Book of Abstracts of the

# 13th Topical Meeting of the International Society of Electrochemistry

## Advances in Electrochemical Materials Science and Manufacturing

7 to 10 April, 2013, Pretoria, South Africa

Workshop, 11 April, 2013

Practical Electrochemical Sensors with Relevance to Africa

*Organized by:*
ISE Division 4 Electrochemical Materials Science
ISE Division 5 Electrochemical Process Engineering and Technology
ISE Region South Africa

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# Symposium Organization

## Electrode Fabrication & Engineering

Giovanni Zangari, *Charlottesville, VA, USA*
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Janice Limson, *Rhodes University, South Africa*
Jessie Pillay, *Mintek, Randburg, South Africa*

## Electrochemical Energy Technologies

Kenneth Ozoemena, *CSIR, Pretoria, South Africa*
Shawn Gouws, *Nelson Mandela Metropolitan University, South Africa*
Hongze Luo, *CSIR, South Africa*
Mmalewane Modibedi, *CSIR, Pretoria, South Africa*
Mkhulu Mathe, *CSIR, Pretoria, South Africa*

# Table of Contents

Oral presentation program

## Dear colleagues, ladies and gentlemen,

On behalf of all the African members of the International Society of Electrochemistry (ISE), the Organising Committee and Symposium Organisers, I warmly welcome you to the 13th Topical Meeting of the ISE hosted by the Council for Scientific and Industrial Research (CSIR) Pretoria, South Africa. This event is quite unique as it is the first time that the ISE is holding a conference in Africa. We have chosen the CSIR as the venue due to its unique position in the national system of innovation and special relationship with electrochemistry, especially on batteries; the famous ZEBRA battery and spinel cathode ($Li_{1+x}Mn_{2-x}O_4$) and anode ($Li_4Ti_5O_{12}$) materials for lithium ion batteries were invented by the CSIR researchers (led by Johan Coetzer and Michael Thackeray) in the late 1970's.

Pretoria (founded in 1855) is one of the South Africa's three capital cities, serving as the executive (administrative) and de facto national capital; the other cities being Cape Town (the legislative capital), and Bloemfontein (the judicial capital). Pretoria is popularly referred to as the Jacaranda City due to the thousands of purple blossom-bedecked Jacaranda trees planted in its streets, parks and gardens. The city is about 50 km from the economic center of the country, Johannesburg. Over the years, Pretoria has greatly been influenced by diverse cultures which can be reflected by the architectural styles found in the city, ranging from the British Colonial Architecture to Art Deco with a good mix of uniquely South African styles. Some of the notable structures of Pretoria that may be of interest to you will include the Union Buildings, Voortrekker Monument, Mahlamba Ndlopfu (the President's House), to mention but a few.

*continue*

The theme of the meeting “Advances on Electrochemical Materials Science and Manufacturing” reflects the constantly increasing importance of electrochemistry in promoting the growth of scientific and technical infrastructure in the field of materials science, engineering and technologies, and the need to sensitise and expose research students and academia to the uniqueness of electrochemistry as a major research and development tool in modern materials science and engineering. The conference consists of three Symposia sponsored by the ISE Division 4 (Electrochemical Materials Science), ISE Division 5 (Electrochemical Process Engineering and Technology) and ISE South African Region. As part of the activities marking this first ISE meeting in Africa, the South African Region of the ISE wishes to recognise and celebrate the contributions made by some academics who have been at the forefront of teaching and research in electrochemistry in the country: Professor Andrew Martin Crouch, Professor Ignacy Cukrowski, Professor Emmanuel Iwuoha, Professor Peter Loyson, Professor Vladimir Linkov, and Professor Tebello Nyokong.

I would like to thank the Organizing Committee, Symposia Organizers and the Executive Committee, sponsors and exhibitors for all their contributions to make this meeting a success. Of course, it is impossible for this meeting to be successful without the key contributors (you, the participants), thanks a million times!

I hope your 13th TM ISE Meeting will be a memorable one.

Kenneth I. Ozoemena
*Chair*
*Organizing Committee*
*13th Topical Meeting of the International Society of Electrochemistry*

# Electrochemistry Excellence Award: Teaching & Research

Recognition by the South African Region of the
International Society of Electrochemistry

## Professor Andrew Martin Crouch

Professor Andrew M Crouch is the Acting Deputy Vice-Chancellor Academic at the University of the Witwatersrand. Prior to this he served as the Dean of the Faculty of Science at WITS for a period of four years. He is a member of the Senior Executive Team of the University who advises the Vice-Chancellor on broad institutional leadership and management. Prior to his appointment at WITS, he was Professor of Chemistry and Associate Dean: Faculty of Natural Sciences at the University of Stellenbosch. Prof Crouch has extensive teaching experience in Chemistry, having taught at the Peninsula Technikon (now Cape Peninsula University of Technology), University of the Western Cape (UWC), Stellenbosch University and various Universities abroad. He has more than 20 years research experience in environmental electrochemistry and its applications, being the author/co-author of more than 140 research papers and a patent. During the past 20 years Prof Crouch supervised and trained 23 Masters, 12 PhD and 6 Post-Doctoral students in Chemistry. He established a Centre for Electrochemistry at the UWC with the assistance of the private sector, which has become the South African Institute for Advanced Materials Chemistry. As Coordinator of the Centre he was awarded a SASOL grant to establish an Endowed CHAIR in Analytical/Applied Chemistry. He was also awarded the Ernst Oppenheimer Memorial Trust Fellowship and Gold Medal (1998) from the Anglo American Chairman's Fund. He is a founding member of the ElectrochemSA, and a lifetime member of the South African Chemical Institute.

## Professor Ignacy Cukrowski

Professor Cukrowski is a Full Professor in the Department of Chemistry, Faculty of Natural and Agricultural Sciences. It is the second time that he has been recognised as an Exceptional Academic Achiever by the University of Pretoria, the first being in 2008. For his PhD (completed at the Marie Curie-Sklodowska University, Lublin, Poland, and which led to numerous patents and publications) Prof Cukrowski designed, built, tested, and optimised a unique voltammetric system with a built-in self-controlling digital logic for ultra-trace analysis on eight channels (working stations) with specially designed electrode systems working in a parallel mode. In 2001 he attained the DSc (Habilitatzion) from the Nicholaus Copernicus University, Torun, Poland, based on results from his work at the University of the Witwatersrand (Wits). Prof Cukrowski is the founder and was for ten years, first president of the Electrochemical Society of South Africa and organised several national and international conferences. He is a member of the South African Chemical Institute. Prof Cukrowski established electrochemistry research laboratories at both Wits and UP. He has supervised about 30 MSc, PhD and Post-doctoral Fellows, published over 90 papers in, and refereed for, 12 international journals. He has delivered over 20 invited plenary and keynote lectures, presented more than 30 seminars and given at least 110 conference presentations across the globe. Prof Cukrowski has been the project leader of numerous research projects organised by amongst others, the NRF, the Technology and Human Resources for Industry Programme (THRIP), the Pebble Bed Modular Reactor (PBMR) project, Sasol, Anglo-American and Chrome International.

## Professor Emmanuel Iwuoha

Professor Emmanuel Iwuoha was admitted as a Fellow of the Royal Society of Chemistry of UK in 1999, Chartered Chemist in 1990, Chartered Scientist in 2005 and Member of the University of Western Cape (UWC) Governing Council since 2005. Also in 2005 he was appointed a Senior (Distinguished) Professor at UWC. In 2013 he became the Chair of Nanoelectrochemistry and Sensor Technology (NEST Chair), under the South African Research Chair Initiative (SARChI). Prof Iwuoha coordinated the development and establishment of the National Nanoscience Postgraduate Teaching and Training Platform (NNPTTP) in 2011. NNPTTP is an inter-university platform that comprises of the University of Western Cape, the University of Johannesburg, the University of Free State and Nelson Mandela Metropolitan University; that offers MSc Nanoscience degree with specialisations in NanoBiomed, NanoChem and NanoPhysics. In 2002 he established SensorLab, which was envisioned to be a smart materials, electrochemical energy, electrocatalysis and sensors research platform, and now provides research facilities for 5 full time lecturers at UWC. From 2004 to 2012 Prof Iwuoha supervised/co-supervised 25 PhD's and 30 MSc's. By 2011 he had 115 cited ISI-listed journal publications; 11 book chapters; 1 encyclopaedia chapter. He has given 13 plenary and keynote presentations including plenary lectures at the 1995 Heyrovsky Discussions on 'Electrochemistry of biologically active compounds and their models'; the 4th World Biosensor Congress of 1996 on 'Organic phase biosensors: kinetics and applications'; and the 2008 Gordon Research Conference on Bioanalytical Sensors. He was a Guest Editor of Anal Lett volume 44, issue 11, 2011.

## Professor Vladimir Linkov

Professor Linkov is the Director of South African Institute for Advanced Materials Chemistry (SAIAMC) at University of the Western Cape, Cape Town, South Africa. After graduation from Moscow State University (MSc, 1987) and Stellenbosch University (PhD, 1995), Vladimir worked as Senior Lecturer and Research Coordinator at SASOL Center for Separation Technology at Potchefstroom University. He was appointed Full Professor at University of the Western Cape (UWC) in 1997 and the same year organized Inorganic Porous Media Group at Chemistry Department. Further, he initiated and currently leads SAIAMC consisting of more than 70 people (including students). He initiated the ESKOM Center for Electrocatalytic Research (ECER), which later became a part of SAIAMC. He initiated the first Hydrogen and Fuel Cell research programme in South Africa (funded by ESKOM) that became the technical foundation of the Hydrogen and Fuel Cell National Strategy (HySA). As a part of HySA development, UWC was selected to host DST Competence Center for System Integration and Technology Validation (HySA Systems). He was South African national representative to Implementation Liaison Committee of the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE). He is a founding Fellow of the Mapungubwe Institute for Strategic Reflection (MISTRA), leading South African think tank (2011- present). Prof Linkov has supervised and co-supervised 52 students, and published more than 200 research publications, including 83 Scopus listed articles, 56 technical reports, and 18 registered patents.

## Professor Peter Leon Robert Loyson

Professor Loyson was the Head of Department of Chemistry at the Port Elizabeth Technikon for 15 years, during which time he ensured quality education within the Department. After the merging of the Technikon with the University, he became Professor of Physical and Analytical Chemistry at the newly established Nelson Mandela Metropolitan University. His interest in electrochemistry dates back to the courses in analytical electrochemistry which he presented for many years at the PE Technikon. It was during this time that he came across polarography; was fascinated by the technique and impressed with its extreme sensitivity and wide applications. He could boast that during the 1970-80's their University's Metrohm polarograph was one of the most used polarographs on the African continent! He presented courses in Corrosion, for the Corrosion Institute of SA, Basic Electrochemistry (part of a short course in Battery Electrochemistry for ESKOM staff), and electrochemistry topics covering theoretical and industrial electrochemistry. Later, he became involved in "industrially driven" research projects, mainly dealing with organic electrochemistry which led to the first doctoral thesis at the PE Technikon, and battery research focusing on miners cap-lamp lead acid batteries that led to another PhD thesis. He was the Chairman of the Eastern Province section of ElectrochemSA and for a number of years organized regular post-graduate research seminars in Electrochemistry. He published a number of peer-reviewed articles, and has been honoured with several awards. His motto "let electrons do the work!" aptly sums up his efforts in electrochemistry.

## Professor Tebello Nyokong

Professor Nyokong holds a DST/NRF professorship in medicinal chemistry and nanotechnology and Director of the DST/Mintek Nanotechnology Innovation Centre (NIC)-Sensors at Rhodes University. She joined Rhodes University in 1992 and has been undertaking research on chemically modified electrodes using phthalocyanines. The modified electrodes are used for analyses of many molecules such as thiols and neurotransmitters. She has also taught Electrochemistry from year 1 to honours. Professor Nyokong has successfully supervised 54 PhD/MSc students and has published over 400 papers. She has received many awards for her research including the following: she was awarded "A" rating by the National Research Foundation (NRF) of South Africa and a medal by the Third World Academy of Science (TWAS) Medal (2013); she was awarded South African Chemical Institute (SACI) Gold Medal (2012); she was awarded Distinguished Professor at Rhodes University and recognized by Royal Society in Chemistry/Pan African Chemistry Network as a Distinguished Woman in Chemistry (2011); she received two honorary doctorates from Walter Sisulu University and the University of South Africa and was inducted into Lesotho Hall of fame (2010); she was awarded NRF President's award as Champion for the transformation in research and L'Oreal-UNESCO award for "Women in Science" as a Laureate representing Africa and the Arab States (2009); she was recognized by the NRF as one of the top three publishing scientists in South Africa (2007); In 2004 she was bestowed with the Order of Mapungubwe (Bronze) by the State President of South Africa, Mr Thabo Mbeki.

# Workshop Schedule

## **Thursday**, 11 April, 2013

### Morning

8:30

**Introduction**
Janice Limson, *Workshop organiser, Head of Biotechnology, Rhodes University, South Africa*

8:40

**Research for short term technology transfer; low-cost technologies**
Sandro Carrara, *EPFL, Lausanne (Switzerland), Professor of Optical and Electrical Biosensors, University of Genoa,* Editor-in-Chief of BioNanoScience

9:40

**Impedance based biosensors for portable transduction technologies**
Pedro Estrela, *Department of Electronic & Electrical Engineering, University of Bath, UK*

10:40

Tea/coffee

11:10

**Opportunities for the commercial exploitation of nanoelectrodes**
Neville Freeman, *NanoFlex Ltd, UK*

12:10

**Electrochemical (bio)sensors based on screen printed electrodes: from the lab to the market**
Pablo Fanjul Bolado, *R&D Director, DropSens, S.L, Spain*

13:00

Lunch

## Afternoon

14:00

**Models for African Technology Transfer**
John Saffell, *Alphasense Limited, UK*

15:00

**Trouble shooting and technical management in sensors manufacture**
Rory Brimecombe, *Senior Technical Manager Diasorin (Medical devices) South Africa*

15:30

Tea/coffee

16:00

**Health Biotechnology Innovation in South Africa**
Tim Newman, *Health Biotechnology at the Technology Innovation Agency of South Africa*

16:30

Open forum discussion

17:00

Close

# Special Meetings and Social Program

## **Sunday**, 7 April, 2013

15:00

**Opening Ceremony**

18:00 to 20:00

**Welcome Reception**

## **Monday**, 8 April, 2013

17:00 to 20:00

**Poster Session and Reception**

## **Tuesday**, 9 April, 2013

18:00

**Departure by bus for the Banquet at Moyo Zoo Lake (Johannesburg)**
Presentation of Electrochemistry Excellence Award: Teaching & Research
Presentation of ISE Division Best Poster Prizes

## **Wednesday**, 10 April, 2013

16:00

**Closing Ceremony**

## **Thursday**, 11 April, 2013

08:30 to 17:00

**Workshop**
Practical Electrochemical Sensors with Relevance to Africa

# Program

# Sunday, 7 April, 2013 - Afternoon

## Plenary Lecture

### Diamond Auditorium

*Chaired by:* Mkhulu Mathe

15:20 to 16:00 page 49

**Tebello Nyokong** *(Departement of Chemistry, Rhodes University, Grahamstown, South Africa)*

Methods of Electrode Surface Modification Using Porphyrin type Molecules and Nanomaterials

16:00 to 16:20 Coffee Break

16:20 to 17:00 Keynote page 53

**Abasifreke Ebong** *(Electrical and Computer Engineering, The University of North Carolina at Charlotte, Charlotte, USA)*, Nian Chen

Pathway to low-cost metallization of silicon solar cell through understanding of the silicon metal interface and plating chemistry

17:00 to 17:40 Keynote page 52

**Sandro Carrara** *(Laboratory of Integrated Systems, EPFL - École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland)*

Electrochemical biosensors and Biomedical Circuits and Systems

17:40 to 18:00 Invited page 115

**Hasuck Kim** *(Department of Energy Systems, DGIST, Daegu, Korea)*, Taek Dong Chung, Yang-Rae Kim, Yuanzhe Piao, Seunghee Woo

Synthesis of three-dimensional graphene/carbon composites and their electrochemical applications

# Monday, 8 April, 2013 - Morning

## Plenary Lecture

**Diamond Auditorium**

*Chaired by:* Emmanuel Iwuoha

08:30 to 09:10 page 47

**Richard G. Compton** *(Department of Chemistry, Oxford University, Oxford, United Kingdom)*, Edward O. Barnes, Baptiste Haddou, Neil V. Rees, Emma Stuart, Yige Zhou

Electrochemical Studies of Nanoparticles

## S1 Electrode Fabrication & Engineering

**Emerald Auditorium**

*Chaired by:* Aba Ebong

09:10 to 09:40 Keynote page 61

**Giovanni Zangari** *(Materials Science and Engineering, University of Virginia, Charlottesville, USA)*, Lok-kun Tsui

$TiO_2$ nanotube photoanodes modified by electrodeposited $Cu_2O$ and $Fe_2O_3$: optimization of photoconversion efficiency

09:40 to 10:00 page 125

**Lukas le Roux** *(Material Science and Manufacturing, CSIR, Pretoria, South Africa)*, Mkhulu Mathe, Kenneth Ozoemena

$Al_2O_3$ coated $TiO_2$ nanotubes based Dye Solar Cells

10:00 to 10:20 page 177

**Abebaw Tsegaye** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Tesfaye Waryo

Electropolymerization and Electrochromism of Poly(4,7-dithien-2-yl-2,1,3-benzothiadiazole) in 1-butyl-3-methylimmidazolium Ionic Liquids

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 163

**Derck Schlettwein** *(Institute of Applied Physics, Justus-Liebig-University Giessen, Giessen, Germany)*

Electrochemically Triggered Deposition of Porous ZnO: a Versatile Method to Realize Textile-Based Solar Cells

11:00 to 11:20 page 113

**Ladislav Kavan** *(Department of Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague 8, Czech Republic)*, Michael Graetzel, Jun-Ho Yum

Cathode for Dye Sensitized Solar Cells Based on Graphene Oxide

11:20 to 11:40 page 128

**Claude Lévy-Clément** *(CNRS-ICMPE, Thiais, France),* Jamil Elias

Optimization of 1-D ZnO Nanostructures for Photovoltaic Applications

11:40 to 12:00 page 144

**Nonhlanhla Mphahlele** *(CSIR, Tshwane University of Technology, Pretoria, South Africa)*, Leskey Cele, Lukas le Roux, Tebogo Masemola, Mkhulu Mathe, Kenneth Ozoemena

Photoelectrochemistry of Metallophthalocyanines / Multi-walled carbon nanotube hybrid for the development of Dye Solar Cells

12:00 to 12:20 page 69

**Jan-Philipp Becker** *(IEK-5 Photovoltaik, Forschungszentrum Juelich, Juelich, Germany)*, Jürgen Hüpkes, Sascha E. Pust

Anodic electrochemical etching of ZnO:Al thin films for solar cell applications

## S2 Electrochemical Sensors

**Ruby Auditorium**

*Chaired by:* Sibulelo Vilakazi

09:10 to 09:40 Keynote page 54

**Emmanuel Iwuoha** *(SensorLab, Department of Chemistry, University of Western Cape, Cape Town, South Africa)*, Priscilla Baker, Abd Almonam Baleg, Nazeem Jahed, Abongile Jijana, Peter Ndangili, Ezo Nxuzani, Rasaq Olowu, Tesfaye Waryo

Smart Nano-Dimensional Dendritic Aptasensor and Quantum Dots-Linked Estrogen Receptor Alpha-Recombinant Protein Biosensor for Real-Time Determination of Estrogenic 17β-Estradiol

09:40 to 10:00 page 78

**Andrew M. Crouch** *(Institute for Molecular Sciences, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa)*

Studies of mixed metal oxide thin films as anode materials for the degradation of phenol

10:00 to 10:20 page 145

**Munkombwe Muchindu** *(Advanced Materials Division, Mintek, Randburg, South Africa)*, Richard Moutloali, Sibulelo Vilakazi

Detection of Cholera Bacteria by an Electrochemical Immunosensor System Conjugated with Gold Nanoparticle-Enzyme for Amplification

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 182

**Winfried Vonau** *(Kurt-Schwabe-Institut, Ziegra-Knobelsdorf, Germany)*, Kristina Ahlborn, Frank Gerlach

Electron conducting glasses as electrode materials

11:00 to 11:20 page 67

**Priscilla Baker** *(Department of Chemistry, University of the Western Cape, Bellville, South Africa)*, Xolani T. Simelane

Label free domoic acid detection at novel polyamic acid based immunosensor systems

11:20 to 11:40

**Emma J. E. Stuart** *(Department of Chemistry, University of Oxford, United Kingdom)*, Richard G. Compton, Jay T. Cullen, Neil V. Rees, Kristina Tschulik, Yi-Ge Zhou

Electrochemical detection and quantification of commercial silver nanoparticles in seawater media

11:40 to 12:00 page 173

**Shane Flanagan** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University , Grahamstown, South Africa)*, Ronen Fogel, Janice Limson, Michael Niland

Normalizing Variability in the Electrochemical Detection of Mycotoxins at Carbon Nanotube Modified Glassy Carbon Electrodes

12:00 to 12:20 page 104

**Euodia Hess** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*

Polyamic acid composites for multiple sensing applications in complex sample matrices

## S3 Electrochemical Energy Technologies

Diamond Auditorium

*Chaired by:* Volker Presser

09:10 to 09:40 Keynote page 56

**M. V. Reddy** *(Department of Physics, National University of Singapore, Singapore, Singapore)*

Updates on novel electrode materials for Li-ion batteries

09:40 to 10:00 page 153

**Elie Paillard** *(MEET - Institut of Physical Chemistry, University of Muenster, Muenster, Germany)*, Enrico Binetti, Peter Bishop, Dominic Bresser, Mark Copley, Stefano Passerini, Marinella Stricolli, Jan von Zamory, Martin Winter

Titanium Oxide Nanoparticles for High Power and Increased Capacity Anodes for Li-ion Batteries

10:00 to 10:20 page 70

**François Béguin** *(Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland)*, Séverine Jouanneau, Cyril Paireau, Encarnacion Raymundo

Cyclability improvement of Si/C composites for Li-ion batteries prepared from polyvinyl alcohol

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 110

**Charl Jafta** *(Energy Materials, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa)*, Ncholu Manyala, Mkhulu Mathe, Kenneth Ozoemena

The Impact of Microwave Treatment on the Oxygen Vacancy Concentration and Electrochemical Performance of $LiMn_{1.5}Ni_{0.5}O_4$ Cathode Material

11:00 to 11:20 page 73

**Dominic Bresser** *(Institute of Physical Chemistry - MEET, University of Muenster, Muenster, Germany)*, Franziska Mueller, Elie Paillard, Stefano Passerini, Martin Winter

New zinc-based anode materials for lithium-ion batteries

11:20 to 11:40 page 119

**Steffen Krueger** *(Institute of Physical Chemistry - MEET, University of Münster, Münster, Germany)*, Richard Kloepsch, Jie Li, Sascha Nowak, Martin Winter

Anodic-Driven Overcharge Issues of Cathodes in Lithium-Ion Battery Fuel Cells

11:40 to 12:00 page 109

**Chinwe Ikpo** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Charl Jafta, Nazeem Jahed, Kenneth Ozoemena, Natasha West

Electrochemical Responses of Composite Olivine Lithium Iron Phosphate Cathode Material for Lithium Ion Batteries

12:00 to 12:20 page 71

**Aiswarya Bhaskar** *(MEET Battery Research Center, Institute of Physical Chemistry, WWU Muenster, Germany)*, Steffen Krueger, Stefano Passerini, Martin Winter

Investigations on High Voltage Spinel-Layered Composite Materials for High Energy and High Power Applications in LIBs

# Monday, 8 April, 2013 - Afternoon

## Plenary Lecture

**Diamond Auditorium**

*Chaired by:* Priscilla Baker

14:00 to 14:40 page 46

**Haruo Akahoshi** *(Hitachi Research Laboratory, Hitachi, Ltd, Ibaraki-ken, Japan)*

Electrochemical copper deposition technology in the electronic industry

## S1 Electrode Fabrication & Engineering

**Emerald Auditorium**

*Chaired by:* Taka Homma

14:40 to 15:00 page 165

**Walther Schwarzacher** *(H. H. Wills Physics Laboratory, Bristol, United Kingdom)*

Microstructure and morphology of electrodeposited Cu films

15:00 to 15:20 page 187

**Marketa Zukalova** *(Department of Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic)*, Pavel Janda, Ladislav Kavan, Jan Prochazka

Compact $TiO_2$ Films Prepared by Sol-Gel Dip-Coating for Dye Sensitized Solar Cells and Other Applications

15:20 to 15:40 page 149

**Bulelwa Ntsendwana** *(Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa)*, Srinivasan Sampath, Omotayo Arotiba, Bhekie Mamba

Towards Photoelectrochemical Technology for Water Treatment: The degradation of *p*-nitrophenol on an Exfoliated Graphite-$TiO_2$ Photoanode

15:40 to 16:00 page 143

**Alireza Moshfegh** *(Department of Physics, Sharif Univ. Tech., Tehran, Iran)*, M. Gholami, O. Moradlou, N. Naseri

Improved photoelectrochemical activity of $TiO_2$ nanotube arrays modified by deposited $Ag_2S$ nanoparticles

16:00 to 16:20 Coffee Break

16:20 to 16:40 page 159

**Mark Rohwer** *(Department of Energy Materials, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa)*, Remegia Mmalewane Modibedi, Kenneth Ozoemena

Microwave-assisted Pechini Synthesis of Pd-Ni Nanocatalyst for Ethanol Electro-oxidation in Alkaline Medium

16:40 to 17:00 page 133

**Katlego Makgopa** *(Department of Chemistry, University of Pretoria, Pretoria, South Africa)*, Kenneth Ozoemena

Electrochemical Properties of Graphene oxide/Manganese Oxide Nanocomposites for Electrochemical Capacitors

## S2 Electrochemical Sensors

Ruby Auditorium

*Chaired by:* Greg Wildgoose

14:40 to 15:00 111

**Abongile Nwabisa Jijana** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Tesfaye Waryo

Spectroelectrochemically Active Carboxylic acid Capped Semiconducting Nano-matrices of Metal Selenides Integrated ER-α, Receptor-sensor for Estrogens

15:00 to 15:20 136

**Audacity Maringa** *(Department of Chemistry, Rhodes University, Grahamstown, South Africa)*, Edith Antunes, Tebello Nyokong

Synthesis and Electrochemical Characterization of Nickel Nanoparticles and their Conjugates with Phthalocyanines

15:20 to 15:40 154

**Jeseelan Pillay** *(Advanced Materials Division, Mintek, Johannesburg, South Africa)*, Sibulelo Vilakazi

Screen Printing Technology: Design and Development

15:40 to 16:00 126

**Ji Won Lee** *(Department of Chemistry, Seoul National University, Seoul, Korea),* Kwan Kim

Isocyanide-Adsorbed Au Nanoelectrode to Detect BiogenicVolatile Organics by Raman Scattering Spectroscopy

16:00 to 16:20 Coffee Break

16:20 to 16:40 99

**Ulrich Guth** *(Dresden University of Technology, Department of Chemistry and Food Chemistry, Dresden, Germany)*, Monika Berthold, Johanna Riedel

Electrochemical determination of dissolved nitrogen containing explosives

16:40 to 17:00 page 150

**Stephen Nyoni** *(Department of Chemistry, Rhodes University, Grahamstown, South Africa)*, Tebello Nyokong

Application of electrochemical techniques to the characterisation of nanofabricated surfaces for sensor development

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## S3 Electrochemical Energy Technologies

Diamond Auditorium

*Chaired by:* Dmitri Bessarabov

14:40 to 15:00 page 167

**Bin Shao** *(Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan)*, Yasuyuki Abe, Izumi Taniguchi

Preparation of $Li_2MSiO_4/C$ (M=Fe, Mn) Nanocomposites by a Novel Synthesis Method for Lithium Battery Cathode

15:00 to 15:20 page 75

**John Cannarella** *(Mechanical and Aerospace Engineering, Princeton University, Princeton, USA)*, Craig Arnold

The effects of mechanical stress on lithium-ion battery capacity fade

15:20 to 15:40 page 160

**Claire Rossouw** *(Department of Energy Materials, Material Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa)*, Mkhulu Mathe, Kenneth Ozoemena, Haitao Zheng

Conductivity Improvement of $LiFePO_4$ Cathode Material via Graphene-Coating and Aluminum-Doping

15:40 to 16:00 page 166

**Kimberly Scott** *(Department of Materials Science & Engineering, ESRG, Rutgers, The State University of New Jersey, North Brunswick, USA)*, Glenn G. Amatucci, Anna Halajko

Fabrication of High Capacity Lithium Alloy Electrodes For Lithium Ion Batteries With The Utilization of Electrodeposition

16:00 to 16:20 Coffee Break

16:20 to 16:40 page 74

**Nicolas Bucher** *(Department of Electrochemistry & New Materials, TUM CREATE, Singapore, Singapore)*, Maria Arkhipova, Irina Gocheva, Steffen Hartung, Harry E. Hoster, Philipp Kratzer, Gerhard Maas, Madhavi Srinivasan

Guanidinium based Ionic Liquids as new Electrolyte for Energy Storage Systems

16:40 to 17:00 page 168

**Pei Kang Shen** *(School of Physics and Engineering, Sun Yat-sen University, Guangzhou, China)*, Chunyong He

A New Method for Synthesis of Self-Doped Graphene as High-Performance Material for Lithium-Ion Batteries

# Tuesday, 9 April, 2013 - Morning

## Plenary Lecture

**Diamond Auditorium**

*Chaired* by: Janice Limson

08:30 to 09:10 page 48

**John Miller** *(JME, Inc., Case Western Reserve University, Beachwood, USA)*

Highly-reversible Electrical Energy Storage: Technologies, Applications, and Societal Impact

## S1 Electrode Fabrication & Engineering

**Emerald Auditorium**

*Chaired* by: Giovanni Zangari

09:10 to 09:40 Keynote page 59

**John Stickney** *(Department of Chemistry, The University of Georgia, Athens, USA)*, David Benson, Kaushik Jagannathan, Youn-Geun Kim, David Robinson, Leah Sheridan

E-ALD of Pd on Au Single Crystals

09:40 to 10:00 page 142

**Remegia Mmalewane Modibedi** *(Materials Science and Manufacturing, CSIR, Pretoria, South Africa)*, Eldah Louw, Mkhulu Mathe, Kenneth Ozoemena

Electrodeposition of Pd on Carbon Paper and Ni Foam via Surface-Limited Redox-Replacement Reactions for Oxygen Reduction Reaction

10:00 to 10:20 page 96

**Guillaume Gotti** *(Department of Electrochemistry, University Paul Sabatier, Toulouse, France)*, David Evrard, Katia Fajerwerg, Pierre Gros

Electrodeposited gold nanoparticles on glassy carbon. Correlation between AuNPs characteristics and $O_2$ reduction kinetics

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 135

**Ncholu Manyala** *(Department of Physics, University of Pretoria, Hatfield Pretoria, South Africa)*, Abdulhakeem Bello, David Dodoo-Arhin, Fabiane Mopeli, Kenneth Ozoemena

Synthesis and Characterization of Graphene Foam Composite for Electrochemical Applications

11:00 to 11:20 page 185

**Elizabeth L. Zeitler** *(Department of Chemistry, Princeton University, Princeton, USA)*, Andrew B. Bocarsly

Carbon Dioxide Reduction by N-heterocycles: Mechanistic investigations

11:20 to 11:40 page 124

**Vasilica Lates** (*Chemical Resource Beneficiation Focus Area, North West University, Potchefstroom, South Africa)*, Anzel Falch, Roelof Jacobus Kriek, Marcelle Potgieter

Gold-silver Nanoparticles for Efficient Electro-reduction of Carbon Dioxide

11:40 to 12:00 page 83

**Fabian Ezema** *(Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria)*, Paul M. Ejikeme, C. D. Lokhande, Asumpta Chinwe Nwanya, Rose Osuji, Paulinus Ugwuoke

Synthesis and Characterization of (NiO-CoO) Composite Thin Film by Chemical Methods

12:00 to 12:20 page 183

**Natasha West** *(Department of Chemistry, University of the Westrn Cape, Cape Town, South Africa)*

The role of spinel phase $LiPtAu_{0.02}Mn_{1.98}O_4$ nano-materials in the enhancement of the current discharge density of lithium-ion batteries

## S2 Electrochemical Sensors

**Ruby Auditorium**

*Chaired by*: Jessie Pillay

09:10 to 09:40 Keynote page 58

**Wolfgang Schuhmann** *(Analytische Chemie - Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Bochum, Germany)*

Bioelectroanalysis. Design of electron-transfer pathways as a basis for biosensors and biofuel cell electrodes

09:40 to 10:00 page 88

**Ronen Fogel** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa),* Lance Ho, Janice Limson

Variability in response of laccase-based nanocomposite electrochemical biosensors: key aspects

10:00 to 10:20 page 72

**Mawethu Bilibana** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Emmanuel Iwuoha, Priscilla Baker

DNA aptamer nanobiosensor for microcystin-LR prepared with sulphonated polyaniline platform doped with silver nanoparticles

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 81

**Pedro Estrela** *(Department of Electronic & Electrical Engineering, University of Bath, Bath, United Kingdom)*, Niklaas Buurma, Andrew Hallett, Simon Pope, Edward Regan, Caleb Wong

Enhancing Impedimetric and Potentiometric DNA Biosensing with Active Sensitisers

11:00 to 11:20 page 82

**Mathieu Etienne** *(LCPME, CNRS, Villers-lès-Nancy, France)*, Wissam Ghach, Alain Walcarius

Communication between Electrode Surface and Whole Cells with Cytochrome C as Redox Shuttle

11:20 to 11:40 page 108

**Tan-Phat Huynh** *(Department of Physical Chemistry of Supramolecular Complexes, Institute of Physical Chemistry, Polish Academy of Science, Warsaw, Poland)*, K.C. Chandra Bikram, Francis D'Souza, Wlodzimierz Kutner, Vladimir Nesterov, Janusz Sobczak, Marta Sosnowska

Conducting molecularly imprinted polymers for selective impedimetric determination of explosive nitroaromatic compounds

11:40 to 12:00 page 132

**Hlamulo Makelane** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Emmanuel Iwuoha

Ultra-Sensitive Electrochemical Nanosensors of Star Copolymer Platform using Polypropyleneimine and Polythiophene

12:00 to 12:20 page 170

**Vernon Somerset** *(NRE, CSIR, Stellenbosch, South Africa)*

Voltammetric Determination of Precious Metals in Environmental Samples

## S3 Electrochemical Energy Technologies

Diamond Auditorium

*Chaired by*: Bruno Pollet

09:10 to 09:40 Keynote page 51

**Dmitri Bessarabov** *(HySA Infrastructure Center of Competence, North-West University, Faculty of Natural Science, CRB, Potchefstroom, South Africa)*

DST HySA Infrastructure Center of Competence: Hydrogen Production and Storage. From Materials to Hydrogen Systems: An Overview

09:40 to 10:00 page 122

**Henrietta W. Langmi** *(HySA Infrastructure Center of Competence, Council for Scientific and Industrial Research, Pretoria, South Africa)*, Dmitri Bessarabov, Mkhulu Mathe, Brian North, Jianwei Ren, Dave Rogers

An Overview of Hydrogen Storage Materials: Making a Case for Metal Organic Frameworks

10:00 to 10:20 page 180

**Jan Van der Merwe** *(Faculty of Natural Science, HySA Infrastructure, North-West University, Potchefstroom, South Africa)*, Dmitri Bessarabov, Christiaan Martinson

Fundamental understanding of PEM electrolyser operation: characterisation tools development

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 130

**Vladimir Linkov** *(South African Institute for Advanced Materials Chemistry, University of the Western Cape, Cape Town, South Africa)*, Shan Ji, Hui Wang, Rongfang Wang

Palygorskite Hybridized Carbon Nanocomposite as PtRuIr Support for the Methanol Oxidation Reaction

11:00 to 11:20 page 155

**Bruno Pollet** *(HySA Systems Competency Centre, SAIAMC, Chemistry, University of the Western Cape, Cape Town, South Africa)*

The Use of Ultrasound in Fuel Cell Technologies – An emerging research area

11:20 to 11:40 page 118

**Cobus Kriek** *(Department of Chemistry, North-West University, Potchefstroom, South Africa)*, Marten Bjorketun, Adri Calitz, Anzel Falch, Vasilica Lates, Marcelle Potgieter, Jan Rossmeisl, Samira Siahrostami, Marthinus Steyn

The electro-oxidation of sulphur dioxide ($SO_2$)

11:40 to 12:00 page 161

**Caroline Rozain** *(CEA Grenoble, Grenoble, France)*, Nicolas Guillet, Eric Mayousse, Pierre Millet

PEM water electrolysis with reduced iridium oxide loadings : influence on kinetic parameters and electrolyserperformances

12:00 to 12:20 page 94

**Eric Gauthier** *(Chemical & Biological Engineering, Princeton University, Princeton, USA)*, Jay Benziger

Gas Management and Multiphase Flow in Direct Alcohol Fuel Cells

# Tuesday, 9 April, 2013 - Afternoon

## S1 Electrode Fabrication & Engineering

**Emerald Auditorium**

*Chaired by*: Mkhulu Mathe

14:00 to 14:20 page 106

**Takayuki Homma** *(Department of Applied Chemistry, Waseda University, Shinjuku, Tokyo, Japan)*, Yasuhiro Fukunaka, Yoko Ishibashi, Jason Komadina

Electrodeposition process to form patterned Si nanostructures

14:20 to 14:40 page 121

**Virginie Lair** (*LECIME - UMR CNRS 7575, ENSCP - Chimie ParisTech, Paris, France)*, Laurent Gaillon, Armelle Ringuedé, Cécile Rizzi, Juliette Sirieix-Plenet

Electrodeposition of Metal Oxides Films in Various Room Temperature Ionic Liquids (RTILs)

14:40 to 15:00 page 157

**William Richard** *(Electrochemical Process, Paul Sabatier University, Toulouse, France)*, David Evrard, Pierre Gros

Electrodeposited 4-nitrobenzene diazonium as a powerful tool for the fine tuning of surface properties

15:00 to 15:20 page 181

**Marcela Vazquez** *(División Electroquímica y Corrosión, INTEMA - UNMdP - CONICET, Mar del Plata, Argentina)*, María Frontini, Thembela Hillie, Remegia Mmalewane Modibedi, Matías Valdes

Electrodeposited $Cu_2ZnSnS_4$ thin films

15:20 to 15:40 page 114

**Mesfin Kebede** *(Materials Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa)*, Niki Kunjuzwa, Mkhulu Mathe, Kenneth Ozoemena, Maje Phasha

Synthesis and Electrochemical Properties of Al-Doped $LiMn_2O_4$ Cathode Materials Using Solution Combustion Method

15:40 to 16:00 page 171

**Zhenlun Song** *(Surface Engineering, Ningbo Institute of Materials Technology and Engineering, Ningbo, China)*, Shoudong Mao, Jing Yu

Electrodeposited amorphous Al-Mn coatings on NdFeB magnet from an $AlCl_3$-BMIC ionic liquid

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## S2 Electrochemical Sensors

Ruby Auditorium

*Chaired by*: Frank Marken

14:00 to 14:20 page 172

**Elaine Spain** *(National Centre for Sensor Research, Dublin City University, Dublin, Ireland)*

Facile Synthesis of Regioselectively Decorated Electrocatalytic Nanoparticles for Highly Sensitivity DNA Detection

14:20 to 14:40 page 91

**Xolile Fuku** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Vilakazi Sibulelo

Quantum dots electrochemical genosensor for breast cancer biomarkers

14:40 to 15:00 page 86

**Marian Filipiak** *(Natural Science and Quality Assurance, Poznan University of Economics, Poznan, Poland)*, Marta Ligaj, Mariusz Tichoniuk

Electrochemical biosensor for the detection of pathogenic bacteria (Aeromonas hydrophila)

15:00 to 15:20 page 162

**John Saffell** *(Alphasense Limited, Great Notley, United Kingdom)*, Ronan Baron, Roderic Jones, Iq Mead

Measuring ppb Gas Concentrations in Air Quality Networks

15:20 to 15:40 page 151

**Modupe Ogunlesi** *(Department of Chemistry, University of Lagos, Lagos, Nigeria)*, Sulaiman Akanmu, Wesley Okiei

Electrochemical Sensor for the Monitoring of Values of Peak Current of Haemoglobins in the Presence of Anti-Sickling Agents and its Application in the Management of Sickle Cell Disease

15:40 to 16:00 page 65

**Omotayo Arotiba** *(Applied Chemistry, University of Johannesburg, Johannesburg, South Africa)*, Rui Krause, Bhekie Mamba, Thabile Ndlovu, Srinivasan Sampath

Bismuth Modified Exfoliated Graphite Electrode Platform for the Voltammetric Detection of Arsenic in Water

16:00 to 16:20 Coffee Break

16:20 to 16:40 page 147

**Kanyisa L. Nohako** *(Department of Chemistry, University of the Western Cape, Bellville, South Africa)*, Priscilla Baker, Emmanuel Iwuoha

Design and Characterisation of Immunosensors developed on Clathrate Compound Platforms

16:40 to 17:00 page 169

**Bongiwe Silwana** *(Department of Chemistry, University of Western Cape, Bellville, South Africa)*, Emmanuel Iwuoha, Vernon Somerset, Charlton Van der Horst

Bismuth film coated SPCE for Electrochemical Stripping Measurement of Platinum Group Metals

17:00 to 17:20 page 178

**Aliki Tsopela** *(LAAS, CNRS, Toulouse, France)*, Céline Christophe, Ricardo Izquierdo, Philippe Juneau, Ahmet Lale, Jérôme Launay, Florent Lefèvre, Isabelle Séguy, Pierre Temple-Boyer, Emilie Vanhove

Electrochemical microsensor for detection of pollutants

17:20 to 17:40 page 141

**Radovan Metelka** *(Department of Analytical Chemistry, University of Pardubice, Pardubice, Czech Republic)*, Kurt Kalcher, Ivan Svancara, Karel Vytøas

Years of Collaboration in the Middle Europe. Part II: (Bio)sensors Based on Screen-Printed Carbon Electrodes

## S3 Electrochemical Energy Technologies

Diamond Auditorium

*Chaired by*: Mark Rohwer

14:00 to 14:20 page 89

**Elzbieta Frackowiak** *(Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland),* François Béguin, Krzysztof Fic

Strategies for enhancing the performance of carbon/carbon supercapacitors in aqueous electrolytes

14:20 to 14:40 page 156

**Volker Presser** *(Department of Energy Materials, INM - Leibniz-Institute for New Materials, Saarbrücken, Germany)*, Jennifer Atchison

Supercapacitors, Pseudocapacitors, and Flow Capacitors: Challenges and Advances of Polymer-Derived Nanoporous Carbons

14:40 to 15:00 page 127

**Joel Lekitima** *(Department of Chemistry, University of Pretoria, Hatfield Pretoria, South Africa)*, Kenneth Ozoemena

Electrochemical Performance of MWCNTs-CoTPyzPz//CB-MWCNTs Asymmetric Capacitors

15:00 to 15:20 page 146

**Njagi Njomo** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa),* Priscilla Baker, Emmanuel Iwuoha, Kenneth Ozoemena

Graphenated Transition Metal Oxides and Poly-(4-styrene sulphonic acid) Doped Polyaniline Nanocomposite Materials for the Development of Asymmetric Supercapacitors

15:20 to 15:40 page 117

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

Novel Nanoporous Carbons Based on Tobacco and Their Electrochemical Properties in Supercapacitors

15:40 to 16:00 page 62

**Qamar Abbas** *(Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland)*, Francois Béguin, Piotr Kleszyk, Paula Ratajczak

Performance of Electrochemical Capacitors with Microporous Carbon Electrodes in New Types of Aqueous Electrolytes

16:00 to 16:20 Coffee Break

16:20 to 16:40 page 176

**Dah-Shyang Tsai** *(Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan)*, Ying-Sheng Huang, Kuei-Yi Lee

Micro-ultracapacitors based on Interdigitated Electrode

16:40 to 17:00 page 107

**Tobias Hutzenlaub** *(IMTEK - Department of Microsystems Engineering, University of Freiburg, Freiburg, Germany)*, Simon Thiele, Roland Zengerle

Calculation of tortuosity in a Li-ion battery cathode based on FIB/SEM tomography

17:00 to 17:20 page 100

**Steffen Hartung** *(Electrochemistry & New Materials, TUM CREATE, Singapore, Singapore)*, Nicolas Bucher, Irina Gocheva, Harry E. Hoster, Madhavi Srinivasan

Effect of Doping and Electrolyte on the Performance of Sodium Manganese Oxides in Sodium Ion Batteries

17:20 to 17:40 page 164

**Matthias Schroeder** *(Institut für Physikalische Chemie - MEET, Westfälische Wilhelms University of Münster, Münster, Germany),* Andrea Balducci, Philipp Isken, Alexandra Lex-Balducci, Stefano Passerini, Martin Winter

On the influence of the electrolyte properties on the performance of Lithium-Ion Capacitors

# Wednesday, 10 April, 2013 - Morning

## Plenary Lecture

Diamond Auditorium

*Chaired by:* Hasuck Kim

08:30 to 09:10 page 50

**Reginald M. Penner** *(Department of Chemistry, University of California, Irvine, USA)*

Lithographically Patterned Nanowire Electrodeposition (LPNE): Advances and Applications

## S1 Electrode Fabrication & Engineering

Emerald Auditorium

*Chaired by*: Walther Schwarzacher

09:10 to 09:40 Keynote page 57

**Daniel A. Scherson** *(The Ernest B. Yeager Center for Electrochemical Sciences, Case Western Reserve University, Cleveland, USA)*, Doe Kumsa

Theoretical Aspects of Pulsed Electrochemical Micromachining

09:40 to 10:00 page 174

**Ralph Sueptitz** *(Chemistry of Fuctional Materials, IFW Dresden, Dresden, Germany)*, Juergen Eckert, Annett Gebert, Margitta Uhlemann

Electrochemical Micromachining of Passive Electrodes – Application to Bulk Metallic Glasses

10:00 to 10:20 page 93

**Jean Gamby** *(Department of Chemistry, CNRS, Paris, France)*, Mohammed Kechadi, Bernard Tribollet

Microchannel Impedance through two antiparallel planar microelectrodes

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 131

**Eldah Louw** *(Department of Chemistry, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa)*, Leskey Cele, Mathe Mkhulu, Remegia Mmalewane Modibedi, Kenneth Ozoemena

Electrochemical deposition and characterization of platinum on carbon paper and Ni foam for methanol oxidation for fuel cell application

11:00 to 11:20 page 79

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

Electrodeposited Polycarbazole Derivatives as Materials for Optoelectronic Applications

11:20 to 11:40 page 90

**Neville Freeman** *(Research and Development, NanoFlex Ltd, Daresbury, United Kingdom)*, Andrew Mount, Ilka Schmuser, Reshma Sultana, Jonathan Terry, Anthony Walton

Fabrication of Commercial Nanoelectrodes: challenges and opportunities

11:40 to 12:00 page 63

**Oluwasesan Adegoke** *(Department of Chemistry, Rhodes University, Grahamstown, South Africa)*, Nyokong Tebello

Characterization and Application of Quantum dots (CdTe@ZnS)-colbalt tetraamino-phthalocyanine Nanoconjugates as Luminescence sensor for superoxide anion

12:00 to 12:20 page 138

**Justus Masa** *(Analytische Chemie, Electroanalytik & Sensorik, Ruhr-Universitaet Bochum, Bochum, Germany)*

Bifunctional catalyst for electrocatalysis of oxygen reduction and water oxidation derived from manganese complexes

## S2 Electrochemical Sensors

Ruby Auditorium

*Chaired by*: Galal Ahmed

09:10 to 09:40 Keynote page 60

**Gregory Wildgoose** *(School of Chemistry, Energy & Materials Laboratory, University of East Anglia, Norwich, United Kingdom)*, Andrew Ashley, Elliot Lawrence, Vasily Oganesyan

Introducing "Electrocatalytic Frustrated Lewis Pairs" for Hydrogen and Small Molecule Activation

09:40 to 10:00 page 137

**Frank Marken** *(Department of Chemistry, University of Bath, Bath, United Kingdom)*, Sara E.C. Dale, Anne Vuorema

Junction Electroanalysis

10:00 to 10:20 page 102

**Martin Henstridge** *(Physical and Theoretical Chemistry, Oxford University, Oxford, United Kingdom)*, Richard G. Compton, Eduardo Laborda

Asymmetric Marcus-Hush Theory

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 92

**Ahmed Galal** *(Department of Chemistry, Cairo University, Faculty of Science, Giza, Egypt)*, Shimaa Ali, Nada Atta, Ekram El-Ads

A novel hybrid nano-scale sensor of perovskites and carbon paste for the determination of neurotransmitters

11:00 to 11:20 page 112

**Kurt Kalcher** *(Department of Chemistry - Analytical Chemistry, Karl-Franzens University, Graz, Austria)*

Electroanalysis with Carbon Paste Electrodes and Related Sensors: 20 Years of One Collaboration in Middle Europe

11:20 to 11:40 page 186

**Yongchun Zhu** *(Department of Chemistry, Shenyang Normal University, Shenyang, China)*

Adsorption and determination of dichromate in aqueous solution based on pine needle powder modified carbon paste electrode by potentiometry

11:40 to 12:00 page 105

**Lance Ho** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa)*, Ronen Fogel, Janice Limson

Examination of the Fouling Resistance Capabilities of a Laccase-based Phenolic Biosensor Utilising Multi-walled Carbon Nanotubes

12:00 to 12:20 page 175

**Christopher Edozie Sunday** *(Department of Chemistry, University of the Western Cape, Bellville, South Africa)*, Emmanuel Iwuoha

A Multi-Signal biocompatible Platform from $[Ru(Bpy)_3]^{2+}$ Ion Exchanged In AuCuG/Perfluorosulfonate Ionomer Composite Films And Its Potential Applications In Electrochemical Sensors.

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## S3 Electrochemical Energy Technologies

### Diamond Auditorium

*Chaired by*: Olaf Conrad

09:10 to 09:40 Keynote page 55

**Kenichiro Ota** *(Green Hydrogen Research Center, Yokohama National University, Yokohama, Japan)*, Akimitsu Ishihara, Koichi Matsuzawa, Shigenori Mitsushima

Transition Metal Oxide Based Materials for Cathode of PEFCs

09:40 to 10:00 page 116

**Joon-Hee Kim** *(Samsung Advanced Institute of Technology, Samsung Electronics Co., Ltd., Yongin-si, Korea)*, Jinsu Ha, Suk-Gi Hong, Yoon Hoi Lee, Jung Ock Park

Development of Mid-temperature PEMFC MEA under the Operating Condition of Low Relative Humidity

10:00 to 10:20 page 77

**Olaf Conrad** *(HySA/Catalysis, University of Cape Town, Rondebosch, South Africa)*, Sharon Blair, Tapiwa Chivengwa, Greg Crymble, Nabeel Hussain, Rushanah Mohamed

Evaluation of application methods and ink parameters for the preparation of catalyst coated membranes for fuel cells

10:20 to 10:40 Coffee Break

10:40 to 11:00 page 84

**Omobosede Fashedemi** *(Department of Chemistry, University of Pretoria, Pretoria, South Africa)*, Kenneth Ozoemena

Non-noble Iron Tetrasulfophthalocynine on Multi-walled Carbon Nanotubes: a Potential Cathode Catalyst in Direct Alcohol Alkaline Fuel Cells

11:00 to 11:20 page 158

**Armelle Ringuedé** *(LECIME, CNRS - ENSCP Chimie ParisTech, Paris, France),* Valerie Albin, Michel Cassir, Virginie Lair, Bianca Medina-Lott, Cyrine Slim

Improvement and Deeper Understanding of Electrical Performances of Molten Salts/Cerium Oxide Composite as Electrolytes for Intermediate Temperature Solid Oxide Fuel Cells

10:20 to 11:40 page 97

**Shawn Gouws** *(InnoVenton, Nelson Mandela Metropolitan University, Port Elizabeth, South Africa)*

Voltammetric characterization methods for the PEM electrolysis evaluation

11:40 to 12:00 page 179

**Minoru Umeda** *(Department of Materials Science and Technology, Nagaoka University of Technology, Niigata, Japan)*, Masahiro Ide, Hironosuke Ikeda, Sayoko Shironita

Scanning Electrochemical Microscopy Study of PEFC Cathode Catalyst after Long –Term Endurance Test

12:00 to 12:20 page 85

**Ernst Ferg** *(Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth, South Africa)*, Francois van Vuuren

An electrochemical study in using EIS of commercial AA alkaline battery capacities

# Wednesday, 10 April, 2013 - Afternoon

## S1 Electrode Fabrication & Engineering

Emerald Auditorium

*Chaired by*: Lukas Le Roux

14:00 to 14:20 page 120

**Pawel J. Kulesza** (*Department of Chemistry, University of Warsaw, Warsaw, Poland)*

Development of Nanostructured Materials Towards More Effective Electrocatalysis, Photoelectrocatalysis and Bioelectrocatalysis

14:20 to 14:40 page 80

**Paul M. Ejikeme** (*Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria)*, Cosmas N. Anyanwu, Viola Egidio, Braccio Giacobbe, John A. Ibemesi, Okechukwu D. Onukwuli, Vito Valerio, Francesco Zimbardi

Factorial Design and Response Surface Methodology in Optimization of Biodiesel Production from Nigerian Non-Edible Oil

14:40 to 15:00 page 134

**Philippe Mandin** *(LIMATB, UBS, Lorient, France),* Zine Derhoumi, Herve Roustan

Bubble over voltage modelling during two-phase electrolysis. Experimental Study

15:00 to 15:20 page 101

**Emma Harvey** *(Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands)*, Wesley Browne, Ben Feringa, Mary Pryce

The Electrochemical Properties of Dithienylcyclopentene Switches and their Cobalt Carbonyl Complexes

15:20 to 15:40 page 140

**Mangaka Matoetoe** (*Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa)*, Emmanuel Iwuoha

Indigo dye incorporated Polyaniline composite's chemical and electrical properties

15:40 to 16:00 page 123

**Mieczyslaw Lapkowski** *(Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland)*, Przemyslaw Data

Optical Properties of Electrodeposited Polyselenophene Derivatives

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## S2 Electrochemical Sensors

Ruby Auditorium

*Chaired by:* Modupe Ogunlesi

14:00 to 14:20 page 129

**Janice Limson** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa)*, Denzil Beukes, Ronen Fogel, Nasheen Ragubeer

Electrochemical sensing of antioxidant properties: screening of bioactive compounds

14:20 to 14:40 page 95

**Eric de Souza Gil** *(Faculty of Pharmacy, Federal University of Goiás, Goiânia, Brazil)*, Fernando Miguel Lino, Luisa Sá, Ieda Torres

Antioxidant activity and electrochemical behavior of alcoholic beverages produced from jabuticaba (Myrciaria jabuticaba)

14:40 to 15:00 page 76

**Arely Cárdenas Robles** *(Investigación y Posgrado, CIDETEQ, Pedro Escobedo, Mexico)*, Carlos Frontana

Voltammetric and Chronoamperometric Evaluation of CUPRAC Methodology for Developing an Electrochemical Sensor

15:00 to 15:20 page 98

**Pierre Gros** *(Laboratoire de Génie Chimique UMR 5503, Université Paul Sabatier, Toulouse, France)*, Clémence Cheignon, David Evrard, Anne Galinier, Fadhila Sekli-Belaidi

PEDOT-based electrochemical microsensor for the assay of ascorbic and uric acids in human blood serum. Highlighting the antioxidant regeneration mechanism using SECM

15:20 to 15:40 page 64

**Fanelwa Ajayi** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Siphelele Zosiwe

A poly (8-anilino-1-naphthalene sulphonic acid) silver nanoparticulate modified bioelectrochemical nanobiosensor system for the analytical determination of rifampicin

15:40 to 16:00 page 139

**Philani Mashazi** *(Advanced Materials Division, Mintek, Randburg, South Africa)*, Nolwazi Nombona, Sibulelo Vilakazi

Design and development of electrochemical biosensing systems for the detection of disease biomarkers for human and animal health

## S3 Electrochemical Energy Technologies

Diamond Auditorium

*Chaired by*: Patrick Nojola Shakes

14:00 to 14:20 page 184

**Krzysztof Winkler** *(Department of Chemistry, University of Bialystok, Bialystok, Poland)*, Ewa Brancewicz, Emilia Gradzka

Chemical synthesis of $C_{60}$-Pd polymer spherical nanoparticles - morphology and electrochemical properties

14:20 to 14:40 page 68

**Ipek Becerik** *(Department of Chemistry, Istanbul Technical University, Istanbul, Turkey)*, Osman Sinan Suslu

$H_3PO_4$ Doped Polybenzimidazole (PBI)-Based Membranes for Direct Methanol Fuel Cell-Internal Combustion Engine Hybrid Systems

14:40 to 15:00 page 148

**Patrick Nonjola** *(Material Science and Manufacturing, CSIR, Pretoria, South Africa)*, Mkhulu Mathe, Remegia Mmalewane Modibedi

Performance and Evaluation of Polysulfone/$TiO_2$ Nanocomposite for Alkaline Fuel Cell Applications

15:00 to 15:20 page 103

**Pilwon Heo** *(Energy Lab, Samsung Advanced Institute of Technology, Yongin, Korea),* Hyuk Chang, Kyoung Hwan Choi, Takashi Hibino, Ki-Hyun Kim, Chanho Pak, Yanbai Shen

Design of $Fe_{0.4}Ta_{0.5}P_2O_7$-based composite electrolyte and electrode materials for high-temperature, low-humidity PEMFCs

15:20 to 15:40 page 66

**Vincenzo Baglio** *(CNR, CNR-Institute of Advanced Energy Technologies (ITAE), Messina, Italy)*, Stefania Siracusano

Sulfonated Polysulfone-based Membranes for PEM Electrolyzer Applications

# Poster Presentations

# S1 Electrode Fabrication & Engineering

s1-001

**Peter Ajibade** *(Department of Chemistry, University of Fort Hare, Alice, South Africa)*, Adebayo Adeniyi

Design, synthesis and photo physical and electrochemical studies of some Ru(II) complexes for application in DSSCs

s1-002

**Olivia Barron** *(Department of Chemistry, SAIAMC, University of the Western Cape, Cape Town, South Africa)*, Vladimir Linkov, Sivakumar Pasupathi, Bruno Pollet

Gas diffusion electrodes for high temperature PEMFCs

s1-003

**Abdulhakeem Bello** *(Department of Physics, University of Pretoria, Hatfield Pretoria, South Africa)*, David Dodoo-Arhin, Mopeli Fabiane, Ncholu Manyala

Non-Covalent Functionalized Graphene Foam as Electrode for Supercapacitors

s1-004

**Przemyslaw Data** *(Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland)*, Wojciech Domagala, Mieczyslaw Lapkowski, Pawel Zassowski

Investigation of Electrodeposited Polymer by Optical and EPR Measurements During Doping Process

s1-005

**Adedayo Fashina** *(Department of Chemistry, Rhodes University, Grahamstown, South Africa)*, Edith Antunes, Tebello Nyokong

Preparation, Photophysical, Electrochemical and Sensing Properties of Luminescent Tetraaminophthalocyanine-grafted Silica Nanoparticles

s1-006

**Yanfang Gao** *(College of Chemical Engineering, Inner Mongolia University of Technology, HuHhot, China)*, Gan Jia, Xiaohui Liu, Yuting Yu, Wen Zhang

Electrosynthesis of Dimethyl Carbonate from CH3OH and CO with [Cu(2,2 Œ-Bipy)Cl2] Catalyst

s1-007

**Julia Kois** *(Materials Science, Tallinn Technical University, Tallinn, Estonia)*

Electrochemical synthesis of CdSe/CdS nanowires for hybrid photovoltaic structures

s1-008

**Virginie Lair** *(LECIME - UMR CNRS 7575, ENSCP - Chimie ParisTech, Paris, France)*, Valerie Albin, Michel Cassir, Olga Halipova, Armelle Ringuedé

Electrodeposition of Gadolinium-Doped Ceria Nanostructured Thin Layers

s1-009

**Mieczyslaw Lapkowski** *(Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland)*, Alina Brzeczek, Wojciech Domagala, Wojciech Kuznik, Przemyslaw Ledwon, Sandra Pluczyk, Krzysztof Walczak

Spectroelectrochemical Properties of Pyrrole Naphthalimide Derivatives and Their Polymers

s1-010

**Jose de Ribamar Martins** *(Instituto de Química, Universidade de São Paulo, São Paulo, Brazil)*, Susana I. Cordoba de Torresi

Electrochromic properties of nanostructured WO3 films in acid and protic ionic liquid electrolytes

s1-011

**Thandeka Mthethwa** *(Department of Chemistry, Rhodes University, Grahamstown, South Africa)*, Edith Antunes, Tebello Nyokong

Synthesis and surface modification of non-spherical gold nanoparticles for optical sensing

s1-012

**Marcelle Potgieter** *(Chemical Resource Beneficiation Research Focus Area, North-West University, Potchefstroom, South Africa)*, Anzel Falch, Roelof Jacobus Kriek, Vasilica Lates

High-throughput combinatorial synthesis and parallel screening of electrocatalysts for oxygen reduction

s1-013

**Alina Pruna** *(Faculty of Physics, University of Bucharest, Bucharest, Romania)*, David Busquets, Daniele Pullini

Electrochemical synthesis and characterization of multi-component nanocomposite of polypyrrole and carbon-based materials

s1-014

**Suelen H. Takahashi** *(Instituto de Química, Universidade de São Paulo, São Paulo, Brazil)*, Susana I. Cordoba de Torresi

Multi Stimuli Electro Conductive Hydrogel and its Application in Controlled Drug Delivery

s1-015

**Izumi Taniguchi** *(Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan)*, Renat Tussupbayev

Preparation of $LiMPO_4/C(M=Fe,Co)$ Nanocomposites by a Combination of Emulsion Drip Combustion and Ball Milling with Heat Treatment

s1-016

**Izumi Taniguchi** *(Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan)*, Maki Hasumi, Bin Shao

Synthesis and Characterization of $Li_2MnP_2O_7$ Cathode Materials for Lithium Batteries

s1-017

**Charl Francois Van Schalkwyk** *(Advance Materials Division, Mintek, Randburg, South Africa)*, Gary Pattrick

The Development and Scale-Up of Enhanced Oxygen Reduction Reaction (ORR) Catalysts for Hydrogen Fuelled Low Temperature PEMFCs

s1-018

**Tesfaye Waryo** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Sibusiso Qwesha

Oxy/ Hydroxy Manganese Electrodeposition on 1-Methyl-3-octylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid - Carbon Paste Electrode

# S2 Electrochemical Sensors

s2-001

**Eric de Souza Gil** *(Department of Pharmacy, Federal University of Goias, Goiânia, Brazil)*, Fernando Miguel de Amorim Lino, Luisa Zaiden de Sá, Paulo Cesar Ghedini, Robson Leite Gonçalves, Matheus Lavorentin Rocha, Ieda Maria Sapateiro Torres

Wines of the world. Their antioxidant capacity estimated by means of DPPH radical scavenging assay and electrochemical index

s2-002

**Fabian Ezema** *(Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria)*, Paul M. Ejikeme, C. D. Lokhande, Asumpta Chinwe Nwanya, Rose Osuji, Paulinus Ugwuoke

Synthesis and Characterization of ZnO-CdO Composite Thin Film by chemical methods

s2-003

**Usisipho Feleni** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa),* Priscilla Baker, Emmanuel Iwuoha

Palladium Telluride Quantum dots Electrochemical Biosensor for Protease Inhibitor Anti-retroviral Drug: Indinavir

s2-004

**Kwan Kim** *(Department of Chemistry, Seoul National University, Seoul, Korea)*, Ji Won Lee

Organic Isocyanide-Adsorbed Gold Nanostructure: ASERS Sensory Device to Detect Volatile Organics

s2-005

**Jan Kruid** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa)*, Ronen Fogel, Janice Limson

Voltammetry in Complex Microbiological Growth Media: Challenges and Recommendations

s2-006

**Abdulkadir Levent** *(Department of Analytical Chemistry, Batman University, Batman, Turkey)*, Zühre Sentürk, Yavuz Yardim

Electrochemical evaluation of ambroxol at a boron-doped diamond electrode and its adsorptive stripping voltammetric determination enhanced by anionic surfactant

s2-007

**Abdulkadir Levent** *(Department of Analytical Chemistry, Batman University, Batman, Turkey)*, Ahmet Altun, Hakan Sahin, Yavuz Yardim

Electrochemical investigations of testosterone hormone using various electrode

s2-008

**Nsovo Mathebula** *(Department of Chemistry, Pretoria, South Africa)*

Nanocomposite Based Immunosensors for Active Tuberculosis

s2-009

**Hazel McArdle** *(National Centre for Sensor Research, Dublin City University, Dublin, Ireland)*, Nihan Aydemir, Clive Evans, Robert Forster, Tia Keyes, Jadranka Travas-Sejdic, David Williams

Real-Time Electrochemical Monitoring of the Polymerase Chain Reaction by Conducting Polymers

s2-010

**Nontle Mniki** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker

Protein Phosphatase immunosensor for the detection of cyanotoxins associated with algal bloom

s2-011

**Janes Mokgadi** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Priscilla Baker, Michael Davies-Coleman, Meryck Ward

Development of electroactive polymer platforms for evaluation of halocarbon adsorption

s2-012

**Bulelwa Mpushe** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Mangaka Matoetoe, Emmanuel Iwuoha, Christopher Edozie Sunday

Spectro-electrochemical interrogation of novel biocompatible nano-platforms for mycotoxin immunosensors

s2-013

**Ezo Nxusani** *(Department of Chemistry, University of the Westrn Cape, Cape Town, South Africa)*, Rachel Ajayi, Priscilla Baker, Emmanuel Iwuoha, Abongile Jijana, Peter Ndangili, Tesfaye Waryo

3-Mercaptopropionic acid capped $Ga_2Se_3$ nanocrystal-cyp3a4 biosensor for the determination of 17-alpha-ethinyl estradiol in water

s2-014

**Lisebo Phelane** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa*), Priscilla Baker

Metal Nanoparticles modified Polysulfone membranes for water treatment

s2-015

**Keagan Pokpas** *(SensorLab, Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Emmanuel Iwuoha, Nazeem Jahed

An investigation of graphene-modified pencil graphite electrodes for the determination of trace metals by anodic stripping voltammetry

s2-016

**Sinazo Qakala** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Emmanuel Iwuoha

Development of Rapid Test Systems of Enzyme and Aptamer Nanobiosensors for Water Estrogens

s2-017

**Sudheesh Kumar Shukla** *(Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa)*, Omotayo Arotiba, Bhekie Mamba, Ajay Kumar Mishra

Application of *in situ* coupled Glucose Oxidase and Poly (propylene imine) Dendrimer for the Amperometric Detection of Glucose

s2-018

**Unathi Sidwaba** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)*, Fanelwa Ajayi, Emmanuel Iwuoha, Abongile Jijana

Development of methacrylate hydrogel nanobiosensor for phenolic endocrine disrupting compound, Bisphenol A

s2-019

**Vernon Somerset** *(NRE, CSIR, Stellenbosch, South Africa)*, Emmanuel Iwuoha, Bongiwe Silwana, Charlton Van der Horst

HRP Inhibition Based Amperometric Biosensor for the Detection of Heavy Metals

s2-020

**Ivan Svancara** *(Department of Analytical Chemistry, University of Pardubice, Pardubice, Czech Republic)*, Kurt Kalcher, Radovan Metelka, Karel Vytras

Years of Collaboration in the Middle Europe. Part I:Electroanalysis with Carbon Paste-Based Electrodes

s2-021

**Oluwakemi Tovide** *(Department of Chemistry, University of the Western Cape, Bellville, South Africa)*, Priscilla Baker, Emmanuel Iwuoha, Nazem Jahed

Graphenated–polyaniline Nanocomposite for Real Time Determination of Polyaromatic Hydrocarbons

s2-022

**Portia Tshikalaha** *(Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa)*, Omotayo Arotiba, Bhekie Mamba

A Dendrimer-Gold Nanocomposite based Immunosensor for the Detection of Cholera Toxin in Water

s2-023

**Charlton Van der Horst** *(Department of Chemistry, University of the Western Cape, Bellville, South Africa)*, Emmanuel Iwuoha, Bongiwe Silwana, Vernon Somerset

Synthesis and characterisation of bismuth-silver amalgam nanoparticles for electrochemical sensor applications

s2-024

**Abd Almonam Baleg** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa)* Nazeem Jahed, Priscilla Baker, Emmanuel Iwuoha

Impedimetry and microscopy of electrosynthetic poly(propylene imine)-co-polypyrrole dendritic star copolymer

# S3 Electrochemical Energy Technologies

s3-001

**Shahul Hameed Abdulrahman** *(Department of Chemistry, National University of Singapore, Singapore, Singapore)*, B.V.R. Chowdari, Mangayarkarasi Nagarathinam, M. V. Reddy, Martin Karl Shreyer, Jagadese J. Vittal

Oxalatophosphates: Novel Inorganic-Organic Hybrid Cathode Materials for Lithium Ion Batteries

s3-002

**Vincenzo Baglio** *(CNR, CNR-Institute of Advanced Energy Technologies (ITAE), Messina, Italy)*

Investigation of a Composite Anode Catalyst in Direct Methanol Fuel Cells

s3-003

**Henryk Bala** *(Department of Chemistry, Czestochowa University of Technology, Czestochowa, Poland)*

Hydrogenation and Corrosion Behavior of $LaNi_5$ Based Alloys with Nickel Partly Sybstituted by Zinc

s3-004

**Dmitri Bessarabov** *(DST HySA Infrastructure Center of Competence, North-West University, Faculty of Natural Science, CRB, Potchefstroom, South Africa)*

Transient Electrochemical Gas Permeability Measurements for PEM Fuel Cells and Electrolysers

s3-005

**Kwinda David** *(Department of Energy Materials, Council for Scientific and Industrial Research, Pretoria, South Africa)*

Electrochemical Performance of co-doped $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Ni, Co) Cathode Materials

s3-006

**Zachary M. Detweiler** *(Department of Chemistry, Princeton University, Princeton, USA)*, Steven Bernasek, Andrew B. Bocarsly

Mechanistic Study of the Heterogeneous Electrochemical Reduction of $CO_2$ at Anodized Indium Metal Electrodes

s3-007

**Anne Lutgarde Djoumessi Yonkeu** *(Department of Chemistry, University of Western Cape, Cape Town, South Africa*), Christopher Arendse, Abd Almonam Baleg, Emmanuel Iwuoha, Gcineka Mbambisa

Novel Poly(propylene thiophenoimine)-co-Poly(ethylenedioxythiophene)Composites of Naphthalene Diimide for Applications in Organic Photovoltaic Cells

s3-008

**Sakumzi Gwicana** *(Department of Chemistry, North West University, Potchefstroom, South Africa)*

PGM based $SO_2$ electrocatalysts for electrolytic hydrogen production

s3-009

**Pilwon Heo** *(Energy Lab, Samsung Advanced Institute of Technology, Yongin, Korea)*, Seong-Woo Choi, Kyoung Hwan Choi, Ki-Hyun Kim, Chanho Pak

Cross-linked polybenzimidazole / $Sn_{0.9}In_{0.1}P_2O_7$ composite membrane for high temperature PEMFCs

s3-010

**Mesfin Kebede** *(Department of Materials Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa),* Mkhulu Mathe, Kenneth Ozoemena, Maje Phasha

Synthesis of high capacity performing 1D-$SnO_2$ anode materials for Li-ion battery

s3-011

**Maria Kourasi** *(Faculty of Engineering and the Environment, University of Southampton, Southampton, United Kingdom)*, Richard Wills

Application of Heteropolyacids in Bifunctional Air Electrodes

s3-012

**Andries Kruger** *(Department of Natural Science, HySA Infrastructure, Potchefstroom, South Africa),* Dmitri Bessarabov, Jochen Kerres, Henning Krieg

Evaluation of novel PBI based membranes for $H_2$ production through $SO_2$ electrolysis

s3-013

**Niki Kunjuzwa** *(Department of Materials and Sciences, Witwatersrand/CSIR, Pretoria, South Africa)*, Neil J. Coville, Mesfin Kebede, Mkulu Mathe, Kenneth Ozoemena

Synthesis of High Energy Density Spinel $LiMn_2O_4$ Cathode for Lithium Ion Battery

s3-014

**Ofentse Makgae** *(Department of Material Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa)*, Patric Nonjola

Synthesis of Quaternary Ammonium Polysulfone-based $TiO_2$ Nanocomposite Anion-Exchange Membrane

s3-015

**Solomon Mamuru** *(Department of Chemistry, Adamawa State University, Mubi, Nigeria)*, Jeffrey Barminas, Alfred Onen, Kenneth Ozoemena

The Impact of Multi-walled Carbon Nanotubes on the Electrochemical and Electrocatalytic Properties of Iron(II)tetrakis(diaquaplatinum) octacarboxyphthalocyanine

s3-016

**Christiaan Martinson** *(Faculty of Natural Science, CRB, DST HySA Infrastructure Center of Competence, NWU, Potchefstroom, South Africa),* Dmitri Bessarabov, Kenny Uren, George van Schoor

Developing Current Switching Method to Evaluate Electrochemical Characteristics of a PEM Electrolyser

s3-017

**Noluthando Mayedwa** *(Department of Chemistry, University of the Western Cape, Cape Town, South Africa),* Emmanuel Iwuoha

Development of Platino-Iridium/Ruthenium Telluride Nanoalloy Electrode Systems for High Performance Ammonia Fuel Cell

s3-018

**Thobile Mhlabeni** *(Department of Energy Materials, The Council for Scientific and Industrial Research, Pretoria, South Africa)*, David Kwinda, Hongze Luo

Improved Electrochemical Properties of$xLi_2MnO_3 \bullet (1-x)LiMO_2$ by $LiCoPO_4$ Surface Treatment

s3-019

**Esterina Modica** *(CNR, CNR-Institute of Advanced Energy Technologies (ITAE), Messina, Italy)*

Ti Oxide Based Catalyst Supports for Low Temperature Fuel Cell

s3-020

**Alireza Moshfegh** *(Department of Physics, Sharif Univ. Tech., Tehran, Iran),* B Mahmoudi, O. Moradlou, Alireza Moshfegh, N. Naseri

Photoresponce of $Cu_2O$ loaded titania nanotube array in water splitting under visible light

s3-021

**Edith Mshoperi** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa)*, Ronen Fogel, Janice Limson

Analysis of the synergistic effect of carbon black and iron phthalocyanine cathode modification in microbial fuel cells

s3-022

**Kudzai Mtambanengwe** *(Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown, South Africa),* Sean Edwards, Ronen Fogel, Richard Laubscher, Janice Limson

Use of microbial fuel cells in the beneficiation of treated algal biomass for bioelectricity production

s3-023

**Nomthandazo Mutangwa** *(CSIR, Institution, Pretoria, South Africa),* Lukas le Roux, Mkhulu Mathe, Kenneth Ozoemena

Electrochemical Capacitors Based on Ultra-large Graphene Oxide and Graphene Sheets Integrated with Metallotetrapyrazinoporphyrazine

s3-024

**Sbongiseni Nkosi** *(Department of Chemistry, Tshwane University of Technologya, Pretoria, South Africa)*, Haitao Zheng

Synthesis of nanostructured $Li_4Ti_5O_{12}$ materials using $TiO_2$ nanoparticles

s3-025

**Nthabiseng Ntholeng** *(Energy Materials, Material Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa)*

Development of High Performance $LiNi_{0.5}Mn_{1.5}O_4$ Spinel

s3-026

**Chinwe Nwanya** *(Solar and Photovoltaic Unit, National Centre for Energy Research and Development, UNN, Nsukka, Nigeria)*, Paul M. Ejikeme, Fabian I. Ezema, Ogbonna U. Oparaku, Rose Osuji, Kenneth O. Ugwu, Paulinus Ugwuoke

Dye-sensitized solar cells using natural dyes extracted from Jathropha curcas and Citrus aurantium Leaves

s3-027

**Shahmahmood Obeidi** *(Institute of Physical Chemistry, MEET, University of Muenster, Muenster, Germany)*, Jan Holtmann, Alexandra Lex-Balducci, Stefano Passerini, Martin Winter

New ceramic separators for Li-ion batteries

s3-028

**Armelle Ringuedé** *(LECIME, CNRS - ENSCP Chimie ParisTech, Paris, France)*, Christel Laberty-Robert, Guillaume Muller

Reduction Mechanisms of Hierarchical Mesoporous Thin Films Anode (NiO-GDC) Fabricated by Sol-Gel Process – Application to Micro-SOFC

s3-029

**Matthias Schroeder** *(Institute for Physcal Chemistry, MEET, Westfälische Wilhelms University of Münster, Münster, Germany)*, Andrea Balducci, Stefano Passerini, Martin Winter

Soft Carbon as anode material for Lithium-Ion Capacitor

s3-030

**Bin Shao** *(Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan)*, Izumi Taniguchi

Synthesis of $Li_2MnSiO_4/C$ Nanocomposites for Lithium Battery Cathode Employing Sucrose as Carbon Source

s3-031

**Sayoko Shironita** *(Department of Materials Science and Technology, Nagaoka University of Technology, Niigata, Japan)*, Tsukasa Sakai, Minoru Umeda, Weiqi Zhang

Reaction Selectivity of Methanol and Oxygen at Pt/C Electrocatalysts Studied by Porous Microelectrode

s3-032

**Ralph Sueptitz** *(Department of Chemistry of Fuctional Materials, IFW Dresden, Dresden, Germany)*, Juergen Eckert, Fedor Fedorov, Annett Gebert, Kristina Tschulik, Margitta Uhlemann

Cobalt Hydroxide Nanowires Electrodeposited in Anodized Aluminum Oxide Templates for Supercapacitor Applications in Energy Storage Nanosystems

s3-033

**Ashton Swartbooi** *(Department of Materials Science and Manufacturing, CSIR, Pretoria, South Africa)*, Dawid Van Vuuren

Development of a High Pressure Solid Polymer Electrolyte (SPE) Electrolyser for the Production of Hydrogen

s3-034

**Thato Tshephe** *(Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa)*, Peter Olubambi, Kenneth Ozoemena, Iakovos Sigalas

Electrochemical Characteristics of Titanium-Manganese-Ruthenium Oxide Composite Electrodes for Electrochemical Capacitors

s3-035

**Shu Lan Wang** *(Wang, Northeastern University, Shenyang, China)*

Unique performance of SnO/Sn/ $Cu_6Sn_5$ three–layer anode for Li ion battery

s3-036

**Haitao Zheng** *(Department of Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR)*, Pretoria, South Africa)

Promotion of Pd/C catalyst for ethanol electro-oxidation by TiO2nanoparticles in alkaline media

# Abstracts of Plenary, Keynote, Invited Oral and Oral contribution presentations

# Electrochemical copper deposition technology in the electronic industry

Haruo Akahoshi
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Copper is the one of the key material in electronic circuit fabrication as a wiring material. Major application of copper electrochemical deposition in the early electronic industry was the printed wiring boards and its through-hole plating for making inter-layer electrical connection. In order to realize high-density wiring, small diameter deep interconnecting holes were required. Primary requirement for the copper deposition in those applications was uniform thickness inside the small holes and the board surfaces. Electroless copper deposition has intrinsic advantage on the uniformity of the deposits. Many attempts had been done to solve the drawback of the electroless copper deposition, instability and poor mechanical properties of the deposits. Proper selection of trace amount additives enabled to give superior mechanical properties and the formulation was applied on many types of circuit boards including very high density multilayer printed wiring boards for super computers. Those additives improved mechanical properties through promoting crystal growth by adsorbing to the plated copper surfaces. Mixed potential theory is a principal theory of the electroless deposition. However it is not always true on the local reaction. The influence of the additives on the local anodic reaction gives quite different results on the uniformity of plated copper thickness. Typical effective additives; Silicate and 2-2'bipyridine show quite opposite behavior on this point.

New movement on copper deposition arose in mid 90' accompanied with new application of copper sub-micron scale wiring on large scale integrated circuit. The feature of the new technology was non-uniform electrolytic copper plating called "super-filling" or "bottom up filling". Local deposition rate was controlled by local accumulation or depletion of adsorbing additives. This technology was extended for larger size via-filling build-up printed wiring boards and TSV (through silicon via) for 3D packaging. A prominent shape deposition and a selective trench filling were demonstrated using electrolytic copper plating solution with specially selected suppressing agent.

[1] Akahoshi, H., Kawamoto, M., Itabashi, T., Miura, O., Takahashi, A., Kobayashi, S., et al. (1995). *IEEE Transactions on Components, Hybrids, and Manufacturing Technology PART-A* , ***18***(1), 127-135.
[2] Haba, T., Suzuki, H., Yoshida, H., Akahoshi, H., & Chinda, A. (2010). *Electrochemical and Solid-State Letters,* ***13***(5), D23-D25.
[3] Nakano, H., Suzuki, H., Haba, T., Yoshida, H., Chinda, A., & Akahoshi, H. (2010). *Proceedings of the 60th Electronic Components and Technology Conference* 612-616.

# Electrochemical Studies of Nanoparticles

Richard G Compton, Emma Stuart, Yige Zhou, Neil V Rees, Edward O Barnes and Baptiste Haddou
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The chemical sensing of single metal nanoparticles (Ag, Cu, Ni, Au) via electroanalytical methods will be described. In particular experiments will be reported in which nanoparticles in solution impact an electrode held under potentiostatic control by virtue of their Borwnian motion. If the applied potential is sufficiently oxidising then the impact leads to current transients of *ca* millisecond duration in which the charge passed indicates the number of atoms in the nanoparticles since the oxidation is shown to be quantitative even for particles as large as *ca* 100 nm. In this way analysis of current time data allows the sizing of nanoparticles and the assessment of their concentration.

In further experiments the tagging of nanoparticle surfaces with electroactive groups and shown to allow the measurement of nanoparticle surface areas. Inferences about nanoparticle size are in good agreement with those from the former type of measurement.

Theory will be reported for the potential dependence of the oxidative current in the first type of experiment will be reported and shown to allow the measurement of the electrochemical rate constants for the metal oxidation reactions which will be compared with the corresponding values for bulk metals.

Last experiments in sea-water media will be reported and the methods shown to allow the monitoring of nanoparticle aggregation in real time.

Acknowledgments: Funding via the Leverhulme Trust is gratefully acknowledged as is collaboration with Mintek, Randberg, South Africa (Robert Tshikhudo, Jessie Pillay and Sibulelo Vilakazi)

# Highly-reversible Electrical Energy Storage: Technologies, Applications, and Societal Impact

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The use of stored energy, from fossil fuels for instance, is fundamental to the generation of electric grid power. To date, however, there has been infrequent use of highly-reversible energy storage to meet the instant demands of the grid, due primarily to the lack of cost-effective energy storage technology. And where such reversible energy storage is being used, it rarely is in the form of stored electricity but rather in the form of chemical energy (batteries), the form of gravitational energy (in an elevated water reservoir), or in the form of mechanical energy (spinning flywheel or compressed air in an underground cavern). With such storage, electricity must first be converted to the storage form then back again to electricity before use, creating conversion losses as well as wear-out, particularly for batteries because chemical storage reactions are generally not fully reversible.

Capacitors, on the other hand, store electricity directly and thus do not suffer losses from energy conversion. Furthermore, capacitor storage relies on physical rather than chemical processes, which are generally highly-reversible and provide long life. Capacitor storage is presently being used in a broad range of applications involving energy conservation, for instance in hybrid diesel-electric city transit buses, where efficiency and cycle life are important. Here vehicle kinetic energy is captured and stored in a capacitor bank during a stopping event and then reused later to accelerate the vehicle. In many applications, capacitor energy storage represents the lowest cost solution over all other available storage technologies.

This presentation first reviews electrochemical capacitor technology (sometimes referred to as supercapacitor or ultracapacitor technology) including types, performance, and comparisons with other storage technologies. Second, popular capacitor energy storage applications are presented. Third, capacitor energy storage for the electric grid is discussed. Development efforts directed towards creating multi-MWh-size capacitor storage systems are reported. Such systems are expected to become commercially available within two years and are projected to provide cost-effective energy storage for the utility power grid. Finally addressed is the potential impact to society of having affordable, highly-reversible grid-scale energy storage.

# Methods of Electrode Surface Modification Using Porphyrin type Molecules and Nanomaterials

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Porphyrin-type molecules such as phthalocyanines (Pcs) are employed as electrode modifiers in order to enhance electrode activity [1]. Nanomaterials such carbon nanotubes (CNTs), quantum dots and metal nanoparticles are employed together with Pcs to enhance electrode activity due to the synergistic effect of these nanomaterials with Pc molecules. Methods of electrode modifications using Pcs alone or the nanocomposites include self-assembled monolayer formation, polymerization, adsorption, grafting or click chemistry. Characterization of the conjugates or surfaces modified by conjugates will be discussed. Methods of characterization include voltammetry, X-ray photoelectron spectroscopy, scanning electrochemical microscopy and other microscopic techniques. The applications of the nanocomposites as electrocatalysts will be discussed.

Reference

1. T. Nyokong in $N_4$-macrocyclic metal complexes: electrocatalysis, electrophotochemistry, and biomimetic electrocatalysis (Eds. J.H. Zagal, F. Bedioui, J-P. Dodelet)

# Lithographically Patterned Nanowire Electrodeposition (LPNE): Advances and Applications

Reginald M. Penner
*Department of Chemistry,*
*Department of Chemical Engineering and Materials Science,*
*and Center for Solar Energy,*
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In this talk we describe a high-throughput method called Lithographically Patterned Nanowire Electrodeposition (LPNE) for patterning the electrodeposition of nanowires onto dielectrics such as glass and polymer surfaces. Photolithography is used to prepare a sacrificial nickel or gold nanoband electrode that is located within a horizontal trench with a width in the 300 nm range. This nanoband electrode can have any two-dimensional pattern on a flat surface. The height of the trench defines the height of the nanowire as it is electrodeposited, and the quantity of electrodeposited material determines the width of the nanowire. Minimum dimensions of 20 nm (height) and 50 nm (width) are obtainable for a variety of electrodeposited materials using LPNE. Many centimeters of nanowire can be patterned onto a glass surface using a single series of LPNE processing steps, providing for ultra-high throughput nanowire fabrication.

LPNE provides a means for preparing nanowires of virtually any material that can be electrodeposited from aqueous solutions. At present, the list of materials we have explored includes metals (Pt, Au, Pd, etc.), metal oxides ($MnO_2$), II-VI semiconductors (CdSe, CdTe), thermoelectric materials ($Bi_2Te_3$, PbTe), and electronically conductive polymers (e.g., PEDOT). In this talk, I'll discuss the state-of-the-art and the key challenges associated with LPNE. One of the challenges is the polycrystalline nature of our electrodeposited nanowires. I'll also illustrate applications for LPNE nanowires related to the detection and emission of light, the preparation of biosensors for cancer makrers and chemical sensors for gases, and as battery cathode materials.

# DST HySA Infrastructure Center of Competence: Hydrogen Production and Storage. From Materials to Hydrogen Systems: An Overview

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The Department of Science and Technology of South Africa developed the National Hydrogen and Fuel Cells Technologies (HFCT) Research, Development and Innovation (RDI) Strategy. The National Strategy was branded Hydrogen South Africa (HySA). The overall goal of HySA is to develop and guide innovation along the value chain of hydrogen and fuel cell technologies in the Republic. The overall vision of the HFCT RDI strategy is to bring about wealth, job and IPR creation through the initiation of new high technology industries based on minerals found on South African soil, especially Platinum Group Metals (PGMs). Allied to this is the goal of the developing cost competitive solution for the generating hydrogen locally focusing on using renewable energy, and the supporting enabling goal of developing a range of high-level skills, generally in accordance with the required human capital development strategy.

HySA has been established consisting of three Centers of Competence - HySA Infrastructure, HySA Catalyst and HySA Systems. The HySA Infrastructure (Hydrogen Production, Storage and Delivery) Center of Competence, HySA Infrastructure in shot, co-hosted by the North-West University (NWU) and Council for Scientific and Industrial Research (CSIR).

The mission of the HySA Infrastructure is to deliver cost-effective technologies for hydrogen production (linked to renewable energy), storage and distribution. The overall aim is to become a significant player in the renewable hydrogen production and storage R&D leading to the development and application of new products, hydrogen storage materials and processes which improve the competitiveness of South African industry and the quality of life of all South Africans.

Our technical objectives include development of hydrogen generation systems and prototypes linked to renewable energy sources as well as hydrogen storage and distribution technologies. Research and development at HySA Infrastructure is driven by the products needs and focused on product development. The overview will be given for the following Key Technologies: PEM Electrolysers and electrolyser systems linked to renewable energy (water and depolarized electrolysis), PEM electrolysers characterization tools, electrochemical hydrogen compression (EHC) and separations, hydrogen storage.

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D. Bessarabov et al., Hydrogen Infrastructure within HySA National Program in South Africa: road map and specific needs, *Energy Procedia*, 29 (2012) 42

# Electrochemical biosensors and Biomedical Circuits and Systems

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Integrated electrochemical Nano-Bio-Sensors [1] for diagnosis and/or treatment of patients with specific physiological conditions (e.g., heart, cardiovascular, cancer diseases) or convalescents is a key factor to provide better, more rationale, effective and ultimately low-cost health care also at home. The ultimate goal of improved health care on those subjects is the extension of the patients' autonomy, the possibility for auto-monitoring, the improvement of their comfort levels and their integration into everyday life. On-line monitoring is also required in professionals and recreational sportsmen training, as well as in elderly and/or disabled citizen care and/or people involved in public utilities (e.g. the public-transportation drivers). For those, it is a key aspect the maintenance of their safety by through embedded systems to alert emergency services in the event of a potentially dangerous situation. Some systems for on-line monitoring are available in the market. They use wearable devices (accelerometers, heartbeat monitoring system, etc). However, all these systems do not measure the human metabolism at molecular level (metabolites). The only available real-time, implantable/wearable systems for metabolic control are limited to glucose monitoring and used only for diabetic patients. However, electrochemical sensors may address so many other molecules, which have crucial relevance in human metabolism in chronic patients. So far, there are no available integrated nano-bio-systems for multi-metabolites, real-time, remote monitoring of the human metabolism. Thus, the aim of this keynote speech is to present an innovative concept for multi-panel, highly integrated, fully implantable, remotely powered and real-time monitoring systems for human metabolism at molecular level. The considered metabolic molecules will be glucose, lactate, glutamate, ATP [2], and anticancer drugs as well as anti-inflammatory ones [3]. In case of drugs, the specificity of electrochemical sensors is improved at system level [4]. The proposed nanotechnology will be based on carbon nanotubes to improve the sensors performance [3, 5]. To pursue their detection, innovative VLSI solutions [6] are discussed including the system remote powering [7]. The new approach is obtained by integrating nano/bio/micro/CMOS/SW/RF systems in three devices: (i) a fully implantable sensors array for data acquisition; (ii) a on-skin intelligent-patch for remote powering and signal processing; (iii) a wearable station (a mobile phone) for data collection, elaboration and storage. The major presented breakthroughs are in the areas of: (i) nano-sensors; (ii) signal analysis; (iii) HW/Bio co-design; (iv) multi-panel metabolites detection; (v) fully implantable sensors; (vi) remote powering; (vi) minimally-invasive biomedical implants.

# Pathway to low-cost metallization of silicon solar cell through understanding of the silicon metal interface and plating chemistry

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Metallization is crucial to silicon solar cell performance. It is the second most expensive process step in the fabrication of a solar cell. In order to reduce the cost of solar cell, the metallization cost has to be cut down by using less metal without compromising the efficiency. Screen-printing has been used in metallizing the commercial solar cell because of the high throughput and low cost at the expense of performance. However, because of the variability in the screen-printed gridlines, the amount of Ag metal used cannot be controlled. More so, the dependence of the contact resistance on doping necessitates the use of low sheet resistance emitters, which exacerbates losses in the blue response and hence the efficiency. To balance the contact resistance and improve blue response, several approaches have been undertaken including, use of Ag pastes incorporating nanoparticle glass frits that will not diffuse excessively into a lightly doped emitter, Ni plating on lightly doped emitter through SiNx dielectric plus NiSi formation followed by Cu and/or Ag plating, light induced plating (LIP) of Ag or Cu on fired through dielectric metal seed layers formed by aerosol or inkjet or screen-printing. All these approaches require excellent adhesion and gridline conductivity to minimize the total series resistance, which impedes the collection of electrons. This paper presents the issues and the pathway to achieving high efficiency using low cost metallization technology involving inkjet-printed Ag fine gridline having 38 μm width and 3 μm height fired through the SiNx followed by Ni and Cu plating. A comprehensive analysis of silicon/metal interface, using high precision microscopy, has shown that the investigated metallization technology is appropriate for the longevity of the device.

# Smart Nano-Dimensional Dendritic Aptasensor and Quantum Dots-Linked Estrogen Receptor Alpha-Recombinant Protein Biosensor for Real-Time Determination of Estrogenic 17β-Estradiol

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17β-estradiol (E2) is the most potent estrogenous endocrine disrupting chemical (EDC). The Food and Agriculture Organisation (FAO) of the United Nations's acceptable daily intake (ADI) of E2 through all sources is 0.05 μg/kg body weight. Very sensitive techniques are, therefore, required for real time determination of E2. Due to the high specificity of receptors and aptamers for their analytes, they have been used in this study to construct ultrasensitive sensor systems for the determination of E2. In the first design a novel quantum dots-biosensor (Au|L-Cyst|SnSe-MPA-QDs|ER-α) was developed on L-cysteine (L-Cyst)-functionalised gold (Au) platform on which mercaptopropionic acid (MPA)-capped tin selenide (SnSe) quantum dots (QDs) and estrogen receptor α-recombinant protein (ER-α) were incorporated. Physiologically the ER-α's ligand binding domain at its c-terminus binds preferentially to 17β-estradiol. In the second design an electrochemical dendritic DNA aptasensor for the determination of E2 was constructed with a 76-mer biotinylated DNA aptamer conjugated to a nano-dimensional generation 2 poly(propylene thiophenoimine)-co-poly(3,4-ethylenedioxythiophene) dendritic star copolymer (G2PPT-co-PEDOT). The 76-mer biotinylated DNA aptamer was synthesised by Systematic Evolution of Ligands by Exponential Enrichment (SELEX). The response dynamics of the sensors were studied by square wave voltammetry (SWV), Bode electrochemical impedance spectroscopy (EIS) and Hall-effect analysis. The response parameters of the sensors showed that they were more sensitive than most other techniques including dissociation enhanced lanthanide fluorescence immunoassay (DELFIA), enzyme-linked immunosorbent assay (ELISA), yeast estrogen screen (YES) and bis(trimethylsilyl) trifluoroacetamide derivatisation (BTD) method.

# Transition Metal Oxide Based Materials for Cathode of PEFCs

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Polymer electrolyte fuel cells are expected for the residential and transportable applications, due to their high power density and low operating temperature. However, a significant cost reduction is needed especially for fuel cell vehicles.

We have reported that partially oxidized group 4 and 5 metal carbonitrides were stable in an acid solution and had a definite catalytic activity for the oxygen reduction reaction (ORR). We have tried to apply group 4 and 5 metal oxide-based compounds to the cathode catalyst. In this paper we will report our recent results of non-precious metal oxide based cathode, mostly partially oxidized Ta and Zr compounds.

Ta and Zr compounds were heat-treated at 800-1200°C under different flowing rate of the $H_2/N_2$ gas mixtures that containing small amount of oxygen to obtain specimens with different oxidation state. After heat treatment, original materials changed to oxides that contained small amount of carbon and nitrogen.

Heat treated powder was mixed with alcohol, Ketjen Black and Nafion. The mixture was dipped on a glassy carbon rod (5 mm diameter) and the working electrode was made. All electrochemical measurements were examined in 0.1 M $H_2SO_4$ at 30°C under atmospheric pressure using a conventional 3-electrode cell. Slow scan voltammetry (scan rate: 5 $mVs^{-1}$) was performed under $O_2$ and $N_2$ atmosphere to obtain the current for the oxygen reduction reaction (ORR).

The catalytic activities of our materials strongly depended on the degree of oxidation (DOO). An appropriate oxidation of materials is essential to have a definite catalytic activity for the ORR. Among these materials, partially oxidized Ta carbonitride (Ta-CNO) and Zr carbonitride (Zr-CNO) had high catalytic activity for the ORR. The onset potentials of them were almost reaching 1.05 V vs RHE that is the onset potential of commercial Pt-C. In the next step, in order to increase current density of ORR, we are trying to use many kind of starting materials, such as metal complexes which contain nitrogen and carbon. The results will be presented at the meeting. Although there is still some difference in the ORR activity from Pt/C catalyst, these materials have great potential for PEFC cathode.

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# Updates on novel electrode materials for Li-ion batteries

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Lithium ion batteries (LIBs) are promising energy storage devices used in portable electronic devices due to high energy density, less self-discharge rate and long shelf-life compared to Ni-MH and Ni-Cd cells. For high-power applications like, back-up power supplies and electric/hybrid electric vehicles, the LIBs need to satisfy several criteria namely, cost-reduction, improvement in the energy density, safety-in-operation at high current charge/discharge rates and improvement in the low-temperature-operation. To satisfy the above conditions researches are being carried out worldwide to find alternative novel low cost, environmental friendly electrode materials. In my talk, i will discuss our recent results novel electrode materials based on intercalation, alloying-de-alloying and conversion and alloying-de-alloying reactions. N,F-doped TiO$_2$, (M$_{1/2}$Sb$_{1/2}$Sn)O$_4$ (M= V,Sn,Sb), MN M= Co,Cr, V and ZnCo$_2$O$_4$ anodes and layered cathodes Li(CoxNiy)O$_2$, LiVPO$_4$F and hybrid inorganic-organic open framework materials. Materials were prepared by various chemical methods. They were well characterized by Rietveld refinement X-ray diffraction, Scanning electron microscope, Transmission electron microscopy, XPS, IR, Raman, density and BET surface area methods. Electrochemical studies were evaluated by cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical spectroscopy techniques

Key words: Anodes; Cathodes; Lithium ion batteries; Electrochemical impedance spectroscopy; characterization technique.

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# Theoretical Aspects of Pulsed Electrochemical Micromachining

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A first principles model is herein presented aimed at simulating the initial stages of pulsed electrochemical micromachining, ECμM, as introduced by Schuster et al. over a decade ago (Schuster et al. *Science* **2000,** 289, 98-101). Our strategy is based on finding solutions to the equations that govern mass transport of all solution phase species coupled to Poisson's equation for the electrostatic potential in solution subject to boundary conditions that relate the potential across the tool|electrolyte and workpiece|electrolyte interfaces to the rates of heterogeneous electron transfer. This complex problem including its moving boundary aspects was solved using COMSOL without assuming an *a priori* separation of double layer charging and Faradaic processes. The results obtained for a Pt tool and Cu workpiece employing conditions similar to those specified by Schuster et al. in their original work were found to be in good agreement with those obtained experimentally.

# Bioelectroanalysis. Design of electron-transfer pathways as a basis for biosensors and biofuel cell electrodes

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The development and application of biosensors and (miniaturized) biofuel cells is based on the fundamental understanding of the properties of the complex molecular architecture of the sensing interface and especially on the design of optimized electron transfer pathways between immobilized enzymes and the electrode surface.

Over the past years we have developed strategies for the synthesis of specifically designed redox polymers, in which we can vary the properties of the polymer backbone as well as the nature and redox potential of the polymer attached redox mediator. By design of the coordination shell of octahedral Os-complexes or the selection of organic redox compounds we are able to predesign the redox polymers that they are optimally adapted to an enzyme which is used as biocatalyst and selective recognition element in biosensors and biofuel cells electrodes.

The presentation will focus on the design and the properties of the redox polymers using combinatorial synthetic approaches, the design of biolelectrochemical interfaces by combining nanostructured electrode materials with a variety of redox enzymes and the mentioned redox polymers. Design concepts for biosensors and biofuel cells are proposed.

# E-ALD of Pd on Au Single Crystals

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Studies of the adsorption and absorption of hydrogen on nanofilms of Pd formed on Au substrates will be discussed. The electrochemical analog of atomic layer deposition (ALD), E-ALD, has been used to form films with from 0.5 ML to 50 ML thickness. The chemistry used to form the films will be briefly described. The thinner films allowed characterization of the hydrogen waves on Pd, with minimal interference from the absorption process. To better characterize the dependence of the hydrogen waves as a function of surface structure, single crystal Au substrates have been used to grow the Pd films. It is evident from these studies that the adsorption of hydrogen is strongly dependent on surface structure, and the history of the electrode. Scanning tunneling images were collected in-situ during several cycles of surface limited redox replacement, used to grow the film. Those results support the layer by layer growth model.

# Introducing "Electrocatalytic Frustrated Lewis Pairs" for Hydrogen and Small Molecule Activation

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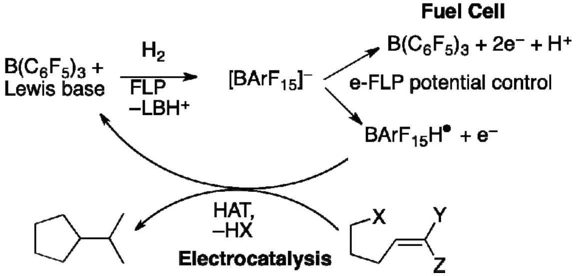

Since their introduction by the pioneering work of Doug Stephan's group,[1] the concept and reactivity of "frustrated Lewis pair" (FLP) chemistry continues to be explored at a phenomenal rate. Conventional FLP chemistry can be used to heterolytically cleave $H_2$ using a suitable sterically hindered Lewis acid/base combination. Activation of small organic molecules such as imines, carbonyls, alkenes and even $CO_2$,[2] is then achieved by coupled proton/hydride transfer, but requires suitably reactive substrates and is usually stiochometric.[2] Our pioneering approach is to combine FLP cleavage of hydrogen with electrochemical oxidation of the resulting Lewis acid-hydride intermediate. Using the archetypal FLP systems $B(C_6F_5)_3$ and $(^tBut)_3P$ we have demonstrated e-FLP activation ***catalytically*** generates either a reactive source of H• (1-electron process) for hydrogen atom transfer (HAT) reactions and small molecule activation; alternatively, by selecting a different applied potential, the hydride can undergo a 2-electron oxidation to effect overall conversion of $H_2$ into 2-electrons and 2-protons with obvious metal-catalyst-free energy applications. The parent Lewis acid is regenerated in either case.
Electronic, steric and electrode substrate effects on the mechanism and kinetics of the electrochemical reactions are also presented.[3,4]

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# $TiO_2$ nanotube photoanodes modified by electrodeposited $Cu_2O$ and $Fe_2O_3$: optimization of photoconversion efficiency

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The conversion of solar energy to hydrogen via photoelectrochemical water splitting is a possible route to satisfy the global need for renewable and clean energy [1]. $TiO_2$ nanotube arrays can be formed by scalable and low energy intensity processes such as electrochemical anodization, and exhibit properties of interest for photoelectrochemical applications, including high surface area, 1D charge transport, and stability in solution and under irradiation [2]. A main challenge towards the use of $TiO_2$ as a photoanode is the wide bandgap (Eg = 3.2 eV), which limits absorption of sunlight to the UV range. In order to extend the absorption spectrum, $TiO_2$ nanotube arrays were modified by electrodeposition of the semiconductor oxides $Cu_2O$ and $Fe_2O_3$ (bandgap ~2.1eV), resulting in sensitization in the visible and a 100% increase in photocurrent conversion [3-4]. To further enhance the efficiency, an improved understanding of the electrochemical and electronic structure of these materials is needed. $Cu_2O/TiO_2$ and $Fe_2O_3/TiO_2$ photoanodes were characterized using the Mott-Schottky technique, to obtain flat band potentials and doping concentrations. Furthermore, the effect of the water concentration in the anodization electrolyte on the photocurrent efficiency of $TiO_2$ nanotubes was investigated: 11 vol% water in ethylene glycol resulted in the highest quantum efficiencies in the UV range. Finally, we investigated various $TiO_2$ nanotube surface cleaning processes to enhance the contact between the semiconductor sensitizers and the $TiO_2$ support, which resulted in an additional enhancement of the efficiency.

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# Performance of Electrochemical Capacitors with Microporous Carbon Electrodes in New Types of Aqueous Electrolytes

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A recent trend in the construction of electrochemical capacitors (ECs) is to utilize safe, cost effective and environmental friendly materials. In this sense, ECs based on neutral aqueous electrolytes using activated carbon electrodes have been investigated in recent years [1-3].

We have investigated a range of 1 mol.L$^{-1}$ sulphate solutions ($Li_2SO_4$, $Na_2SO_4$, $MgSO_4$, $K_2SO_4$, $Al_2(SO_4)_3$, $BeSO_4$ and $(NH_4)_2SO_4$) in three- and two-electrode cells, taking into account the wettability of microporous carbon electrodes at room temperature. The highest power has been observed with the less solvated potassium ions (from $K_2SO_4$), in good agreement with the contact angle measurements.

The electrochemical characteristics, i.e., capacitance, resistance, efficiency and self-discharge of supercapacitors have been evaluated by floating at room temperature. From these measurements, we can conclude that these electrochemical capacitors can operate with high efficiency up to 1.6V. However the stability window is limited in case of $Al_2(SO_4)_3$ and $BeSO_4$ due to the very low pH values. The results show that such kind of electrochemical capacitors are promising environment friendly energy storage systems for future.

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# Characterization and Application of Quantum dots (CdTe@ZnS)-colbalt tetraamino-phthalocyanine Nanoconjugates as Luminescence sensor for superoxide anion

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Quantum dots (QDs) are of interest for research and practical applications because of their high surface-to-volume ratio, narrow emission wavelength, broad absorption spectra and their quantum confinement. Encapsulating core CdTe QDs into an inorganic shell such as ZnS, as used in this work (denoted as CdTe@ZnS) have been reported to reduce the toxicity of QDs core containing cadmium chalcogenide materials. It has also been indicated that the fluorescence quantum yields improve once the shell is deposited around the core. The optical properties of QDs, makes them unique nanomaterials for multiplex and ultrasensitive applications in optical sensor technology [1]. However, to fully exploit their properties, surface modification of the QDs using macrocylic compounds such as cyclodextrin, crown ether, porphyrin and calixarene in well-defined non-covalent or covalent interactions to form the specific host-molecule complexes has garnered considerable interest [2,3]. Therefore, in order to explore novel strategies for the surface modification of QDs for tailored sensor delivery with improved sensitivity and selectivity, we report here on the conjugation of thiol-capped CdTe@ZnS QDs to colbalt tetraamino-phthalocyanines (CoTAPc). The nanoconjugate is tested for its ability for sensing superoxide anion $O_2^{\bullet-}$. $O_2^{\bullet-}$ is a reactive oxygen specie, formed as a reduced intermediate of molecular oxygen through enzymatic reactions associated with normal metabolism, but has been reported to be associated with various pathological conditions. The conjugation of CoTAPc to CdTe@ZnS QDs for the fluorescence recognition of $O_2^{\bullet-}$ is reported here for the first time.

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# A poly (8-anilino-1-naphthalene sulphonic acid) silver nanoparticulate modified bioelectrochemical nanobiosensor system for the analytical determination of rifampicin

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Rifampicin is a first-line antitubercular drug effective against actively growing *Mycobacterium tuberculosis.* Resistance of the mycobacterium to rifampicin among tuberculosis (TB) patients results from inadequate or inappropriate dosing of treatment or using low quality medication. It is therefore necessary to develop reliable methods for determining the rifampicn metabolic profile of patients at point of care for proper dosing. Herein an efficient rifampicin bioelectrochemical nanosensor device is illustrated. It consists of cytochrome P450-2E1 (CYP2E1) immobilised on electroactive nanocomposites of poly (8-anilino-1-napthalene sulphonic acid) (PANSA) and silver nanoparticles (AgNPs) stabilized in polyvinylpyrrolidone (PVP). The performance of the rifampicin nanobiosensor (Au/AgNPs-PANSA/CYP2E1) was interrogated amperometrically. The biosensor gave a dynamic linear range of 2-14 µM, a sensitivity of 1.40 µA/µM, detection limit of 0.05 µM and the parameters $K_M$, $K_M^{app}$ and $I_{MAX}$ were estimated to be 5.0 µM, 1.25 µM and 1.78 x $10^{-6}$ µA respectively. The peak serum concentration of RIF of 5 µg/mL (6 µM) obtained 4 - 8 hr after administration of 600 mg rifampicin, was found to be within the linear range of the nanobiosensor, suggesting that the nanobiosensor can be applied to systems with concentrations from 0.05 µM and above; thus making it suitable for the determination of rifampicin in serum.

# Bismuth Modified Exfoliated Graphite Electrode Platform for the Voltammetric Detection of Arsenic in Water

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Arsenic has become a priority pollutant owing to its very high toxicity and numerous sources which include naturally occurring minerals and mining activities. Although several reports on the electrochemical detection of arsenic using stripping voltammetry exist, the quest for electrodes or modified electrodes that can yield a lower detection limit is ongoing. These electrodes should also possess intrinsic selectivity towards other heavy metals interferences. In line with this quest, we present the sensing of arsenic on a bismuth modified exfoliated graphite electrode. Bismuth film was electrodeposited onto an exfoliated graphite (EG) electrode by holding the potential at -600 mV in 0.1 M $HNO_3$ supporting electrolyte containing 5 mM $Bi_2O_3$. Modification of the electrode resulted in an increase in the electroactive surface area and consequently peak current enhancement in $Ru(NH_3)_6^{+2/+3}$ redox probe. The redox reaction of $Ru(NH_3)_6^{+2/+3}$ was also diffusion controlled as confirmed by cyclic voltammetric experiments. The electrochemical response of As (III) was first investigated on the EG-Bi electrode using cyclic voltammetry. Square wave anodic stripping voltammetry was performed with the modified electrode in As (III) solutions and the peak current was proportional to As (III) concentration. A detection limit of 5 µg $L^{-1}$ was obtained from a pre-concentration time and potential of 180 s and -600 mV respectively. The obtained detection limit is lower than the WHO recommended arsenic limit of 10 µg $L^{-1}$ in water, making this method suitable for field application. No measurable reduction in analytical performance of the modified electrode was observed in the presence of other heavy metal ions except copper.

Keywords: arsenic, exfoliated graphite, Square wave anodic stripping voltammetry, bismuth modified electrode

# Sulfonated Polysulfone-based Membranes for PEM Electrolyzer Applications

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A Polymer Electrolyte Membrane (PEM) based on non-perfluorinated polymers as an alternative to Nafion was investigated for application in a PEM water electrolyzer.The sulfonated polysulfone (SPSf) was synthesized using trimethyl silyl chlorosulfonate as the sulfonating agent in a homogeneous (solution) phase of chloroform.

A single cell PEM electrolyzer was investigated by polarization, impedance spectroscopy and chrono-amperometric measurements. The single cell based on non-perfluorinated polymer was compared to a cell with Nafion 115 membrane. Concerning MEA preparation procedure, an $IrO_2$ oxygen evolution catalyst was directly deposited onto one side of the membrane by a spray-coating technique.The anode catalyst loading was 2.5 mg $cm^{-2}$. A Ti mesh (Franco Corradi, Italy) was used as the backing layer. A commercial 30% Pt/Vulcan XC-72 (ETEK, PEMEAS, Boston, USA) was used as the catalyst for the $H_2$evolution.The cathode was spread on a carbon cloth backing layer (GDL ELAT from ETEK) with a Pt loading of 0.6 mg $cm^{-2}$.The electrochemical activity of these MEAs was analyzedin a temperature range from 25 °C to 80 °C.

The results indicate promising performance of polymer electrolyte membrane based on sulfonated polysulfone for application in a PEM electrolyzer.

Acknowledgment

The research leading to these results has received funding from the European Community's Seventh Framework Programme (7FP7/SP1-JTI-FCH.2011.2.7) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement ELECTROHYPEM n° 300081.

# Label free domoic acid detection at novel polyamic acid based immunosensor systems

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Domoic acid (MW 310 g/ml) is a neurotoxin which causes amnesic shellfish poisoning (ASP), and can bioaccumulate in marine organisms such as shellfish, anchovies, and sardines that feed on the phytoplankton known to produce this toxin. Unfortunately domoic acid is not destroyed by cooking or freezing and ingestion causes severe allergic reactions in some people. A maximum permitted level of 20 ppm domoic acid in whole shellfish has been adopted by many countries (including Canada, New Zealand, Northern USA).

Novel immunosensor platforms have been prepared by co-polymerisation of polyamic acid (PAA) and with polypyrrole (Ppy). The voltammetric evaluation of the PAA-Ppy composites indicated that the amine and carboxylic acid electrochemistry was retained in the electrochemical signature of the composite but that diffusion was attenuated by incorporation of the Ppy. Spectroscopic evidence (Raman and FTIR) and morphology (AFM and SEM) confirmed the equilibrium composition of a novel composite platform. C=O and C-N strectches (1800-2000 $cm^{-1}$) as well as N-H stretching frequencies (3800 $cm^{-1}$) observed in the spectrum of the equilibrium composite.

Domoic acid antibody was immobilised on the PAA/Ppy platform by incubation and the resultant immunosensor showed a highly selective response to domoic acid (PBS, pH=7). The antibody antigen binding event was characterised by an oxidation peak at 761 (vs Ag/AgCl) not evident in the absence of domoic acid. A decreasing trend in oxidation peak current at domoic acid concentrations in the lower micromolar range, was observed with good correlation in the calibration curve ($r^2$= 0.9925). This was corroborated by an increase in the admittance response of the immunosensor to domoic acid in the same concentration range. Immunosensor response and mechanism of electrochemical interaction will be discussed as well immunosensor response to real samples of commercially available shell fish.

Keywords: Immunosensors, toxins, shell fish, admittance, real sample analysis.

# $H_3PO_4$ Doped Polybenzimidazole (PBI)-Based Membranes For Direct Methanol Fuel Cell-Internal Combustion Engine Hybrid Systems

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Proton exchange membrane fuel cells (PEMFCs) are suitable for the requirements of mobile applications:low temperature operation allows for arbitrary interruption of operation without major energy losses and the specific power is significantly higher than that of the other fuel cells (FCs). The methanol crossover is still one of the major obstacles for a commercialization of PEM- direct methanol fuel cell (DMFC) leading to a serious decrease in the cathode performance, thus, to a loss in overall FC efficiency. Nafion® is the membrane material of choice for most FC applications. However, Nafion is costly and does not work particularly well in a DMFC because of its high methanol permeability (crossover). Methanol, that is not oxidized electrochemically at the anode, permeates through the membrane and is oxidized chemically by oxygen (from air) at the cathode, resulting in significant FC performance degradation. Therefore, there is extensive literature related to the development of new membrane materials with reduced methanol permeability, such as phosphoric acid-doped polybenzimidazole (PBI). So far, $H_3PO_4$-doped PBI membranes suggested for FC applications is one of the most successful polymer membranes. Methanol crossover rate is lowered by one order of magnitude in comparison to Nafion. PBI is an amorphous thermoplastic polymer with a glass transition temperature of $425–436^{0}$C. It is determined that the methanol crossover rate by permeation measurements to be less than 10 mA cm$^{-2}$ at 150°C and a 50/50 methanol/water feed.

On the other hand, the combination of different power sources like an engine, a battery or a FC to meet a single propulsion demand constitutes a hybrid system. The hybrid electric vehicle (HEV) is such a hybrid configuration. Apart from regenerative breaking, a HEV increases the efficiency by reasonable load leveraging between an internal combustion engine (ICE) and a battery, which have inverse efficiency characteristic with respect to load. In this study, the operation of a DMFC, containing $H_3PO_4$- doped PBI, with an ICE in a hybrid system is investigated in terms of fuel efficiency. The current work has a potential for fuel saving because the engine’s waste heat is utilized in pre-conditioning of methanol for the FC and in postconditioning of the FC’s anode exhaust for the engine. The operation of the cell at higher temperature with PBI membranes improves catalyst activity and mass transfer increasing cell efficiency. But the fuel feed to this type of membrane must be in vapor phase. Methanol solution can be evaporated by the engine coolant. The endothermic reaction enthalpy for this conversion is recovered from engine’s exhaust gas. The system efficiency increases with the cell’s fuel utilization, as long as the cell’s efficiency is higher than the engine’s efficiency. To increase the system efficiency with load, the current density of the FC should not be increased beyond the point where where the cell and engine efficiency meet.

# Anodic electrochemical etching of ZnO:Al thin films for solar cell applications

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Doped zinc oxide is a wide bandgap semiconductor which is widely used as a transparent front electrode in optoelectronic devices such as thin-film solar cells. Among the various types of transparent conductive oxides (TCOs), aluminum-doped zinc oxide (ZnO:Al) has the advantage of high stability against hydrogen plasma, very high charge carrier mobilities, and high transmission of light in the visible and near infra-red wavelength range. In addition, it can easily be roughened for light scattering purposes due to its good etching properties [1].

This contribution focusses on the texturing of sputter-deposited ZnO:Al thin films by means of anodic polarization in an aqueous electrolyte at potentials around +2 V vs. standard hydrogen electrode [2]. The polycrystalline structure of the ZnO:Al gives rise to lattice defects and grain boundaries within the material. This structural heterogeneity affects its optoelectronic properties and its etching behavior. We found that the grain boundaries are preferred etch sites and propose a mechanistical model which explains the heterogeneous dissolution process of these layers.

Moreover, the selectivity of the electrochemical etching process allows for the analysis of the chemical composition of the grain boundaries. We found a pronounced change in the Al concentration at the grain boundaries as compared to the bulk material. The investigations might give hints for the effect of the grain boundaries on the electronic conduction mechanisms in the material.

The anodic surface texturing was conducted in different electrolytes under various conditions and different resulting structures were observed. An interpretation of the different dissolution processes is developed. The resulting layers were extensively investigated regarding their morphological, optical and electronic properties.

Furthermore the electrochemical treatment was combined with chemical etching in HCl. The resulting topographies have proven to be beneficial for the utilization as front contacts in Si thin film solar cells due to their very good light scattering ability.

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# Cyclability improvement of Si/C composites for Li-ion batteries prepared from polyvinyl alcohol

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With a theoretical capacity of 3580 mAh/g (corresponding to the $Li_{15}Si_4$ alloy), silicon appears as a promising anode material for lithium-ion batteries in replacement of graphite (372 mAh/g). However, the lithium insertion into silicon is accompanied by a high volumetric expansion (~280%), leading to the disintegration of particles and loss of contact with the current collectors during charge/discharge cycling; the reversible capacity decreases while the irreversible one increases.

Silicon/carbon (Si/C) composites have been proposed in literature to tentatively solve these problems. The carbon matrix in which silicon is dispersed is able to accommodate the repeated volume changes and to improve the electrical contacts. Although promising properties of these composites are often described, most of the suggested solutions are not adapted for applications, in particular because the electrodes thickness is generally very low.

In this presentation, polyvinylic alcohol (PVA) has been used as water soluble and environment friendly precursor to coating silicon nanoparticles by the spray drying technique. Then PVA is cross-linked by oxidative treatment in air at 200°C and the composite is further pyrolyzed at 1050°C under nitrogen flow to get a Si/C composite. Compared to a Si/C composite without cross-linking step of PVA, the carbonisation yield is considerably enhanced and the cycleability of electrodes with PVDF binder as-well.

In another set of experiments, the Si/PVA composite has been carbonised in presence of a small amount (<5wt%) of iron. Using Raman spectroscopy, it is shown that iron plays as a graphitisation catalyst which favours the development of an ordered carbon structure of high electrical conductivity. This type of carbon also leads to an enhancement of cycleability as compared with simply pyrolyzed PVA.

The last strategy was the use of other binders such as polyacrylic acid (PAA) and carboxymethyl cellulose. Thick electrodes of very good cycle life could be prepared from Si/C composites together with PAA binder. Such electrodes were able to withstand 100 galvanostatic cycles at a capacity of 800 mAh/g.

# Investigations on high voltage spinel-layered composite materials for high energy and high power applications in LIBs

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The application of Li-ion batteries in HEVs is at present mainly limited by the lack of appropriate electrode materials, which offer simultaneously high power and high energy densities together with very good cycling stability. Doped Li-Mn-spinels of general formula $LiM_xMn_{2-x}O_4$, M = Cr, Fe, Co, Ni, Cu etc. are promising candidates for cathode materials due to their high operation voltage (close to 5V vs. $Li/Li^+$) and good rate capability due to the spinel structure which facilitates a three dimensional Li-diffusion [1]. Out of these, $LiNi_{0.5}Mn_{1.5}O_4$ is outstanding due to its superior electrochemical performances [2].

The $LiNi_{0.5}Mn_{1.5}O_4$ is synthesized by a sol-gel method reported in literature [3]. The precursor is then annealed at 600°C followed by heating up to 1000°C with a holding time ~1 min to obtain $LiNi_{0.5}Mn_{1.5}O_4$. The obtained material has a particle size of 3-4 μm and belongs to the $Fd\bar{3}m$ space group as revealed by SEM and XRD analyses respectively. The prepared $LiNi_{0.5}Mn_{1.5}O_4$ is cycled between 3.5-5.1 V at a rate of C/2 and exhibits capacity retention of 96% after 100 cycles together with a high rate performance (see figure 1). Several other synthesis routes were tried and later optimized to prepare layered- $LiNi_{0.5}Mn_{1.5}O_4$ composites which combine high voltage as well as high capacity by utilizing also the possibility of second lithium intercalation into the spinel component. The details on the cycling stability, high rate performance and specific energy density of these composite materials will be discussed in comparison with the parent spinel and layered components.

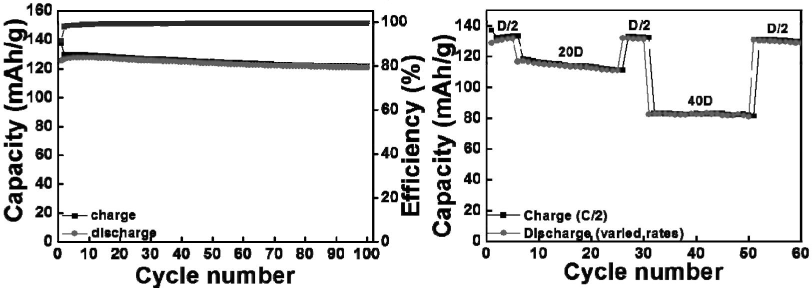

Figure 1: Cycling stability and rate capability of $LiNi_{0.5}Mn_{1.5}O_4$ synthesized at 1000°C

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# DNA aptamer nanobiosensor for microcystin-LR prepared with sulphonated polyaniline platform doped with silver nanoparticles

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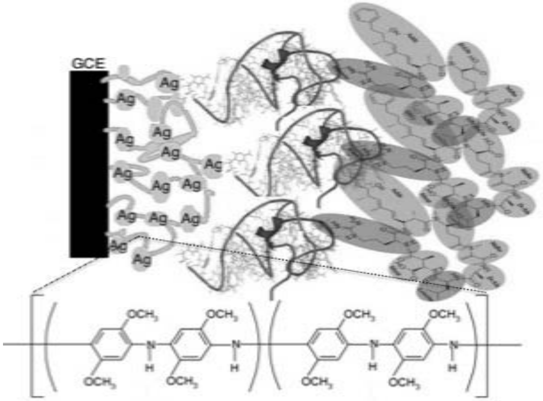
We developed a Cyanobacteria toxins-specific aptamer nanobiosensor on metallised polymeric electrode transducers. Cyanobacteria toxins are classified according to their mode of action into hepatotoxins (e.g. microcystins), neurotoxins (e.g. anatoxins) and skin irritation. Based on the fact that there is a lack of fast reporting diagnostic tools for algal toxins produced by fresh water blue-green algae which kills fish, shellfish, humans, livestock and wildlife. The nanoscale electrochemical biosensors that we prepared use aptamers as molecular recognition elements based on the advantages of aptamers over antibodies. Antibodies are more thermally sensitive, and denaturation of antibodies is usually irreversible. The use of aptamers offers a wide range of assay conditions. The binding of aptamers with their targets usually relies on specific conformations, such as G-quaduplex and hairpin. Conformational variations before and after the formation of aptamer-ligand complexes offer a great possibility and feasibility for the construction of aptamer-based biosensors. Owing to their oligonucleotide nature, they could interact with range of molecules include microcystin, thus fabricate versatile oligonucleotides machines for either biosensing or other clinical applications. In study will detail the properties and the selection methods of aptamers, progress in engineering biosensors, and the prospect of water toxin dictation. Hence, we develop an aptameric nanobiosensor system on the self-reporting thiol terminated 6-carbon spacers 18-bases guanine aptamer. The sensor conductive platform is based on sulphonated Poly (2, 5-dimethoxyaniline) (PDMA) with metal silver nanoparticles.



# New zinc-based anode materials for lithium-ion batteries

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Although tremendous research efforts are currently focused on the development of new battery technologies such as lithium-air or lithium-sulfur, lithium-ion batteries are still the technology of choice for modern electronic and automotive applications.

However, with respect to the anode side, further advances in terms of energy and power density will certainly rely on the development of new materials, offering an enhanced specific capacity and high rate capability. Nanostructuring of inorganic active materials has been proven to allow highly promising progress for the development and design of advanced electrode materials, resulting in shorter diffusion pathways for electrons and lithium-ions as well as a decreased current density per unit surface area of the active material [1]. Currently, most research efforts in the field of high capacity anode materials focus on the investigation of alloying materials, as for instance silicon or tin, or conversion materials, such as cobalt or iron oxide [2,3]. Very recently, we have reported on the beneficial combination of these two lithium storage mechanisms in carbon coated $ZnFe_2O_4$ nanoparticles, showing a specific capacity of more than 1000 mAh $g^{-1}$ and a superior electrochemical performance for applied specific currents up to more than 7.5 A $g^{-1}$ [4]. Nevertheless, in order to further increase the energy density of such materials, we have developed a new synthesis for transition metal doped zinc oxide. These materials offer specific capacities of more than 800 mAh $g^{-1}$ while allowing, at the same time, a lithium uptake at significantly lower potentials [5].

Here, we will report on our latest results obtained for these new lithium-ion anode materials and highlight the influence of the doping agent as well as the importance of electronically conductive percolating networks.

Acknowledgement

Financial support from the European Commission in the ORION project (229036) under the Seventh Framework Programme (7th FWP) is gratefully acknowledged.

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# Guanidinium based Ionic Liquids as new Electrolyte for Energy Storage Systems

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One of the greatest concerns in the field of energy storage is safety, especially for applications in electrically powered vehicles. Organic electrolytes in batteries are still considered unsafe, as they are easily inflammable. In recent years, ionic liquids (IL) have attracted much attention. Their low vapor pressure makes them attractive as flame resistant electrolytes. A great variety of ionic liquids has been tested both in lithium and sodium ion batteries. However, the biggest challenge for the application of ionic liquid as electrolyte remains their high viscosity and the resulting low ionic mobility of dissolved charged carriers, i.e. lithium and sodium ions.

This problem could be solved by a new generation of Guanidinium based ionic liquids. These ionic liquids generally have a relatively low viscosity, which makes them a promising candidate for next generation electrolytes. Furthermore, they exhibit a great structural variety that allows tailoring their characteristics to the needs of the respective application.

Electrochemical stability, impedance, transference number and charge / discharge capacities of newly synthesized Guanidinium based ionic liquids have been measured. A coin cell set-up was used for most of the tests. First investigations indicate good performance, both in singular electrochemical measurements and in tests in coin cells. As can be seen in Fig. 1, for slow C-rates this ionic liquid provides the same capacity as commercially available organic electrolytes. Ionic mobility in these ionic liquids will be further optimised by a systematic variation of substituents, so that a comparable capacity will also be provided for higher C-rates.

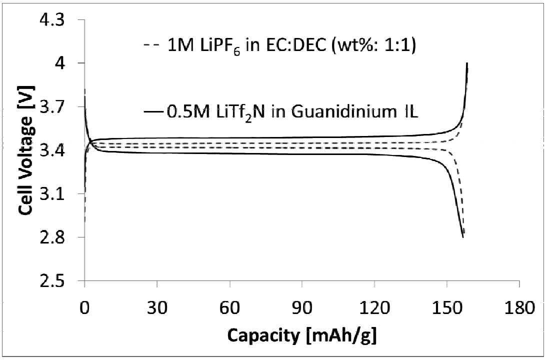

**Fig. 1.** Charge-discharge curves of commercial electrolyte vs Guanidinium based IL in a Li/$LiFePO_4$ cell at a current rate of 0.025 mA/g

# The effects of mechanical stress on lithium-ion battery capacity fade

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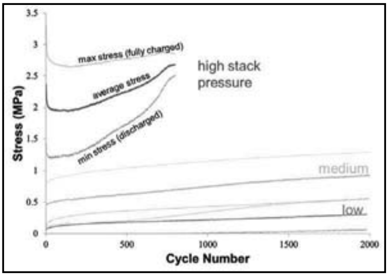
The development of lithium-ion batteries with longer service lives is critical for the economic viability of emerging applications such as electric vehicles and grid level storage. In this work the effects of mechanical stress on lithium-ion battery life are investigated by monitoring the stack pressure and electrochemical capacity of constrained lithium-ion (LCO-C) pouch cells. Stack stress is found to be a dynamic quantity, fluctuating significantly over the life of the cell due to electrode expansion and SEI growth (Figure 1). Variations in initial stack pressure, an important controllable manufacturing parameter, are shown to produce very different stress evolution characteristics over the lifetime of the cells. Lithium-ion cells manufactured with higher levels of stack pressure are found to exhibit shorter cycle lives, although small amounts of stack pressure lead to increased capacity retention over unconstrained cells (Figure 2). Post mortem analysis of these cells suggests a coupling between mechanics and electrochemistry in which higher levels of mechanical stress lead to higher rates of parasitic electrolyte decomposition (SEI growth), while layer delamination is responsible for the capacity fade in unconstrained cells. Mechanical degradation of the separator is also observed in all cells. These results indicate that changes in the mechanical aspects of cell design and manufacturing can lead to improved lithium-ion battery cell life.



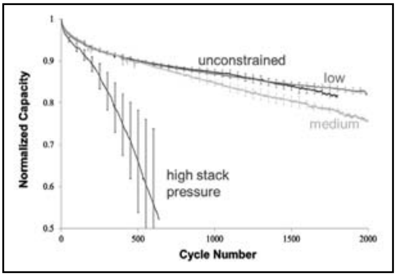


Figure 1 (left): Stress evolution of pouch cells with different initial stack pressures. Figure 2 (right): Capacity retention of pouch cells with different initial stack pressures.

# Voltammetric and chronoamperometric evaluation of CUPRAC methodology for developing an electrochemical sensor

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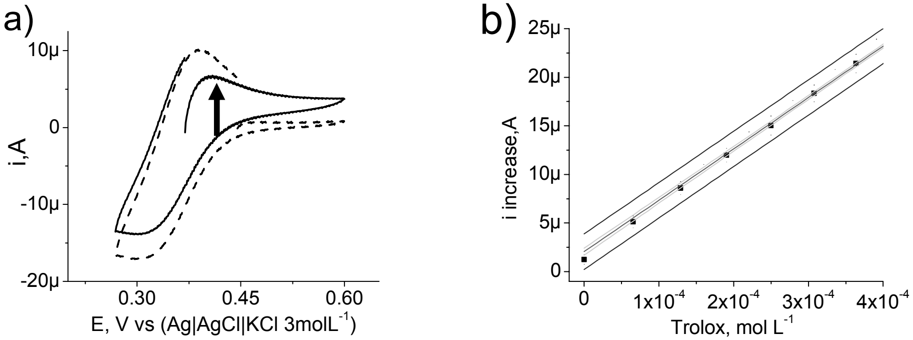
Antioxidants are naturally occurring compounds able to either destroy oxidant substances or prevent their formation, by eliminating Reactive Oxygen Species (ROS) and in this way reduce oxidative stress in living organism[1]. Evaluation of Total Antioxidant Capacity (TAC) in a sample is a convenient measure for comparing antioxidant properties. One of the methods more used for TAC determination uses Cupric Reducing Antioxidant Capacity (CUPRAC), eq. 1[1,2].

$$nCu^{2+} + 2nNc + AO_{red} \leftrightarrow n[Cu(Nc)_2]^{+} + AO_{ox} \qquad \text{Eq. 1}$$

In this method, the species $[Cu(Nc)_2]^{+}$ is the one of interest in the determination and can be electrochemically detected, instead of the classical spectrophotometric method[2]. This option allows determining TAC in samples when there are spectroscopic limitations (e.g. fats, oils or emulsions). In this work results on voltammetric and chronoamperometric performances of this methodology are presented along with TAC determination of pure molecules and samples of commercial teas.These studies will be used for developing a CUPRAC-based electrochemical sensor.



**a)**Cyclic voltammetry of $3x10^{-3}molL^{-1}$ Cu(II) in 1.2 $molL^{-1}$ $NH_4^{+}CH_3COO^{-}$ at different concentrations of added Trolox: 0 $molL^{-1}$(dashed line) and $1x10^{-4}molL^{-1}$(solid line) ($v$=100$mVs^{-1}$). **b)**Chronoamperometric calibration curve of oxidation current increase, at different concentrations of Trolox ($\tau$=0.1s, $E_{app}$=0.5V vs Ag|AgCl|KCl 3$molL^{-1}$, WE: glassy carbon 0.07$cm^2$).

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# Evaluation of application methods and ink parameters for the preparation of catalyst coated membranes for fuel cells

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Polymer Electrolyte Fuel Cells (PEFCs) have shown great potential as future electricity generating devices, and are the leading technology candidate in transport and portable power applications. It is a key mandate for the HySA/Catalysis Centre of Competence to deliver market ready fuel cell applications in the near future. One important step to reach this goal is the development of the knowhow to produce high quality membrane electrode assemblies (MEA) of consistently high performance in large quantities.

One of the common ways to prepare an MEA is by using a so called catalyst coated membrane (CCM) technique. This technique entails the application of the catalyst layer directly onto the membrane, prior to combining it with gas diffusion layers.

In this project, the electrochemical performance of CCM based MEAs prepared via various techniques was investigated. In the first technique, the catalyst layer was coated onto the membrane by direct spraying. In the second technique the catalyst layer was applied by decal transfer after screen printing on an appropriate substrate. In both cases, a range of application parameters and substrates were evaluated.

Alongside this, an extensive study of the catalyst ink utilised in both applications techniques was performed. The influence of the mixing method on the dispersion and the nature of the ink components (ionomer and catalyst) was investigated. Furthermore an evaluation was made of the rheological behaviour and coating quality of inks prepared with different dispersion solvents and component ratios.

# Studies of mixed metal oxide thin films as anode materials for the degradation of phenol

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Transition metal oxides are versatile materials to effect various oxidative or reductive processes. This is due to the ability of these materials to operate in various oxidation states, lending them the ability to both accept and donate electrons. It is well established that the synthesis methods for these materials have a large effect on the reactivity of the materials, especially in instances where metal oxides are used as electrode materials. The synthesis methods induce structural, surface and textural differences which affect the catalytic ability of the materials. Mixed metal oxides show even more variation towards electrochemical efficiency. Recent studies have shown that the electro-catalytic activity and chemical or mechanical stability of oxide electrodes are enhanced by incorporating/doping other metal ions into the oxides. The catalytic properties of existing known metal oxide catalysts can be enhanced by tailoring of the micro- and nano-structure. Characterization of the surface properties of electrodes covered with conductive metallic oxide films is therefore of fundamental importance for understanding their electrochemical behaviour. A systematic investigation was therefore undertaken to study the surface characteristics of a range of compositions of mixed metal oxides of $SnO_2$, $TiO_2$, $RhO_2$, $RuO_2$, $Ta_2O_5$ and $IrO_2$ as thin films with electro-catalytic properties. Various mixed metal oxides electrodes namely, $Ti/SnO_2$-$RuO_2$-$IrO_2$, $Ti/RhO_2$-$IrO_2$ and $Ti/Ta_2O_5$-$IrO_2$ were prepared by sol-gel techniques and anodization techniques and evaluated for their ability to oxidize phenol in aqueous solutions. These metal oxide materials are excellent electronic conductors at anodic potentials. They also have high surface roughness and some internal porosity as observed by SEM, RBS and AFM, which is equivalent to a large number of electro active sites. The electrochemical oxidation of phenol in an aqueous solution is a complex transformation involving several transfer steps of oxygen atoms and electrons. The oxidation rate of phenol was found to depend on the nature of the anode material. It was found that the oxidation rate not only depend on the chemical composition of the anode, but also on the oxide morphology as revealed by the dependence on preparation procedure.

Electrochemical oxidation using these electrodes show that phenol yielded intermediate ring compounds as hydroquinone, benzoquinone, catechol and carboxylic acids such as malic, malonic and oxalic.

# Electrodeposited polycarbazole derivatives as materials for optoelectronic applications

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In era of novel nanoelectronics, flexible and rollable highly stable electronic displays are needed. For that π-conjugated organic polymers possessing mechanical flexibility and tailoring properties due to structure modification are fast growing area for optoelectronic application. Carbazole and its derivatives have been known for many years as components of opto- and electroactive materials, mainly due to their high hole transporting capabilities and strong fluorescence. Their bluish photo- or electroluminescence is a result of the large enough band gap of the biphenyl unit. These properties are especially valuable for perspective materials, when these compounds are used as monomers in syntheses of conjugated macromolecules for optoelectronics. The derivatives were investigated and the electrochemical and optical properties of these compounds were measured, with attempts to made correlation to their π-electron conjugation lengths.

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# Factorial Design and Response Surface Methodology in Optimization of Biodiesel Production from Nigerian Non-Edible Oil

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Experimental design and response surface methodology (RSM) were applied in optimization of biodiesel production from *Azadiracther indica* seed oil (AISO). A 2nd order model equation correlating the response to reaction process variables was obtained. Essential Regression/Essential Experimental Design (ER/EED), Version 2.207 software was employed in the design and analysis of results. Biodiesel was produced using the optimum conditions and characterized for compliance with international standards. Results show that the saponification and iodine values of the oil were 192.371±1.4, 68.165±0.9, respectively. The value of $R^2$ for the developed correlation was 0.932. The optimum conditions for biodiesel synthesis using RSM were: temperature, molar ratio (methanol:oil), catalyst concentration and time of 52°C, 10:1, 0.97(wt% on oil), and 68min, respectively. The viscosity and density (at 40°C), oxidation stability, flash point and cold filter plug point of the biodiesel obtained from AISO by conducting fresh experiments at the optimum reaction conditions were 4.927mm$^2$/s, 862.0kg/m$^3$, 8.83±0.6h, 180.0±1.8°C, 12.0±0.3°C, respectively, while the copper strip corrosion determined using EN ISO 2160 (3h, 50°C) showed that it conformed to strip No 1a (slightly tarnish). The results of most parameters conform to ASTM 6751-08 and EN 14214 standards.

Key Words: *A. indica*, oxidation stability, copper strip corrosion, central composite design, response surface methodology, fatty acid profile.

# Enhancing Impedimetric and Potentiometric DNA Biosensing with Active Sensitisers

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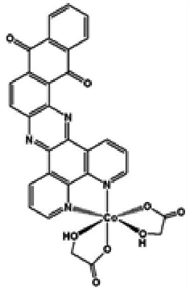
Biosensors for DNA (genosensors) are of significant interest because they address the need for rapid diagnosis of genetic disorders and infections by pathogens. Electrochemical genosensors can be miniaturised more readily than optical sensors and are suitable for use with portable instrumentation by minimally trained clinical personnel.

We present here the combination of two strategies towards sequence-selective DNA detection, viz. intrinsically sequence-selective electrochemical detection of DNA hybridisation and detection of double-stranded DNA by electronically active molecules. A capture strand of DNA is immobilised on an electrode, using immobilisation procedures which have previously been optimised for DNA detection using electrochemically impedance spectroscopy [1]. Following hybridisation, an electronically active molecule binds to the duplex DNA on the electrode that acts as a “sensitizer” for electrochemical detection.



Co aqphen complex

We have used electronic absorption spectroscopy to screen multiple Co-aqphen complexes and have shown the anthraquinone group to significantly increase the binding affinity compared to other complexes [2].

Electrochemical impedance spectroscopy (EIS), cyclic voltammetry and open circuit potential (OCP) measurements were carried out following the binding of the Co aqphen complex to dsDNA by intercalation.

EIS shows that the increase on charge transfer resistance upon hybridization is strongly enhanced in the presence of the Co aqphen sensitizer. The presence of the sensitizer is also observed by OCP measurements, which adds an additional DNA detection mode allowing, for example, internal control of readout. Control EIS and OCP experiments with ssDNA show that the sensitizer does not bind to ssDNA and hence is fully suitable for DNA hybridization sensing. The sensitizer thus provides enhancement of electrochemical DNA detection and highlights structural features favouring selectivity in sensing, paving the way towards a new generation of point-of-care electrochemical biosensors for genotyping.

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# Communication between Electrode Surface and Whole Cells with Cytochrome C as Redox Shuttle

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Recently, whole cells have received considerable attention in fabricating biosensors, bioreactors and biofuel cells, due to the easy and fast communication with their surrounding environment. In this regard, the utilization of a whole cell as host of intracellular enzymes provides a system with high efficiency and stability [1]. Its ability to oxidise different substrates and to transfer electrons either directly [2] or mediated by chemical redox shuttles [3,4], has improved the development of electrochemical cell-based biosensors. The limitation point for these biosensors is the toxicity of the chemical shuttles (*e.g.,* $FeCN)_6^{3-}$) used to improve the bioelectrochemical communication between bacteria and the electrode which can cause damages in cell envelope [3]. In addition, the electrochemical biosensors require the immobilization of whole cells to retain the microorganisms in close proximity to the electrode surface for higher reactivity and stability of the electrochemical communications [5]. In this work, we are studying the electrochemical communication of *pseudomonas fluorescens* CIP 69.13 mediated with Cytochrome C redox shuttle and encapsulated in sol-gel films for construction of environmental biosensing systems.

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# Synthesis and Characterization of (NiO-CoO) Composite Thin Film by Chemical Methods

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We use simple and economical chemical methods such as chemical bath deposition for the deposition of nanocrystalline nickel-cobalt oxides (NiO-CoO) films. The deposition of (NiO-CoO) films were deposited on non-conducting glass substrates. Paramount on the deposition is the optimisation of bath deposition parameters such as the pH of bath, deposition temperature and annealing temperatures. After the deposition, the films are annealed in air to improve the film properties. The films are characterised using physico-chemical techniques such as SEM, AFM, FT-Raman and spectrophotometers. The resistivities of the films were obtained using two point probe and we studied the hydrophilicity of (NiO-CoO) thin films using contact angle measurement.

# Non-noble Iron Tetrasulfophthalocyanine on Multi-walled Carbon Nanotubes: a Potential Cathode Catalyst in Direct Alcohol Alkaline Fuel Cells

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In the emerging fuel cell technology, the research towards non noble metal based catalysts for hydrogen oxidation and oxygen reduction is a field of intense research [1]. The oxygen reduction (ORR) which takes place at the cathode is of particular importance in the fuel cell since it is a multi- electron reaction and a good control of the number of electrons involved is mandatory for the efficiency of the overall system. The desired reaction pathway is one which involves a direct transfer of 4 electrons to produce hydroxide ion in the alkaline medium. Since the first report by Jasinki [2], $MN_4$ macro cycles (M= Transition metals) such as phthalocyanines (MPc) and porphyrins (MP) are known to catalyze the electrochemical ORR in alkaline and acidic media. Iron and Cobalt phthalocyanines have drawn great interest as alternative cathode catalysts to Pt-based systems in ORR [3]. These catalysts however require a conductive support. As the overall efficiency of a fuel cell catalyst is not governed only by the intrinsic activity of the catalyst, the micro or nano structural nature of the catalyst which allows an optimal contact with the active sites is also very important.

The potential of carbon nanotubes (CNTs) as catalyst support has been demonstrated [4]. MPc and MP complexes can easily absorb on CNTS via non covalent p-p interactions facilitating electron transfer processes and stabilizing the systems. CNTs also provide a high surface area controlled by their characteristics which include number of walls, number of nanotubes in a bundle and diameter size. The nanostructured hydrophobic derivative of Iron (II) tetrasulfophthalocyanine has been synthesized and characterized [5]. The complex was incorporated on both hydroxyl and sulfonated functionalized multiwalled carbon nanotubes. These have been tested for their ORR activity in alkaline medium. Their activities have also been compared to that of commercial platinum catalyst. Their resistance to alcohol cross over in high concentration of methanol suggests they can be among the leading non noble cathode catalysts in direct alcohol alkaline fuel cells.

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# An electrochemical study in using EIS of commercial AA alkaline battery capacities

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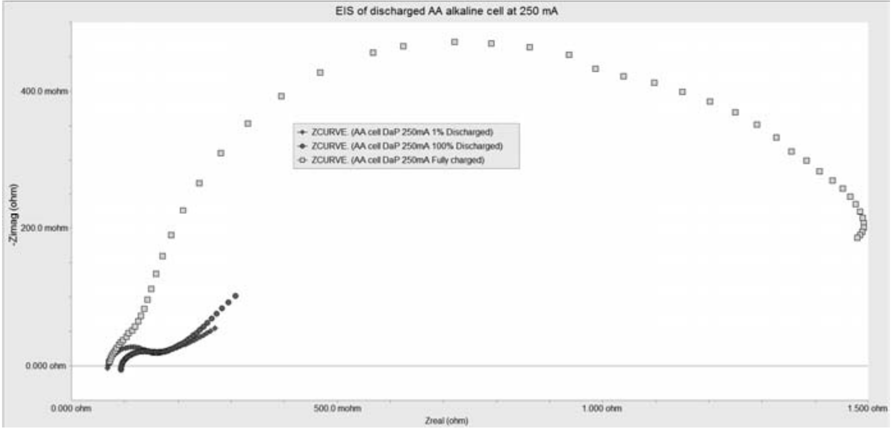
A comparative performance study was done of seven commercially available AA alkaline primary batteries that are readily available from larger South African retail stores. The study considered three IEC discharge capacity specifications testing that included an intermittent 3.9 Ω toy test, an intermittent 1 A photo flash test and a continuous 250 mA test. The study considered the achievable Ah capacity for each battery type subjected to the three test specifications in term of their cost of purchase by the consumer (Ah/Rand) and the amount of anode material (Ah/g Zn). Electrochemical Impedance Spectroscopy (EIS) was done on the different types of batteries at different state of charge (SoC) during the various types of intermittent discharge testing.

The results showed that for a specific low capacity drain application, the more expensive battery was not necessarily more cost efficient. Whereas for high power applications such as a photo flash, the more expensive battery did prove to be more cost efficient. The EIS study of the different types of alkaline batteries did show some unusual impedance anomalies of the fully charged batteries, which disappeared, once the cells' were subjected to a slight discharge as shown in the figure below. The EIS study also showed that there were noticeable changes in the batteries internal and cell resistances as the SoC decreased with little or no variation between the various battery types. A suitable equivalent circuit model was used to describe the changes in the electrochemical character of the alkaline batteries as they were subjected to the discharge testing.



# Electrochemical biosensor for the detection of pathogenic bacteria (*Aeromonas hydrophila)*

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Two electrochemical biosensors for the detection of bacteria *Aeromonas hydrophila* are presented. *Aeromonas hydrophila* is a foodborne human pathogen of emerging importance very much distributed in aquatic environment and isolated from variety of foods [1]. Pathogenicity of *Aeromonas hydrophila* is associated with a presence of the gene aerolysin therefore specific and effective tool for its detection can be the DNA probe of a sequence complementary to this gene. Carefully selected by standard procedures DNA probe at the sequence 5' GTCAAGACGGTGGTGGGCTG was used as a sensing element in the presented biosensors. The detection layer of biosensor 1 was a gold electrode covered with self-assembled monolayer (SAM) consisting of mercaptohexanol and DNA probe [2]. The detection layer of biosensor 2 was a carbon paste electrode (CPE) or carbon paste electrode modified with multi-walled nanotubes (MWCNT) containing covalently immobilized DNA probe. Design of detection layers and concentration of DNA probe in the recognition layer as well as all reaction parameters influencing hybridization event including hybridization time, concentration of target DNA, contamination of non-complementary DNA in the sample were investigated in detail and optimized. Several electroactive hybridization indicators were examined with both detection layers and two of them were selected for the final determinations: daunomycin (carbon paste electrode) and Hoechst 33258 (gold electrode). Both biosensors were used for the detection of pathogenic strains of *Aeromonas hydrophila* in infected food samples (fishes, vegetables, radish sprouts). All samples contained also some other bacterial strains. Minimal DNA concentration isolated from infected samples enabling the detection of *Aeromonas hydrophila* was 2.0 μg/cm$^3$ (biosensor 1) or even 0.8 μg/cm$^3$ (biosensor 2 MWCNT). Obtained results were related to the PCR analysis of all investigated samples.

Implementation of appropriate DNA probe into a detection layer makes electrochemical biosensors an effective analytical tool very useful in the detection of various bacterial infections of foods, a fundamental point for the microbial safety of food and the quality assurance, priority for the food industry and for the consumers.

Acknowledgement
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# Normalizing Variability in the Electrochemical Detection of Mycotoxins at Carbon Nanotube Modified Glassy Carbon Electrodes

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Mycotoxins are low molecular weight secondary fungal metabolites which when ingested, inhaled or adsorbed through the skin adversely affect human and animal health. Ochratoxin A and citrinin are two of the most prominent known mycotoxins produced from a number of fungi, particular among the genera *Aspergillus*, *Penicillium* and *Fusarium*. These fungi readily contaminate a large variety of commodities including cereals, groundnuts, dried fruit, spices and coffee [1]. As ochratoxin A and citrinin are both potent nephrotoxins exhibiting carcinogenic properties [2], the development of a rapid screening platform for the cost effective monitoring of these mycotoxins in foodstuffs is required.

In this study, the application of carbon nanotube modification of glassy carbon electrodes was evaluated with respect to the voltammetric detection of ochratoxin A and citrinin. Enhanced sensitivity towards the tested mycotoxins by electrodes modified with carbon nanotubes was observed, and assigned to the introduction of oxygen functionalities and defect sites onto the nanotube surface through oxidative acid treatment. The heterogeneity in surface chemistry and topology of the modified electrodes induced variability in the anodic detection of these compounds. Hence, we additionally report on a method to normalize the variability across heterogeneous surface preparations through the measurement of double layer capacitance as an indication of electrode surface area [3].

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# Variability in response of laccase-based nanocomposite electrochemical biosensors: key aspects

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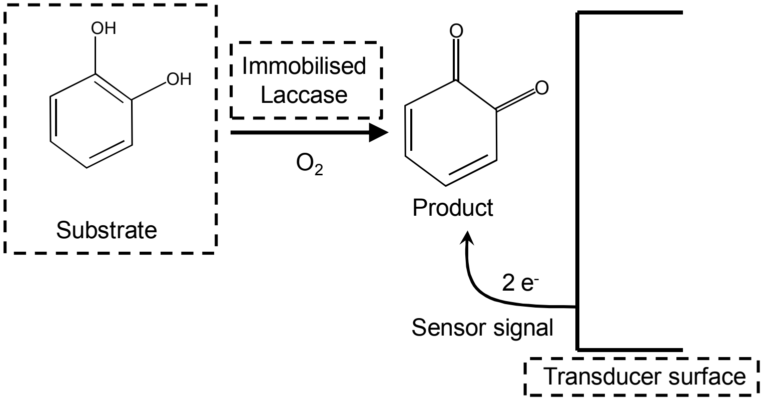
A major concern regarding the adoption of electrochemical laccase biosensor technologies for routine monitoring of phenolic compounds is the variability in biosensor response. This is noted both between different biosensor configurations, as well as the substrate undergoing monitoring. Substrate-specific variation in biosensor responses is especially concerning, given the wide array of phenolic compounds and the variety of effects that this class has on both human health and the environment.

This presentation critically assesses biosensor response variability at key stages of biosensor process development: (1) selection of biorecognition agent, (2) the immobilisation of the biorecognition onto an electrochemical transducer, (3) assessment of different substrates at the fabricated biosensor and (4) modification of the biosensor transducer with multi-walled carbon nanotubes to produce a nanocomposite laccase-based biosensor.



Graphical abstract: Generalised scheme depicting signal generation during the employment of an electrochemical laccase biosensor to detect a substrate,in this case, 1,2-dihydroxybenzene (catechol). Areas highlighted in dashed boxes will be the topics discussed during the presentation.

# Strategies for enhancing the performance of carbon/carbon supercapacitors in aqueous electrolytes

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Electricity storage is one of the key issues to widespread the renewable energies and to enhance the energy efficiency in automotive applications. Two complementary electrochemical systems are currently considered, the batteries for their high energy density (up to 180 Wh/kg for commercial Li-ion batteries) and supercapacitors (or electrochemical capacitors or ultracapacitors) for their high power density (15 kW/kg) and lower stored energy than batteries (5 Wh/kg). The main developed technology for supercapacitors is based on charging an electrical double-layer (EDL) at the electrode-electrolyte interface of high surface area carbons. The main disadvantages of the later are a relatively low energy density and safety issues related with the use of organic electrolytes.

The presentation will describe alternative solutions for developing environment friendly carbon/carbon supercapacitors where pseudocapacitive contributions play together with the EDL capacitance in protic aqueous electrolyte, giving rise to a possible enhancement of energy density. A new source of pseudocapacitance involving a redox electrolyte is demonstrated by high surface area carbons. The later is based on the interface formed by species with a large variety of oxidation states, e.g., iodine, bromine, vanadium, and gives rise to capacitance values as high as 250 F $g^{-1}$ at 1 A $g^{-1}$ for 1 mol $L^{-1}$ KI aqueous solution. Electrochemical hydrogen storage in the negative electrode of carbon/carbon capacitors in neutral aqueous electrolytes, e.g., alkali sulfates, is another source of pseudocapacitance. The voltage (and consequently the energy density) is considerably enhanced by comparison with systems in basic or acidic electrolytes owing to an important overpotential for di-hydrogen evolution at the negative electrode. Beside, a pseudocapacitive contribution related with hydrogen storage appears at the highest voltage values, i.e., when the potential of the negative electrode becomes lower than the equilibrium reduction potential of water.

# Fabrication of Commercial Nanoelectrodes: challenges and opportunities

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Nanoelectrodes have been the subject of intense research interest for more than a decade and the theoretical benefits of nanoscale electrochemistry have broadly been borne out experimentally. What is clear from the literature is that the fabrication of such devices is extremely challenging and it is likely that some of the discrepancies in empirical data are the consequence of the difficulties experienced in controlling the physical manifestations of the final structures. In this paper we examine an approach to the fabrication of nanoelectrode structures and some of the issues and opportunities which have resulted. Specifically we will report on an approach to nanoelectrode fabrication which addresses issues which are germane to commercial exploitation. Specifically:

1) A reliable approach to fabricate nanoscale electrodes which offers:
    a. Reliable, reproducible manufacture;
    b. Drop in replacement for a 'conventional' electrode;
    c. An engineering approach to electrode design;
    d. Flexibility in terms of electrode material.
2) A practical, user friendly platform with:
    a. Standard operating procedures for use;
    b. A sufficient level of understanding (in terms of performance);
    c. Ability to utilize common working practice.
3) A platform which offers the ability to utilize a wide range of process techniques and materials

Some of the design considerations, materials chemistry and physical chemistry involved in attempting to meet such specifications will be discussed.

# Quantum dots electrochemical genosensor for breast cancer biomarkers

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Breast cancer is a disease in which malignant (cancer) cells form in the tissues of the breast. According to statistics from the Cancer Association of South Africa (CANSA), breast cancer is the most common cancer among South African women. Cancer cells produce deoxyribonucleic acids (DNA), ribonucleic acids (RNA), proteins and metabolites as potential biomarkers. Breast cancer is signified by over expression of the Human Epidermal Growth Factor Receptor 2 (HER2) protein which is encoded by the *ERBB2* gene. Detection of this gene is therefore an important clinical procedure in cancer screening practise. Cancer screening for detection, risk assessment diagnosis and prognosis are based on three main assay platforms (genomic, proteomic and metabolic/metabolomic profiles). Genomic technologies including DNA microarrays, polymerase chain reaction (PCR)-based assays, and fluorescence *in situ* hybridization (FISH) permit the determination of genetic materials associated with cancers and tumours. DNA-based biomarkers originate from genetic mutations, loss of heterozygosity (LOH), microsatellite instability (MSA), and DNA methylation. RNA-based biomarkers are mostly mRNAs found in tissues and bodily fluids. Using DNA microarrays, it is possible to identify biomarkers that are differentially expressed in malignant tissues including breast tumours. The challenge for medical diagnostics industries is how to translate the DNA microarrays technology into reliable tools for clinical applications. A variety of nanomaterials such as nanoparticles, nanowires, and nanotubes have been used for constructing DNA sensors. In this work, an electrochemical-DNA genosensors was constructed using the nanomaterials (e.g. quantum dots). Nanocrystals have been utilized for enhancing the signals by increasing the number of immobilized probe DNA molecules. The electrochemical properties and structural morphology of the nanomaterials were determined using cyclic voltammetry (CV), square wave voltammetry (SWV), electrochemical impedance (EIS) and transmitted electron microscopy (TEM). The conductivity of the material was determined using uv-visible and fluorescence. The band gap of the material which is defined as the energy distance between the valence and conduction bands was calculated to be 3.3 eV and 3.5 eV respectively. The values obtained confirmed the conductivity of the material, to be that of a semiconductor. A target DNA labeled with $Ga_2Te_3$ nanomaterials was hybridized with amine-modified probe DNA covalently bound to the mercaptoacetic acid monolayer on the gold surface. The sensitivity and detection limit of the genosensor was calculated from CV and EIS and was found to be $2.42 \times 10^{-6}$ A/nM, $0.66 \times 10^{-6}$ Ω/nM and $4.22\times10^{-5}$ nM respectively.

# A novel hybrid nano-scale sensor of perovskites and carbon paste for the determination of neurotransmitters

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Perovskite of the type $ABO_3$ immobilized on carbon paste electrode (CpE/$SrPdO_3$) is introduced as a novel electrochemical sensor with unique long term stability (over two months) and low detection limit for determination of dopamine (DA) in biological fluids. In this work we compared the performance of CpE/$SrPdO_3$ to electrodeposited palladium nanoparticles modified CpE (CpE/Pd) that exhibited higher electrocatalytic activity toward DA. The prepared perovskite was characterized by XRD and SEM; XRD data showed the formation of the cubic perovskite phase with a secondary phase of $SrPd_3O_4$. We used cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy for the electrochemical characterization of CpE/$SrPdO_3$. DA could be detected in the two linear ranges of 7–70 $\mu$mol $L^{-1}$ and 90–160 $\mu$mol $L^{-1}$ with low detection limits of 9.3 nmol $L^{-1}$ and 25 nmol $L^{-1}$, respectively, and good correlation coefficient of 0.9981. It is possible to determine simultaneously DA, ascorbic acid (AA) and uric acid (UA) as common interferences in human fluids with large separation of the peak potentials. This method is simple, sensitive and successfully applied for direct determination of DA in human urine samples with excellent recovery results. CpE/$SrPdO_3$ showed high reproducibility, enhanced sensitivity, selectivity and anti-interference ability.

# Microchannel Impedance through two antiparallel planar microelectrodes

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In recent years, development of miniaturization technology was increasing, due to the well known advantages and the crucial need for technology to get the micrometer scale measurements and to improve sensitivity of detection methods [1]. Among the various microsystems developed for "laboratory on chip", contact free microelectrodes in microsystem is a very interesting method for detection because of the absence of direct contact between the electrodes and the solution microchannel. The present work describes new results using a contact free impedance device, which permit to reach a best understanding of the free contact transduction [2].

Measurements were carried out through a Polyethylene Terephthalate (PET) microchannel photoablated having a trapezoidal cross-section shape with a depth of 45 µm, a width of 100 µm and a length of 1,4 cm. The distance separation between both microchannels is 100 µm center to center. The microband of PET is carried out in the following way: microchannels are coated with gold nanoparticules with an average size of 19 nm and a standard deviation of 2 nm. The detection is achieved using hydride carbon ink/gold nanoparticules electrodes, thermally laminated by a polyethylene terephthalate/polyethylene terephthalate (PET/PET) layer with thickness of 35 µm at 135°C and a pressure of 2 bar. The distance separation in the PET band between the two planar microelectrodes and the main microchannel is equal to 5 µm and the detection surface area per microelectrode is 88 µm x 100µm [3]. Study was carried out by the impedance measurement in alternative mode (ac) through the two microelectrodes at frequency range from 1 MHz to 1 Hz with 0,1 V amplitude, in order to have the electrical behavior of the overall microsystem and to extract the specific microchannel response. The corrected impedance diagrams were plotted by soustracting PET layer impedance contribution from the global microdevice response. This operation allows a clear observation of solution microchannel impedance such as, resistance, capacitance and diffusion phenomenon in microchannel.

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# Gas Management and Multiphase Flow in Direct Alcohol Fuel Cells

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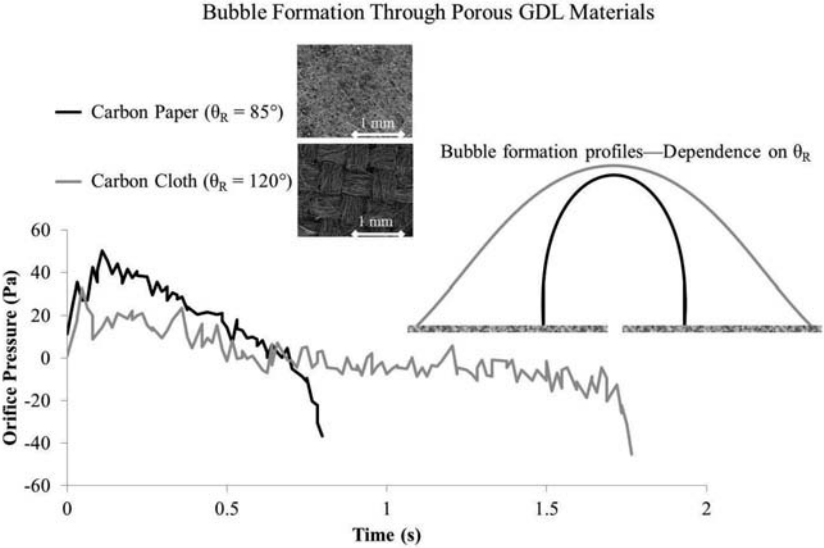
Direct Alcohol Fuel Cells (DAFCs) have the potential to compete with current battery technology due to the high energy density of the alcohol fuels. The limiting factor is primarily the power density of the fuel cell itself. Power density may be improved by considering the impact of electrode design on multiphase transport in the electrodes. Carbon dioxide gas is generated at the anode where its accumulation interferes with liquid fuel delivery. This work has taken a fundamental approach to characterize the gas and liquid distribution of the electrode materials. We then use these properties to understand the transport processes and provide insight into the best methods and electrode designs for gas management. Control of multiphase flow within the electrode is a strategy by which we can optimize flow channel configurations and material properties to minimize the impact of carbon dioxide gas on power output.



# Antioxidant activity and electrochemical behavior of alcoholic beverages produced from jabuticaba (Myrciaria jabuticaba).

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Jabuticaba is a widespread Brazilian fruit that presents vast quantities of antioxidants, being anthocyanin the most important. Therefore, fermented beverages produced from Jabuticaba, in the same way as wine, represent a potential source of antioxidants. In spite of the wide variety of methods available to determine the antioxidant activity of foodstuffs and other vegetal samples, the development of novel methods is still the research focus of many different groups. Electroanalytical methods have emerged as an alternative to determine the antioxidant activity. The aim of this study was to evaluate the antioxidant capacity of red, rose and white fermented beverages, as well as the brandy, "bagaceira", all of them produced from Jabuticaba fruit, comparing it to red and white wines. Traditional spectrophotometric methods (Folin-Ciocalteu, ABTS) and voltammetric methods (CV, DPV and SWV) were used to make this evaluation, and the results are respectively presented on Figure 1 and Table 1.

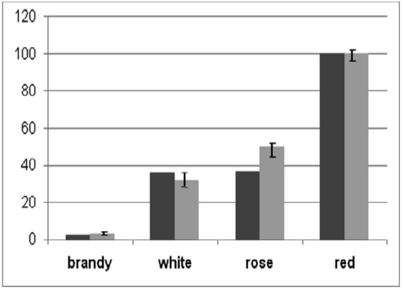

**Figure 2.** Relative total phenol content (■) and ABTS (■) radical scavenging activity obtained for different jabuticaba alcoholic beverages.

**Table 1**. Electrochemical parameters, $E_{pa}$ and $I_{pa}$ obtained for different alcoholic beverages in pH 5.0 0.1 Phosphate buffer.

| Parameter | Brandy | White | Rose | Red |
|---|---|---|---|---|
| $E_{p1a}$ (V) | - | 0.321 | 0.326 | 0.326 |
| $I_{p1a}$ (μA) | - | **3.95** | **4.63** | **4.9** |
| $E_{p2a}$ (V) | - | 0.444 | 0.434 | 0.437 |
| $I_{p2a}$ (μA) | - | **3.81** | **4.26** | **5.20** |
| $E_{p3a}$ (V) | - | 0.739 | 0.744 | 0.727 |
| $I_{p3a}$ (μA) | - | 3.14 | 2.89 | 3.03 |
| $E_{p4a}$ (V) | - | 0.865 | 0.874 | 0.849 |
| $I_{p4a}$ (μA) | - | 3.51 | 3.10 | 3.15 |

(n = 3)

All the fermented beverages presented large quantity of phenolic compounds, according to all methods herein used, while the brandy did not. The DP voltammograms obtained for red, rose and white samples of fermented beverages presented two well defined and intense peaks 1a, at Ep1a ~ 0.32 V and 2a, at Ep2a ~ 0.44 V, and also two small peaks, 3a and 4a, respectively at 0.73 V and 0.87 V. Nevertheless, owing to the strong passivation effect during process 1a and 2a, such further peaks showed to be partially suppressed, appearing only as a shoulder upon the overall amout of phenolics. The electrochemical parameters and spectrophotometrical methods show great concordance. Thus, the voltammetric methods were demonstrated to be useful tools for the analysis of antioxidants in beverage samples.

# Electrodeposited gold nanoparticles on glassy carbon. Correlation between AuNPs characteristics and $O_2$ reduction kinetics.

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The electrocatalytic properties of gold nanoparticles (AuNPs) for the oxygen reduction reaction (ORR) have been extensively studied for many years [1], especially for fuel cells applications [2]. Most works have been performed in acidic or basic media. Comparatively very few papers have been concerned with ORR in neutral solutions [3] although it is of critical importance in the field of clinical biology analysis, particularly for oxidative stress evaluation. In this context we examined the improvements of ORR kinetics by means of AuNPs-modified glassy carbon electrode (AuNPs-GC) in NaCl-$NaHCO_3$ (0.15M/0.028M – pH=7.4) neutral solution to be close to blood ionic composition.

Several AuNPs electrodeposition methods were used, namely cyclic voltammetry (CV), and constant potential electrolysis (CPE) with or without stirring to get homogeneous deposits. For each electrodeposition condition, the ORR kinetics was evaluated through the cathodic heterogeneous electronic transfer coefficient (βn) values deduced from either Tafel plot or Koutecky-Levich method. The results confirmed that that AuNPs-GC induces significant improvements of the ORR kinetics compared to unmodified electrode. The highest βn were reached by performing CPE at low potential (-0.5V/Ag/AgCl) for 30 minutes. The related AuNPs were quite small (~20nm) with a relatively high density (800 NPs/$\mu m^2$).

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# Voltammetric characterization methods for the PEM electrolysis evaluation

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There is a global need to find alternatives to the current fuel crises. This paper will give an overview of past and current studies done on Alkaline and PEM electrolysis in particular the later type of electrolysis. Electrolysis is a chemical reaction that produces electrical energy via an electrochemical process. The electrical energy is the driving force needed for chemical reaction.

During the process of water electrolysis, the water molecule is decomposed into hydrogen and oxygen when an electric current is passed through the system.

Anode reaction: $2H_2O \rightarrow 4H^+ + 4e^- + O_2$
Cathode reaction: $4H^+ + 4e^- \rightarrow 2H_2$
**Overall reaction:** $2H_2O \rightarrow 2H_2 + O_2$

Electrolysis is considered to be one of the cleanest methods of producing hydrogen (Qi, 2008)[1]. A brief overview between alkaline (Atlam & Kolhe 2011)[2]and PEM electrolyser (PSO-F&U, 2008, p66)[3] will be discussed in this paper discussing their effectiveness to produce hydrogen sufficiently.

This trend comes into effect because of the high capital cost associated with PEM electrolyser units, which is being pushed by expensive materials that are used to manufacture the membrane, and the costs associated with the PGM metals used as catalysts in PEM electrolyser units. This compared to the lower capital cost for the manufacturing of alkaline units.

In this paper special emphasis will be given regarding the catalyst material needed to produce hydrogen and oxygen in a PEM electrolysis unit.

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# PEDOT-based electrochemical microsensor for the assay of ascorbic and uric acids in human blood serum. Highlighting the antioxidant regeneration mechanism using SECM

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Oxidative stress has been one of the most widely studied biochemical processes for the last decades. It is the consequence of an excessive production of highly reactive oxygen and nitrogen species [1] and leads to aging processes which are known to be amongst the potential causes for cataract, cancers, cardiovascular and degenerative diseases (Parkinson, Alzheimer). One of the main antioxidant defense systems involves low molecular weight antioxidants [2]. Among them, ascorbic (AA) and uric (UA) acids are present in highest concentrations in most biological fluids and may thus be considered as biochemical markers in a lot of pathologies (preeclampsia, neonatal hypoxia, coronary heart diseases…) [3]. The main electrochemical approach to study antioxidant properties concerns the development of sensors to perform rapid and accurate assays for early biomedical diagnosis. In this context many electrode surface modifications have been proposed to optimize both selectivity and sensitivity [4]. Nevertheless their analytical performances were almost determined in model solutions and/or in particular experimental conditions which did neither reflect the healthy human situation nor integrate the possible interactions between antioxidants.

We recently evaluated poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrode to simultaneously assay ascorbic and uric acids as well in aqueous solution [5] as in blood serum [6]. For the first time the sensitivity of the sensor towards UA was found to vary depending on whether AA was present in the sample or not [7]. This phenomenon was supposed to be the consequence of an EC' mechanism resulting from a spontaneous redox reaction coupled to the electrochemical step, thus regenerating UA close to the electrode surface. We present here preliminary results highlighting this antioxidant regeneration mechanism by scanning electrochemical microscopy (SECM). Finally this synergic effect has been taken into account for the analysis of 15 blood serum samples. The accuracy of the resulting sensor has been satisfactorily evaluated by comparison with data obtained with reference analytical methods.

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# Electrochemical determination of dissolved nitrogen containing explosives

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Electrochemical methods based on voltammetry are well suited for fast and cheap determination of explosives like TNT (trinitrotoluene) in the soil of abandoned military training ground. Up to now their common use is failed mainly due to the necessary detection limit and poor reproducibility of electrochemical electrodes.
Electrochemical carbon electrodes produced by industrial like methods as screen printing and vapor deposition were investigated. The electrodes, 3 mm in diameter were tested in a three electrode arrangement by linear sweep voltammetry and differential pulse voltammetry in aqueous solution with small concentrations of TNT and DNT (dinitrotoluen).

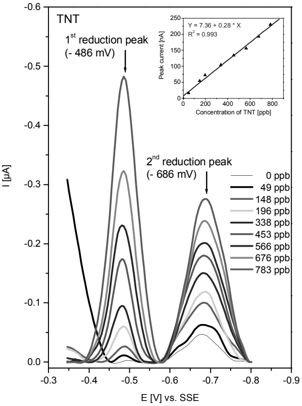

Fig. 1 Determination of TNT on screen printed carbon electrode by differential pulse voltammetry (DPV) in 0.1M $KNO_3$/0.1M KCl solution (counter electrode Pt)

We could show (Fig. 1) that nitro compounds are active species that can be reduced electrochemically in two steps on unmodified carbon electrodes. The detection limit was found to be lower than 5 ppb TNT with the sensitivity of 0.44 nA/ppb. The methods are suited to determine TNT and DNT simultaneously. Such electrodes can be fabricated cheaply in a large scale with controlled thickness, diameter and uniform quality. The sensitivity of screen printed electrodes for the determination of TNT and DNT did not change after storage in air or in 0.1 M PBS (phosphate buffer solution pH 7.4) for at least 2 months.

# Effect of Doping and Electrolyte on the Performance of Sodium Manganese Oxides in Sodium Ion Batteries

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Sodium Ion Batteries (NIBs) have the potential to combine low costs for energy storage with a comparable performance to the currently dominating Lithium Ion Battery (LIB). The biggest challenge for electrode materials for NIBs is the size of the sodium ions. As the ionic radius of sodium is 30% larger than lithium, this puts additional strain on crystal structures to reversibly intercalate and de-intercalate the sodium ions. Solutions to these problems might not only pave the way for commercial sodium ion batteries in the future, but it might also enhance understanding of similar problems in LIBs and therefore improve their performance.

Promising cathode materials that can accommodate the large sodium ions and provide good capacities are layered structures like sodium manganese oxides. However, high capacity fading remains a problem. The purpose of our work is to examine the effect of dopants and different electrolytes on the cycle stability of $Na_xM_yMn_{1-y}O_{2+z}$ (M=Co, Ni, etc.).

The sodium manganese oxides were synthesized to deliver small particles with a high surface area as can be seen in Fig. 1. As the SEM picture shows, particle size varies between roughly 100 – 500 nm. The structure is layered (see Fig. 1 and 2), with manganese ions being octahedrally surrounded by oxygen ions, and the planes being filled with sodium ions.

These materials were tested in a coin cell set-up against sodium metal. Cyclic voltammetry was performed, and charge / discharge behavior of these cells was measured to determine their capacity and cycle stability.

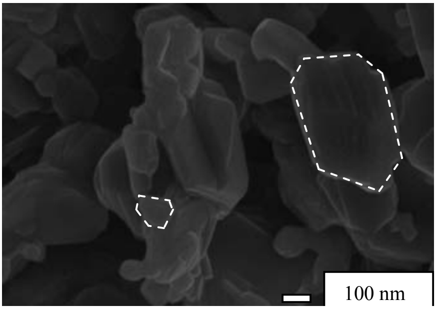

**Fig. 1.** SEM image of layered Na-Mn-oxide

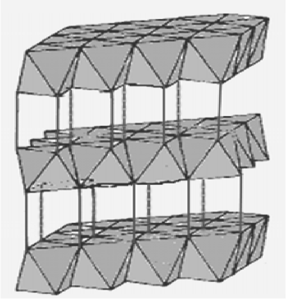

**Fig. 2.** Crystal structure of layered N oxide

# The Electrochemical Properties of Dithienylcyclopentene Switches and their Cobalt Carbonyl Complexes

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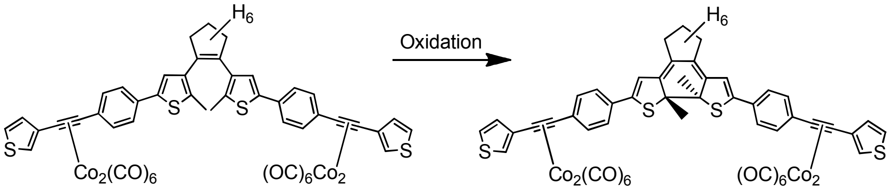
Dithienylcyclopentene switches can undergo reversible ring closing and opening processes, following irradiation with UV and visible light, respectively. Ring closing or ring opening of these switches can also be induced via electrochemical means [1, 2] and a combination of the photo- and electro-processes can be used for the development of molecular wires [3, 4] and non-destructible write-read-erase memory devices [5,6]. We have focused our attention into the investigation of the factors effecting the direction of electrochemical switching of dithienyl-perhydro and –perfluoro cyclopentene switches, appended with ethynyl-thiophene and –ferrocene substituents, using cyclic voltammetry and UV-vis/NIR spectroelectrochemistry. The effect of incorporating $Co_2(CO)_6$ and $Co_2(CO)_4$dppm moieties onto these compounds, on the electrochromic behaviour of the molecular switches, was also examined. Furthermore, IR spectroelectrochemistry techniques were utilised to monitor the effects of the oxidation processes on the cobalt carbonyl moieties.



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# Asymmetric Marcus-Hush Theory

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The theory of electron transfer kinetics underpins the quantitative understanding of the theory of electrochemical sensors, batteries, fuel cells, solar cells etc. We present recent developments in the theory of electrode kinetics.

The asymmetric form of Marcus theory [1] has been applied to the kinetic study of several redox couples including the one-electron reductions of 2-methyl-2-nitropropane, cyclooctatetraene and europium(III) using mercury microhemispheres as working electrodes [2].

The predecessor of this model, the *symmetric* Marcus-Hush (SMH) model, has previously been shown to perform poorly when fitting the voltammetry (both cyclic and square wave) of solution-phase redox systems despite its success in reproducing the curved Tafel plots commonly observed for electroactive monolayers [3]. Conversely, the ubiquitous Butler-Volmer (BV) model has been found to better parameterise experimental voltammetry in the solution phase, but performs poorly as a model for the electrode kinetics of electroactive monolayers. The BV model also allows little insight into the underlying electron transfer process.

The asymmetric Marcus-Hush (AMH) model removes the assumption of the SMH model that the Gibbs energy curves of both the reactants and products have the same curvature [4]. This new model rationalizes the rate of electron transfer in terms of a reorganisation energy, $\lambda$, and an asymmetry parameter, $\gamma$. This parameter is a function of the relative magnitudes of the inner and outer sphere reorganisation energies and the average force constants in the oxidised and reduced species and takes values $-1 \leq \gamma \leq 1$. When $\gamma = 0$ the asymmetric model reduces to its symmetric counterpart.

The additional flexibility of the AMH model has allowed accurate fitting of the voltammetry of both solution-phase [2] and surface-bound [5] redox systems while retaining the physical insights available through Marcus theory.

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# Design of $Fe_{0.4}Ta_{0.5}P_2O_7$-based composite electrolyte and electrode materials for high-temperature, low-humidity PEMFCs

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Proton-exchange membrane fuel cells (PEMFCs) have been considered to be most suitable for vehicle and residential applications. However, many challenges such as complicated water management and expensive materials cost still remain for realizing wide commercialization of PEMFCs. Especially, the challenges in electrolyte materials have been tried to achieve through development of anhydrous proton conductors capable of operating at elevated temperatures (>100 °C) and at low relative humidity (<40%).

Recently, we announced an anhydrous proton conductor, $Fe_{0.4}Ta_{0.5}P_2O_7$ (FTPO), showing high proton conductivity in even non-humidified conditions. The conductivity of FTPO was 0.06 (100°C), 0.127 (150°C), 0.186 (200°C), and 0.248 S $cm^{-1}$ (250°C ) at different temperature [1]. An cell with FTPO electrolyte of 1mm thickness showed a power density of 170 mW $cm^{-2}$ at 200 °C and non-humidified condition. However, in the previous study, pellets made of FTPO powder was used as an electrolyte due to the difficulty in preparing sintered compacts of this material. Forming composites of inorganic and organic materials is known as one of the most promising methods to solve above problem.

In this study, we first investigated the proton-conducting properties of an inorganic-organic composite material based on FTPO under high-temperature and low-humidity conditions. Sulfonated polystyrene-b-poly(ethylene/butylene)-b-polystyrene (sSEBS) was used as starting organic binder. And then, we designed a composite cathode using a mixture of FTPO and sSEBS as an ionomer and analyzed its microstructure and polarization properties. Finally, we evaluated the performance of fuel cell using the optimized FTPO-sSEBS composite as an electrolyte and Pt-FTPO-sSEBS/C electrode as a cathode, wherein we are focusing the cell performance at the temperature range of 50 and 150 °C under unhumidified (or low humidity conditions).

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# Polyamic acid composites for multiple sensing applications in complex sample matrices.

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Polyamic acid/polypyrrole polymer blends have been developed to produce novel sensing platforms for the detection of volatile organic pollutants in aqueous media. The influence of synthesis conditions on the porosity, structural, and mechanical properties have been investigated. The polymer composites retained the functional moieties of polyamic acid with enhanced mechanical properties compared to those of the parent polyamic acid. Copolymerization with polypyrrole significantly improved the porosity morphology and electrochemistry of polyamic acid. Cyclic voltammetry (CV), Osteryoung square wave voltammetry (OSWV), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) experiments were conducted on electrodeposited polyamic acid/polypyrrole composites. The concentration effect was evidenced as a completely new reduction peak at +350mv (vs Ag/AgCl) indicating the formation of a novel polymer composite. Evidence from SEM and AFM provide good support for the kinetic evaluation of interfacial electrochemistry.

The polymeric composites were used as semiconducting platforms in the development of luciferase biosensors. The biosensor kinetics was evaluated using electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM). The responses to model volatile organic compounds viz. naphthalene and flouranthene have been studied in order to determine the limit of detection and linear range of the enzyme biosensors.

Keywords: polyamic acid, polypyrrole, volatile organic compounds, electrochemistry, SEM, EIS, EQCM, luciferase, biosensor.

# Examination of the fouling resistance capabilities of a laccase-based phenolic biosensor utilising multi-walled carbon nanotubes

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Phenolic compounds include numerous global priority pollutants and therefore, it is crucial to monitor such compounds in the environment[1]. However, high fouling rates utilizing electrochemical biosensors limit the development of such a device for commercial use. Fouling is a result of a passivating polymeric layer forming during the deployment of the sensor, which limits re-use of the biosensor[2].

In this study, the modification of glassy carbon electrode transducer surfaces with acid functionalised, multi-walled carbon nanotubes (MWCNT) were assessed for their applicability to improve the operational parameters and fouling resistance of a laccase biosensor[3]. MWCNT samples with different extents of functionalisation were tested for their fouling resistance towards a selection of substrates possessing differing fouling behaviours. Fouling resistance was assessed by comparing both electrochemical measurements in the absence of laccase (cyclic voltammetry) and changes in biosensor kinetics upon re-use of the biosensor (chronoamperometry).

Glassy carbon electrodes modified with MWCNT functionalised for four hours provided the most stable sensor surface for laccase modification amongst the biosensor configurations examined, relative to unmodified GCE.

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# Electrodeposition process to form patterned Si nanostructures

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Patterned nanostructures of Si have been attracting much attention as components of MEMS, semiconductor and photovoltaic devices, etc. For their fabrication, dry processes such as VLS (vapor liquid solid) and CVD (chemical vapor deposition) have been mainly applied. We have attempted to develop electrochemical processes to fabricate various micro & nano structures, featuring their precise controllability and ability to form uniform deposits. In this work, we attempted to develop electrodeposition process to fabricate patterned Si nanostructures such as array of nanopillars. Since the reduction potential of silicon oxide is quite negative, aqueous electrolyte system is difficult to apply. Therefore organic solvent such as propylene carbonate and ionic liquids have been applied [1, 2]. In this study, we used room temperature ionic liquid, trimethylhexyl ammonium ($TMHA^+$) bis-trifluorosulfonyl imide ($TFSI^-$) as electrolyte [3], which contained $SiCl_4$ as the source of Si. Sputter deposited Au/n-Si(100) wafers were used as substrates, on which patterning was carried out using UV-nanoimprint lithography (UV-NIL). Electrodeposition of Si was carried out potentiostatically to the patterned substrates, and as a result, it was confirmed that uniform deposition of Si nano patterns were obtained. The results of TEM, electron diffraction, XPS and Raman spectroscopy indicated that the deposited Si was amorphous, containing O and C. It was also confirmed that such contents of O and C, as well as uniformity of the deposits, were considerably affected by the temperature of the electrolyte during the deposition.

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# Calculation of tortuosity in a Li-ion battery cathode based on FIB/SEM tomography

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Tortuosity is regarded as one of the most important parameters to characterize a porous medium [1]. In the past, the tortuosity of Li-ion battery cathodes was usually calculated by expressing it as a function of the porosity via the Bruggeman equation. However, there is considerable doubt concerning the accuracy of this relation. We present a new method to calculate tortuosity. The starting point is the 3D reconstruction of a $LiCoO_2$ cathode created from FIB/SEM images with three phases, the active material domain, carbon-binder domain and pore space [2]. Pore size distributions, as determined by this work, suggest that a significant number of pores in the carbon-binder domain cannot be resolved by FIB/SEM. This conclusion is additionally supported by experimental data generated by Stephenson et al. [3]. To account for this, we propose a nanoporous carbon-binder domain with the following experimentally derived parameters [3]: i) 65% porosity. ii) Li-ion diffusivity or conductivity of 5% compared to the pore space filled with electrolyte. We compute joint effective diffusivities for pore space and carbon-binder domain for all three spatial directions. From this we calculate tortuosity values of 4.2 (x direction), 6.1 (y direction, the through-plane direction) and 5.7 (z direction). These values are consistent with experimental values for Li-ion cathodes reported previously [3].

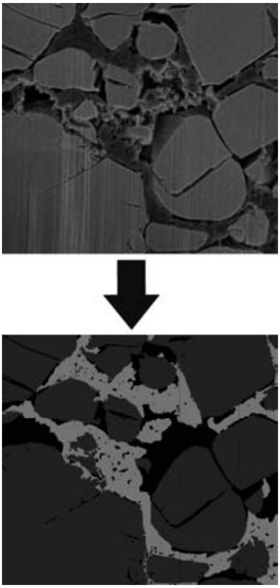

***Figure 1:*** *3D reconstruction by FIB/SEM tomography with a subsequent segmentation step enables the calculation of tortuosity. Pore space (black), active material domain (dark grey) and carbon-binder domain (light grey) are specified by their respective color.*

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# Conducting molecularly imprinted polymers for selective impedimetric determination of explosive nitroaromatic compounds

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New electrochemical sensors for selective determination of several explosive nitroaromatic (NT) compounds were fabricated by integration of conducting molecularly imprinted polymer (MIP) recognition films and resistance impedimetric transducers. The films were deposited on Pt disk electrodes from solutions of newly designed and synthesized bis(2,2'-bithienyl)-(4-aminophenyl)methane **1** functional monomer and each of different NT templates, i.e., 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and 2,4-dinitrotoluene (DNT), at the mole ratio of **1**:NT equal to 1:1 by potentiodynamic electropolymerization. Both theoretical DFT calculations at the M062X/3-21G* level and experimental fluorescence titrations indicated 1:1 stoichiometry of the **1** and NT pre-polymerization complexes formed in solution. Completeness of the template extraction from the MIP films was confirmed by the disappearance of XPS signals of the N atom of the -$NO_2$ groups. The NT recognition signals of the template-extracted MIP films were transduced to the changes of the film resistance using electrochemical impedance spectroscopy (EIS) under non-faradaic and batch-solution injection-analysis conditions. The limit of detection of these chemosensors was in the range of 8 to 30 nM indicating that they are suitable for practical determination of nitroaromatic explosives at toxic concentration (~10 nM). Moreover, selectivity of the sensors was determined by molecular cross-imprinting.

# Electrochemical Responses of Composite Olivine Lithium Iron Phosphate Cathode Material for Lithium Ion Batteries

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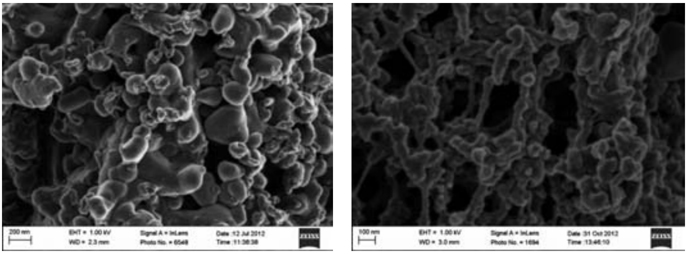
The exponential growth in portable electronics as well as increasing environmental concerns around the globe has attracted worldwide research and development for improved energy storage devices. Lithium ion batteries are the power sources of choice for consumer electronics, electric vehicles and renewable energy plants [1-2]. Current research is centered on the cathodes because they are the real bottlenecks in lithium ion battery development. In this study, composite cathodes consisting of lithium iron phosphate, derivatised carbon nanotubes and polyaniline nanomaterials ($LiFePO_4$/CoNiCNT-PA - Fig. 1b) were developed. The intercalation kinetics, lithium ion diffusion dynamics, rate performance, cyclability and electrochemical properties of these new cathodes will be presented and results compared with those of pristine $LiFePO_4$ (Fig. 1a).



a b

**Fig. 1**. SEM images of (a) Pristine $LiFePO_4$ (b) Composite $LiFePO_4$/CoNiCNT-PA.

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# The Impact of Microwave Treatment on the Oxygen Vacancy Concentration and Electrochemical Performance of $LiMn_{1.5}Ni_{0.5}O_4$ Cathode Material

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The electrochemical performance of $LiMn_{1.5}Ni_{0.5}O_4$ as a lithium ion battery cathode material is intricately linked to the (i) presence of $Mn^{3+}$ ions, (ii) doping/substitution, (iii) degree of disorder, and (iv) impurities [1]. It is common knowledge that the $Mn^{3+}$ ion is electrochemically active, however, a portion of the $Mn^{3+}$ ions may also form $Mn^{2+}$ through the disproportion reaction; $Mn^{2+}$ dissolves into the electrolyte at elevated temperatures, causing significant capacity loss during cycling. To enhance the cyclability and eliminate the impurities in the $LiMn_{1.5}Ni_{0.5}O_4$, a commonly adopted approach is to partially substitute Ni and/or Mn with metallic elements, such as Ti, Fe, Cr, Ru, or Mg [2]. The preferred synthesis strategy for the high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel should be able to (i) control the amount of the $Mn^{3+}$ in the final lattice structure, and hence the site disorder, (ii) limit the amount of the $Li_yNi_{1-y}O$ impurity, and (iii) maintain its high voltage (4.8 – 5.0 V) and achieve capacity close or better than the theoretical value of ~ 147 mA.h.g$^{-1}$.

In our study, $LiMn_{1.5}Ni_{0.5}O_4$ precursor cathode material was treated with microwave irradiation in order to study its effect on the oxygen vacancy concentration and thus on the cycle stability and capacity of the material. This presentation will describe the effect of microwave irradiation on the cathode material in terms of spectroscopy (XRD, XPS), microscopy (SEM) and electrochemistry (CV, galvanostatic charge-discharge test, and EIS).

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# Spectroelectrochemically Active Carboxylic acid Capped Semiconducting Nano-matrices of Metal Selenides Integrated ER-α , Receptor-sensor for Estrogens

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Small nanoscale materials show intrinsic properties beyond the point of being close to 1Å in size. The semiconducting novel thiol capped metal selenide based nanocrystals were synthesized and grown at room temperature. These nanocrystals posed a size average spherical crystal diameter of 30 nm and particle size diameter of 2 nm as supported by transmission electron microscopy studies. These semiconducting matrice nanomaterials showed good size dependent electron mobility, good electro-activity, electronic conductivity and good photolumniscence properties. Surface passivation of these materials with biocompatible ligands such as amines and carboxylic acids makes them popular in the fields of bio-engineering, biosensing and biological tagging and other applications. This work reports a novel semiconducting metal selenide matrixed estrogen-α receptosensor for estrogen E2. The electron induced protein-receptor-sensor was initially characterized by a dynamic linear range at micro concentration from 0.57 µM to 13.3 µM for E2, an LOD of 0.173 µM, an amperometric biosensor sensitivity of 2.8 µA/µM and an electrochemical response time of 1.2 seconds. The sensor was selective towards estrogens due to ER-α binding; which is selective to estrogen, showing greater affinity towards the ligand estradiol.

# Electroanalysis with Carbon Paste Electrodes and Related Sensors: 20 Years of One Collaboration in Middle Europe

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In this contribution, two decades of scientific collaboration between the two electroanalytical groups, (i) the Institute of (Analytical) Chemistry at the KFU Graz and (ii) the Department of Analytical Chemistry at the UPa, are reviewed. Having started in 1993, the join research work with carbon paste-based electrodes and related sensors has so far resulted in more than 50 scientific papers, a series of principal reviews (see *e.g.* [**1**,**2**]), several book chapters, up to the very first monograph in the field released last year [**3**]. Besides publication activities, the experimenation with CPEs had also been the main subject of many Master and PhD theses of students from both Universities (nearly 100 texts altogether) and of numerous other collaborations throughout the Europe, as well as overseas.

The join research work in the mid and late 1990s had been been focused on numerous topics, such as the development and testing of new methods employing chemically and biologically modified CPEs and proposed for the determination of toxic inorganic ions, glucose (series of papers), biological amines, some pharmaceuticals, etc. Besides, special characterisation of carbon pastes had also been of interest, including microscopic studies by OM and SEM. Also, in our labs, the first prototypes of screen-printed electrodes (SPEs) were manufactured; often, based on the already existing concepts from measurements with carbon pastes.

Then, in the 2000s, the individual directions mentioned above were further followed and some new started. Regarding the latter, especially the pioneering work on the bismuth based electrodes and sensors should be reminded, as our contribution to one momentarily popular area of the modern “green analytical chemistry”. Recent years were mainly in the sign of compiling the above-mentioned reviews and books; nevertheless, all distinct research activities forming our international profile went to a further progress; typically, hand in hand with newest trends: use of nanomaterials, sputtered layers of metals, electrospinning, or ecologically oriented electroanalysis.

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# Cathode for Dye Sensitized Solar Cells Based on Graphene Oxide

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The dye sensitized solar cell (DSC) is an attractive alternative to solid state photovoltaics [1,2]. The generic device is a photoelectrochemical DSC with sensitized nanocrystalline titanium dioxide photoanode, electrolyte solution with a redox mediator and the counterelectrode. The latter is typically a film of Pt nanoparticles on F-doped tin oxide (FTO) and the former is the triiodide/iodide couple in aprotic electrolyte medium. Recently, this couple was exchanged with Co(III/II)-based redox mediators [3,4]. The obvious motivation consisted in enhancing the voltage of DSC. Graphene nanoplatelets (GNP) exhibit high electrocatalytic activity for Co(III/II) based mediators [5,6]. Graphene oxide (GO) showed almost no activity as DSC cathode, resembling the properties of basal plane pyrolytic graphite. However, the activity of GO improved dramatically upon reduction with hydrazine and/or heat treatment. The reduced GO or GO/GNP composite films are favored by excellent adhesion to FTO and by higher stability against aging. All GO-containing films were firmly bonded to FTO which contrasted with the poor adhesion of sole graphene nanoplatelets to this support. The activity loss during long-term aging was considerably improved, too. Enhanced stability of GO-containing films together with high electrocatalytic activity is beneficial for application in a new generation of dye-sensitized solar cells employing $Co(bpy)_3^{3+/2+}$ as the redox shuttle.

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# Synthesis and Electrochemical Properties of Al-Doped $LiMn_2O_4$ Cathode Materials Using Solution Combustion Method

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$LiMn_2O_4$ spinel is a promising candidate for the positive (cathode) electrode in rechargeable lithium ion batteries (LIB) [1]. $LiMn_2O_4$ has got high attention because of its low cost, low toxicity, safety and high voltage compared to that of layered $LiCoO_2$, $LiNiO_2$ commercialized cathode materials for LIB. The most known drawback of $LiMn_2O_4$ is its capacity fading during repeated charge/discharge cycling [2]. One of the strategies to reduce the capacity fading of $LiMn_2O_4$ cathode materials is cation substitute of small amount of Mn ions in the crystal. Aluminium-doped lithium manganese oxide $LiAl_xMn_{2-x}O_4$ ($0 \leq x \leq 0.5$) spinel cathode materials were synthesized using corresponding metal nitrates and urea as starting precursors by solution combustion method. The morphology, structural and electrochemical properties of the as-synthesized cathode materials were examined by means of scanning electron microscopy (SEM), X-ray diffraction (XRD) and charge/discharge cycle battery tester.
It was found that aluminium doping showed great influence on their electrochemical properties and crystal structure. The synthesized $LiAl_xMn_{2-x}O_4$ cathode materials display a spinel structure exhibiting a small shift in peak position due to differences in size between Al ions and Mn ions. Partial cation doping of manganese in the host structure by aluminium (Al) ions yielded successful improvements to get stabilized electrode without any rapid capacity loss. The characteristics of stabilizing the discharge capacity by the synthesized samples are compared and the possible mechanisms will be reported.

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# Synthesis of three-dimensional graphene/carbon composites and their electrochemical applications

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Recently, graphene-based composite materials have attracted intense interest because of graphene's unique structure and extraordinary properties such as robustness and excellent electronic conductivity. We studied on the facile synthesis of composites made of graphene and multiwalled carbon nanotube (MWNT) or Vulcan carbon, which represented a new type of graphene based composites. The advantage of this synthesis method is the composite nanomaterials can be produced directly from graphene oxides through an *in situ* chemical reduction. A graphene-MWNT composite modified electrode exhibited good performance in terms of the electrocatalytic reduction of $H_2O_2$; a sensor constructed from such an electrode showed a good linear dependence on $H_2O_2$ concentration in the range of $2 \times 10^{-5}$ to $2.1 \times 10^{-3}$ mol/L. The detection limit was estimated to be $9.4 \times 10^{-6}$ mol/L. (Fig.) Also, we prepared graphene with Vulcan carbon composites to improve the mass transport by introducing necessary channels in the support. Graphene layers tended to form agglomerates when used in fuel cells, so a nano-sized spacer could separate some fraction of agglomerated graphene layers. So, Vulcan carbon was added as to enhance electrocatalytic activities of PtRu catalysts for methanol oxidation and thereby overall fuel cell performance. Experimental results showed that Vulcan carbon is effectively placed between graphene sheets, resulting in more triple-phase boundaries available for electrochemical reaction and better mass transport in the catalyst layer. We believe that this work could be one of the interesting concepts helpful for developing new supporting material in fuel cell application. Experimental details and results will be discussed.

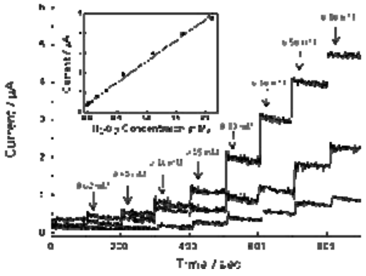

Fig. Addition of increasing concentration of $H_2O_2$ in 0.01 M PBS. Operating potential: -0.4 V.

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# Development of Mid-temperature PEMFC MEA under the Operating Condition of Low Relative Humidity

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Low temperature polymer electrolyte membrane fuel cell (PEMFC) using Nafion® membrane has been widely studied for fuel cell vehicles (FCVs). Recently, however, operation at mid-temperature (120 °C) and low relative humidity ($RH \leq 40\%$) is attracting attention in order to simplify the fuel cell systems. In such conditions, the membrane is dehydrated easily, and it becomes difficult to maintain suitable proton conductivity in membrane and catalyst layer. In order to bring up the voltage of MEAs that operate under low RH condition to the same level of MEAs that operate under high RH, it is important to retain water content in membrane and catalyst layer. Thus, to achieve the desired performance from the MEAs that operate under conditions of 120 °C and RH below 40%, it is necessary to design the membrane and electrodes so that water retention property within the MEAs is enhanced.

To add water retention ability in electrodes, materials which have water absorbing ability were dispersed in the catalyst layer. The MEAs were assembled to minimize membrane and electrode interface resistance, and the cells were operated at 120 °C with hydrogen/air which were humidified to RH of 40% or below. Electrochemical impedance spectroscopy, cyclic voltammetry and I-V polarization were performed to analyze changes in the catalyst layer during the cell operation. The changes in resistance and overpotential indicated that cell performances were influenced by the degree of water content in catalyst layer. The water content affected the active Pt sites and various resistances such as, ohmic, proton transport and charge transfer resistances. In this study, the optimum composition and structure of catalyst layers with high water content for operation at 120 °C will be discussed.

# Novel Nanoporous Carbons Based on Tobacco and Their Electrochemical Properties in Supercapacitors

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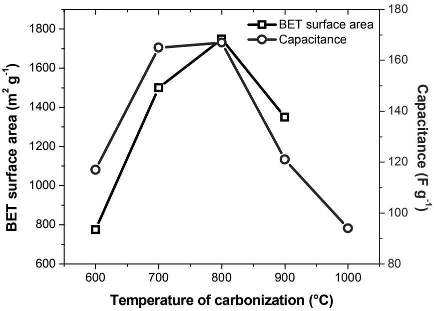
Novel porous carbons for supercapacitors, with a well-targeted porosity, were manufactured by one-step simultaneous carbonization and self-activation of tobacco. The advantages of tobacco plant are a well-organized agriculture, easy harvesting of well-described materials, and the possibility of using wastes, e.g. stems. The most important is the presence of elements, in the structure of tobacco, such as sodium and potassium, which are able to take an active participation in the self-activation process. Among several tobacco species the most promising was tobacco Burley.



The carbons were manufactured in a temperature range from 600°C to 1000°C under nitrogen atmosphere and further washed with HF and HCl to remove the inorganic matter. The tobacco Burley samples carbonized at 600°C are relatively rich in oxygen, 16–18 %; the BET specific surface area is 775 m$^2$g$^{-1}$. The carbon manufactured at 800°C possesses the highest BET specific surface area of 1749 m$^2$g$^{-1}$ among all samples pyrolyzed at various temperatures. While the pyrolysis temperature rises to 900°C, the BET specific surface area drops to 1316 m$^2$g$^{-1}$ and the oxygen content to 5–6 %. The other interesting feature is a very narrow pore size distribution (PSD) for tobacco carbonized at 600°C, with only ultra-micropores (<0.7 nm). The material pyrolyzed at 900°C possesses wider micropores, but in comparison to the industrial carbon DLC SUPRA 30 (Norit) it has definitely a much narrower PSD which is perfectly adapted to the electrolytes used for supercapacitors.

The carbons were implemented in supercapacitor cells with 1 mol dm$^{-3}$ neutral ($Li_2SO_4$), acidic ($H_2SO_4$) and organic ($TEABF_4$ in acetonitrile) electrolytes. Their capacitance values are higher than for most commercially available carbons. The maximum values were 169 Fg$^{-1}$ (0.8 V) in $Li_2SO_4$ and 143 Fg$^{-1}$ (2.7 V) in organic electrolyte for the sample prepared at 800°C. The best value of 218 Fg$^{-1}$ (0.8 V) was achieved in acidic medium with the carbons manufactured at 600°C. The graph shown above demonstrates a parallel dependence of BET surface area and capacitance in 1 mol dm$^{-3}$ $Li_2SO_4$ at 0.8 V vs. carbonization temperature.

Acknowledgements: The Foundation for Polish Science (Fundacja na rzecz Nauki Polskiej) is gratefully acknowledged for financial support of the research.

# The electro-oxidation of sulphur dioxide ($SO_2$)

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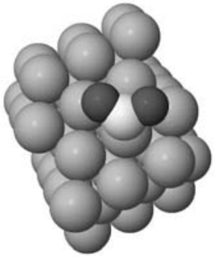
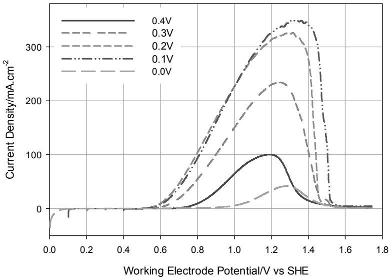
As a well-known gaseous pollutant $SO_2$ is not per say known as a source of energy. However, in the presence of water $SO_2$ can be electro-oxidised at the anode of an electrolyser to produce hydrogen ions, which in turn can be reduced at the cathode of the electrolyser to produce hydrogen gas (a known energy carrier). This reaction occurs at a standard potential of 0.16 V compared to 1.23 V for the regular water oxidation reaction, making it an interesting proposition for hydrogen production. Indications are that the greatest stride towards the development of an effective electrolyser, for the electro-oxidation of $SO_2$, requires the development of an enhanced anode electro-catalyst.

Current electrocatalyst experimental research and development efforts include single electrode electrochemistry studies on polycrystalline Pt, Pd, Rh and Au, with combinatorial studies that will be initiated in 2013. Conducting Koutecky-Levich and Levich investigations for the different polycrystalline metals are proving to be extremely problematic, which is probably due to the incoherent absorption of sulphur and sulphur containing intermediates on the surface of the electrode. This is clearly indicated by the change in the electrochemical behavior of the system, which is directly linked with the pre-conditioning of the electrode. Results obtained thus far on the experimental electrochemical investigation as well as current insights gained from a theoretical investigation, employing density functional theory (DFT), on the trends of the potential electro-catalytic activity of different metals for the electro-oxidation of $SO_2$, will be communicated. Current physical electrochemical observations would seem to be supported by the theoretical DFT calculations.



**DFT modeling of $SO_2$ on platinum.**



**Electro-oxidation of $SO_2$ on platinum.**

# Anodic-Driven Overcharge Issues of Cathodes in Lithium-Ion Battery Full Cells

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In the field of electrochemistry the cell voltage is one of the most important factors for determining the state of charge of a lithium-ion battery. However, the capacity determining objects of a lithium-ion battery full cell are the anode and cathode, which are usually tested as single components in half cells vs. $Li/Li^+$. As a consequence the electrode potentials can be measured. Unfortunately, with the combination of anode and cathode in a full cell, only the cell voltage as a difference between anode and cathode potential can be measured. Therefore, no exclusive information of the anode or cathode state of charge can be gained. Especially for the cathode which suffers a lot from overcharge issue, lsuch as $LiCoO_2$, this may cause problems, since it possesses a critical voltage of ~4.2 V where the structure is known to deteriorate.

In this work a previously proposed model is proved, which investigated the anodic influence on the cathodic overcharge issues during extended cycling. [1] Especially the end of charge points are focused (Fig.1), since the highest cathode potentials are present at fully charged cell chemistry. The effects of active surface area and the type of the anode as well as the electrode balancing in full cells are highlighted. Beside thermodynamic influences between the electrodes, the kinetics of the cells are also affected by the anodic nature

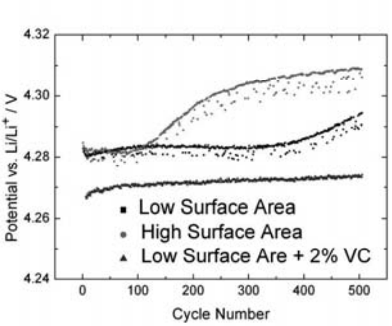

Fig. 1: End of charge Potentials of LCO cathodes in full cells depending on the cell chemistry. All cells were cycles in 1M $LiPF_6$ EC:DMC 1:1 (by wt) electrolyte.

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# Development of Nanostructured Materials Towards More Effective Electrocatalysis, Photoelectrocatalysis and Bioelectrocatalysis

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Recently there has been growing interest in fuel cells as alternative sources of energy. Presently, low-temperature hydrogen-oxygen fuel cells are probably the most promising and the best known system. The most commonly considered electrocatalytic systems utilize precious platinum and, therefore, there is a need to minimize contents of Pt (e.g. by activating it with certain metal oxo species including polyoxometallates of tungsten) as well as to look for alternate molecular catalysts comprising metalloporphyrins or N-chelates combined with Ru-based chalcogenides, and bifunctional materials inducing reduction of both oxygen and hydrogen peroxide intermediate. Electrocatalytic systems that would be useful in biological media, or the systems utilizing biocatalysts (enzymes), have to operate in neutral solutions. Unless highly specific and expensive enzymes, belonging to a group of proteins with the copper active centers (such as bilirubin oxidase or laccase) are considered, the reduction of oxygen in neutral media is a two-step process suffering from the formation of hydrogen peroxide as undesirable intermediate product. Under such condition, the problem can by addressed through application of Prussian Blue supports, in addition to classic and fairly cheap enzymes such as peroxidases or catalases (combined with macromolecular catalysts such as metalloporphyrines). Finally, broad utilization of hydrogen-oxygen fuel cells would require development of effective means of hydrogen production and storage. In this context, the visible-light induced photelectrocatalytic water splitting is an important concept that will be addressed in this presentation as well. We have found that modification of a regular mesoporous $WO_3$ film with colloidal gold nanoparticles resulted in a significant improvement of the delivered photocurrent. This improvement is related to changes in electric properties of the overall electrode due to particular features of gold nanoparticles coated with catalytically active phosphomolybdates adsorbates.

Our research interests also concern development of the direct alcohol fuel cells as alternative technology to hydrogen based electrochemical energy systems. For example, ethanol can be ideally oxidized to carbon dioxide thus delivering 12 electrons. But realistically the reaction is rather slow at ambient conditions. We are going to describe a concept of utilization of functionalized titanium dioxide, tungsten oxide or zirconium oxide matrices (by admixing them with polyoxometallate-modified gold nanoparticles) for supporting and activating noble metal nanoparticles (Pt, Pt-Ru or Pt-Rh) during electrooxidation of ethanol. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account improvement of overall conductivity (due to the presence of nanostructured gold) at the electrocatalytic interface (formed by metal oxide support), as well as and possibility of specific Pt-metal oxide or Pt-Au electronic interactions and existence of active hydroxyl groups on transition metal oxo species.in the vicinity of catalytic Pt sites.

# Electrodeposition of Metal Oxides Films in Various Room Temperature Ionic Liquids (RTILs)

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Room temperature ionic liquids (RTILs) are attracted electrolytes because they present a wide electrochemical window. Moreover they have high chemical and thermal stability, high conductivity and they can dissolve a large variety of organic and inorganic compounds due to their tunable chemical and physical properties. Therefore, RTILs have found many applications in electrochemistry and especially for electrodeposition of nanocrystalline metals and semiconductors. But so far, quite few works were devoted to the effect of addition of RTILs for inorganic material synthesis, especially for electrodeposited metal oxide thin films [1].

Cerium oxide (or ceria, $CeO_2$) is a promising metal oxide material for the surface treatment of different metals and alloys, because of its corrosion resistance in aggressive media. Because inorganic crystals chemical reactivity, electronic structure, bonding, and surface energy are directly related to their surface morphology, the ability to tune their shape is a challenging research. It is generally achieved by a precise control of the growth conditions, for a given composition of the solutions or by using various techniques and experimental conditions [2, 3, 4].

This work deals with the cathodic electrodeposition and characterisation of cerium oxide films by molecular oxygen activation onto stainless steel substrates via Ce(III) nitrate in imidazolium based RTIL). The influence of the nature of RTIL's cation of has been studied. Smooth and adherent cerium oxide thin films have been obtained and SEM and XRD characterizations have been carried out to determine the morphology and the thickness of the obtained films. The deposited oxide films are composed of small particles of cerium oxide lying on a dense and compact amorphous phase.

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# An Overview of Hydrogen Storage Materials: Making a Case for Metal Organic Frameworks

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One of the major challenges facing the transition to a Hydrogen Economy is the development of a suitable storage medium for hydrogen. Conventionally, hydrogen is stored as compressed gas or cryogenically as a liquid. In order to meet future targets hydrogen needs to be stored in a safe and compact manner by combining the gas with other materials either chemically or physically. Hydrogen storage is therefore an extremely active area of research worldwide with many different materials being examined for use in the storage of hydrogen. Research efforts are focused on enhancing hydrogen storage capacity, thermodynamics and kinetics of hydrogen uptake and release, and cycle life of the materials. Materials that store hydrogen chemically which have been investigated extensively include metal hydrides (e.g. $MgH_2$), complex hydrides (e.g. $LiAlH_4$), amides/hydrides (e.g. $LiNH_2/LiH$) and amidoboranes (e.g. $LiNH_2BH_3$). Physisorption materials (e.g. carbon nanostructures and zeolites) have also received considerable attention. In the past decade, there has been growing interest in metal organic frameworks (MOFs) as hydrogen storage materials due to their well-defined structure, tunability, high porosity and large specific surface area. This presentation provides an overview of different hydrogen storage materials along with our research work on MOFs.

# Optical Properties of Electrodeposited Polyselenophene Derivatives

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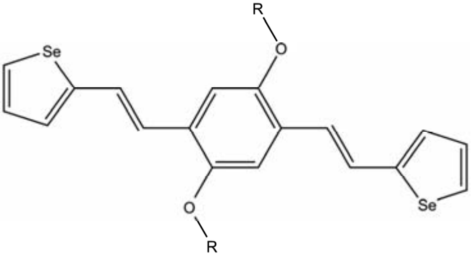
PTh (polythiophene) was one of the first well designed and characterized stable π-conjugated conducting polymer composed of a five-membered ring[1]. Introduction of the alkyl group to PTh led to enhancement of solubility of PTh without losing the essential π-conjugation system of PTh[2]. There are few investigation of polyselenophene chemical and electrochemical analysis[3]. During investigation changing of electronic and optical properties of selenophene compounds was observed. The analysis of selenophene compound were associated with examination of influence of alkyl chain to obtained polymer during electrochemical polymerization. Four of (E,E)-1,4-dialkoxy-2,5-bis[2-(selenophen)-2-yl)ethenyl]benzene derivatives have been electrochemical polymerized and characterized (Fig.1). Large optical differences in comparison of branched alkyl substituents to linear one were observed.



R=Me (1), iPr (2), Bu (3), Hex (4)

Figure 1. Investigated compounds.

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Acknowledgements
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# Gold-silver Nanoparticles for Efficient Electro-reduction of Carbon Dioxide

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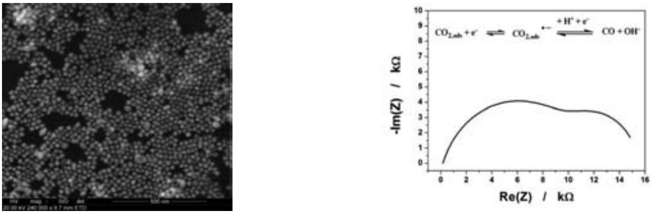
Carbon dioxide electro-reduction ($CO_2$ER) has been studied the last few years employing various metallic electrodes and electrolytes for the conversion of $CO_2$ to different components of the fuel pool, which include alcohols, aldehydes, hydrocarbons and carboxylic acids. $CO_2$ER, however, still suffers from high over-potential as well as the competing hydrogen evolution reaction (HER). Despite the large number of papers on $CO_2$ER little research have been conducted on gold nanoparticles (NPs), with even less on gold-based alloys as catalysts for these reactions. Silver has been studied as a cathode material in an electrolysis cell converting a mixture of $CO_2$ and $H_2O$ to syngas, and recent studies show the superior activity of different core-shell nanoparticles (NPs) over the classic monometallics or NP alloys for the preferential oxidation of CO in the presence of hydrogen or vice versa [2].

With the above in mind, Au@Ag core-shell NPs and Ag decorated Au NPs have been synthesized and tested for $CO_2$ER. The degree of coverage of the cuboctahedral Au NPs with Ag ranged from a thick Ag layer (a true core-shell structure) to an incomplete Ag layer (the so called Ag decorated Au NPs). The morphology of these new materials was confirmed by UV-spectroscopy, high-resolution TEM and electrochemical characterization. The correlation between the morphology of the Au-Ag particles and the efficiency of $CO_2$ER was followed with linear sweep voltammetry. Rotating-ring disk electrode studies allowed the determination of the onset potential for $CO_2$ER and thereby the over-potential required for this reaction. Through electrochemical impedance spectroscopy (EIS) improved discrimination between $CO_2$ER and HER was obtained as well as evidence for the dependence of the reaction mechanism on the morphology of the catalyst. The results showed that the Au@Ag NPs present higher stability during long-term electrolysis, which indicates that this new material could be a promising catalyst for $CO_2$ER.



SEM images of Au@Ag NPs and EIS spectrum recorded for $CO_2$ER at Au NPs.

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# $Al_2O_3$ coated $TiO_2$ nanotubes based Dye Solar Cells

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The talk will discuss findings on our investigations on the effect of *$Al_2O_3$-coated $TiO_2$ nanotubes* on the efficiency of dye solar cells (DSCs). The $TiO_2$ nanotubes were prepared via an anodisation method with the $Al_2O_3$ coating applied by means of a sol-gel dip coating method [1,1]. $TiO_2$ nanotube arrays were synthesised in an organic neutral electrolyte [2] consisting of $H_2O$, $NH_4F$ and ethylene glycol (EG) at an applied voltage of 60 V for 6 hours. The resulting tubes had an average length of 15 µm, diameter of 45 nm and wall thickness of 15 nm.
Scanning electron microscope (SEM) micrographs showed that anodisation at these conditions yields nanotubes with smooth walls and hexagonally shaped, closed bottoms.
Initial x-ray diffraction (XRD) diffractograms suggest that the as anodised nanotubes were amorphous and were then annealed at 450 °C for 2 hours in air. Subsequent diffractograms following annealing showed an improvement to crystalline anatase $TiO_2$ nanotubes.
High-resolution transmission electron microscope (HR-TEM) images suggested that the nanotube walls consisted of individual nano-sized $TiO_2$ crystallites.
Atomic force microscopy (AFM) showed that the average nanotube diameter decreased after sol-gel deposition (from 45 to 17 nm), which suggests that the nanotubes are coated with a layer of $Al_2O_3$. This was confirmed by HR-TEM, in conjunction with selected area electron diffraction (SAED) and XRD analyses. It showed the coating of the nanotube walls with a thin layer of amorphous $Al_2O_3$ with a thickness between 4 and 7 nm. Ultraviolet-visible (UV-vis) absorbance spectra showed that the dye-adsorbability of the nanotubes is enhanced by the $Al_2O_3$.
The DSCs were assembled with a 15 µm thick layer of bare $TiO_2$ nanotubes and the efficiency was determined by means of photocurrent density – voltage (I – V) measurements. The measurements indicated a photon-to-light conversion efficiency of 4.56% for the uncoated $TiO_2$ nanotubes and increased to 4.88% (7% increase) after coating the nanotubes with a layer of alumina.

Keywords: anodisation, efficiency, photocurrent density, Dye solar cells, $TiO_2$ nanotubes, alumina

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# Isocyanide-Adsorbed Au Nanoelectrode to Detect Biogenic Volatile Organics by Raman Scattering Spectroscopy

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Volatile organic compounds (VOCs) are numerous, varied, and ubiquitous. In nature, much of VOCs arise from plants, and the biogenic VOCs dominate over the anthropogenic ones. The biogenic VOCs include the isoprenoids (or terpenoids) such as isoprene and monoterpenes, as well as alkanes, alkenes, carbonyls, alcohols, esters, and acids. Recently, isoprene ($C_5H_8$), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$) have received a great attention since these VOCs can produce tropospheric ozone ($O_3$) in the presence of nitrogen oxide. The early detection of biogenic VOCs is thus a challenging task. This is especially because biogenic VOCs are very reactive and their concentrations are usually very low in ambient air. There are several methods to detect biogenic VOCs, including flame ionization detection, mass spectrometry, photoionization detection, electron-capture detection, and ozone chemiluminescence detection. Among them, the flame ionization detection and mass spectrometry are most widely used for the quantification of biogenic VOCs. So far, no device has yet been developed to use vibrational spectroscopy, however, probably due to their low detectability.

Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the Raman scattering cross sections are dramatically enhanced for the molecules adsorbed thereon. Due to its higher enhancement factor, SERS has been applied to many areas of science and technology including chemical analysis. When a molecule is adsorbed on the SERS-active surfaces, its electronic structure changes noticeably, resulting in the shifting and splitting of spectral lines. Further spectral change can occur by the application of an external electric field. For instance, the peak position of the NC stretching band in the potential-dependent SERS spectrum of 2,6-dimethylphenylisocyanide (2,6-DMPI) is sensitive to the electrode potential. We found recently that a similar NC stretching peak shift can occur even when a 2,6-DMPI-adsorbed Au nanoaggregate is exposed to polar organics like acetone and ammonia, even though the SERS peaks of polar organics cannot be identified probably due to their low adsorption strength and/or their intrinsically small Raman cross sections [1].

We illustrate in this work that the NC stretching band of 2,6-DMPI adsorbed on a poly(ethylenimine)-capped Au film is very susceptible even to the kind of biogenic VOCs exposed, such as isoprene, farnesol, and (+)-α-pinene, suggesting that the isocyanide-adsorbed noble metal nanostructures can be used as a platform for a biogenic VOC sensor operating via SERS. To our knowledge, this is the first report, informing the applicability of SERS, though indirect, in the detection of biogenic VOCs.

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# Electrochemical Performance of MWCNTs-CoTPyzPz//CB-MWCNTs Asymmetric Capacitors

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Recently, capacitor materials based on phthalocyanines with high specific capacitance have been reported [1, 2]. In this study, the capacitive performance of an asymmetric capacitor comprising of functionalized multi-walled carbon nanotube and metallotetrapyrazinoporphyrazine (MWCNT-MTPyzPz) composite as cathode was evaluated. The composites were made from either acid functionalized MWCNT (MWCNTaf) or phenyl functionalized MWCNT (MWCNTPhNH$_2$) and Cobalt (II) tetrapyrazinoporphyrazine or Fe(II) tetrapyrazinoporphyrazine.

An asymmetric capacitor cell, MWCNTaf-CoTPyzPz//CB-MWCNTaf, where the anode was carbon black-acid functionalized MWCNT (CB-MWCNTaf) showed an energy density of 8.5 Wh.kg at a power density of 4.3kWkg$^{-1}$ calculated from charge discharge curves (Figure 1). This asymmetric capacitor showed good energy efficiency and an excellent cycle stability at 200mA.g$^{-1}$.

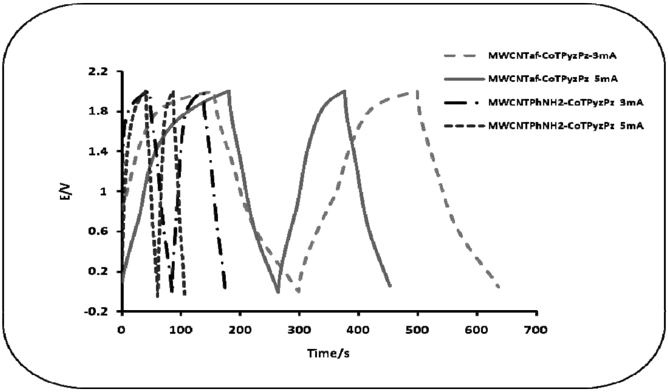

Figure 1. Charge-discharge profiles of MWCNTaf-CoTPyzPz//CB-MWCNTaf and MWCNTPhNH$_2$-CoTPyzPz//CB-MWCNTPhNH$_2$.

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# Optimization of 1-D ZnO Nanostructures for Photovoltaic Applications

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One dimensional (1-D) ZnO nanostructures are intensively investigated due to their properties and various potential applications, including solar cells. The electrochemical deposition of ZnO based on the reduction of molecular oxygen is a low cost method, easily scalable and well suited to obtain arrays of vertically aligned ZnO-NWs (nanowires) [1, 2], ZnO-NTs (nanotubes) [3] and ZnO Urchins [4] with controlled dimensions. Their morphology, electrical and optical properties are promising to develop new types of solar cells based on the concept of semiconductor sensitization of nanostructured wide-band gap oxides [5]. This is well illustrated by the ZnO-NWs(NTs)/CdSe/CuSCN (extremely thin absorber) ETA-solar cells made by electrodeposition of ZnO and CdSe and solution casting of CuSCN [6]. An overview of our efforts developed to increase the conversion efficiency of the ETA-solar cell is presented. Strategies to reduce the thickness of CdSe shell without decreasing the solar light absorption will be discussed [7, 8], as well as the effects of the dimensions of ZnO nanowire diameters on the light scattering, and their influence on the photon harvesting of ZnO/CdSe core-shell NWs [9]. Optimizing the photon harvesting is found to be a successful strategy to increase the energy conversion efficiency of the ZnO-NWs/CdSe/CuSCN ETA-solar cell up to 3.2 % [10].

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# Electrochemical sensing of antioxidant properties: screening of bioactive compounds

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Voltammetric methods of analysis represent a potentially simple and rapid option for screening of large numbers of crude plant and algal samples in the search for novel antioxidants. These methods also hold particular value for studies aimed at unraveling antioxidant mechanisms, including metal binding processes. The wider adoption of these methods is, however, still limited.

Here we provide a critical assessment of voltammetric methods for identifying antioxidants through a comparison with more established DPPH and Folin Ciocalteu assays in a study of ninety nine crude samples of marine algae. Furthermore we examine the extension of this method to guide the isolation of pure antioxidant natural products from the marine brown alga *Sargassum elegans* (Suhr). The application of adsorptive stripping voltammetry studies for probing metal-ligand interactions of antioxidant compounds of plant origin is also examined.

Results suggest that voltammetric methods can identify potential antioxidants in crude samples studied with a higher degree of confidence than DPPH or the FC method alone and represents a potentially viable screening method for marine algal samples. The methods employed further served to guide the isolation of four pure compounds with strong antioxidant potential. Metal binding assays with several compounds including curcumin and capsaicin support voltammetric methods for identifying metal binding interactions of toxicological significance.

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# Palygorskite Hybridized Carbon Nanocomposite as PtRuIr Support for the Methanol Oxidation Reaction

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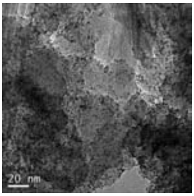
Direct methanol fuel cells (DMFCs) become an active research area since it is low toxic, easy for storage and refilling and no fuel reformer is required[1]. Currently, the use of carbonaceous support materials dominates the field of electrocatalyst for fuel cells due to its high conductivity, relatively high corrosion resistant and porous structures. Unfortunately, the corrosion of carbon supports resulting from the electrochemical oxidation in DMFC operating conditions has been identified to be the major contributor to the low catalyst performance, durability and reliability[2]. Palygorskite (PLS) is a $SiO_2$ based porous material possessing high surface area with high stability [3]. Compared to porous carbon materials, PLS is much cheaper due to its accessibility and its high stability, which makes it a potential candidate as a new support material for use in electrocatalyst for DMFC. However, PLS has low electrical conductivity and cannot be used as electrocatalyst support material 'directly'.

It was found that Carbon NanoTube (CNT)-supported ternary PtRuIr electrocatalysts formed very small particle sizes and showed excellent activity towards the MOR[4]. In this paper, the principal objective of the investigation was to develop a simple and low cost method of preparing PLS and carbon hybrid composite support materials (C-PLS). Subsequently, PtRuIr nano-sized alloy particles were deposited on its surface and evaluated towards the MOR. The morphology and electrocatalytic properties of synthesized PtRuIr/C-PLS were also investigated. The results show that the C-PLS composite appears to be a promising support material for DMFC electrocatalysts.



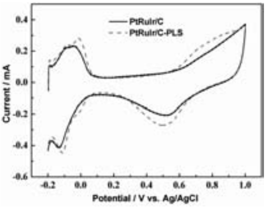


Figure 1, TEM of PtRuIr/C-PLS

Figure 2, Cyclic voltammograms of PtRuIr/C and PtRuIr/C-PLS catalyst in 0.5 mol/L $H_2SO_4$

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# Electrochemical deposition and characterization of platinum on carbon paper and Ni foam for methanol oxidation for fuel cell application

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There are various methods used to prepare fuel cell (FC) catalysts. The electrochemical deposition method is well known for the fabrication of nanostructured catalysts for energy materials[1]. Electrochemical atomic layer deposition (ECALD) method was chosen in this study for the deposition of Pt nanostructures onto FC gas diffusion layer (GDL). The typical GDL for fuel cells, carbon paper was chosen as a substrate for the deposition of Pt. Ni foam was selected because it performed better than Ni mesh as electrode substrate in alkaline fuel cells [2]. Electrochemical evaluation and morphological studies were carried out on the electrodeposited Pt. Cyclic voltammograms of the electrodeposited Pt nanostructures showed features characteristic of polycrystalline Pt electrodes. SEM/AFM images showed good quality deposits that uniformly covered the substrates and EDX confirmed the presence of Pt. The ease, flexibility and cost effectiveness of this method for preparing nanostructured catalysts makes it advantageous for application in fuel cell.

Table 1. Summary of the important activity indicator of methanol oxidation reaction

| **Catalyst** | **Maximum currentdensity (mA/cm$^2$)** | **Onset Potential (V)vs. Ag/AgCl** | **$I_f/I_r$** |
|---|---|---|---|
| Pt/Carbon paper | 0.85 | 0.35 | 4.30 |
| Pt/Ni foam | 5.94 | 0.35 | 2.16 |

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# Ultra-sensitive electrochemical nanosensors of star copolymer platform using polypropyleneimine and polythiophene

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Due to the global challenges for mapping and monitoring polyaromatic hydrocarbons (PAHs) which are released as liquid and gaseous effluents during the processing of fossil fuel (coal, oil and tar), several methods have been applied in their detection such as HPLC, GC and electrochemical methods. Ultra-sensitive nanosensors receive a lot of attention in research with novel dendrimeric smart nanocatalysts being sought for the modern technology advancements to provide highly sensitive electrochemical nanosensor platforms for monitoring and mapping PAHs. In our study, novel copolymer consisting of poly(propylene imine) generation 3 dendrimer and 2-thiophene carboxaldehyde were prepared chemically to achieve G3PPT according to methods modified from literature. Electrochemically, generation 3 poly(propylene imine)-polythiophene (G3PPT-co-P3HT) star copolymer Au electrode was obtained. The star copolymers electro-polymerization mechanism, structure, and properties were intensively investigated in view of their multiple potential technological due to their conductivity. The constructed nanosensors platform were studied and characterized by cyclic voltammetry (CV), alternating current voltammetry (ACV), Square wave voltammetry (SWV), $^1$HNMR and Fourier Transform infra-red spectroscopy (FTIR).

Keywords: ultra-sensitive nanosensor, ac voltammetry, polyaromatic hydrocarbons, star copolymer

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# Electrochemical Properties of Graphene oxide/Manganese Oxide Nanocomposites for Electrochemical Capacitors

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Electrochemical capacitor has become a focus of attention of many researchers for decades due to their potential application as energy storage devices owing to their high energy density, great power density and long cycle life [1,2]. Electrochemical capacitor, also known as supercapacitor or ultracapacitor, is well recognised for its application in a variety of everyday applications including laptop computers, cell phones, and hybrid electric vehicles. These devices store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudocapacitors) [2,3]. Various materials such as carbon materials, transition metal oxides, metal hydroxides and polymeric materials have been explored for supercapacitor application [4]. As one of the green supercapacitor electrode materials, $MnO_2$ shows potential to replace $RuO_2$ due to its high specific capacitance, environmental compatibility, low cost, and abundance in nature. To improve the electrochemical performance, the strategy of direct deposition of $MnO_2$ on large-surface area materials, such as carbon blacks, carbon nanotubes, activated or mesoporous carbons, is quite promising. Recently, graphene oxide (GO), has been widely investigated as a suitable support for $MnO_2$ [5,6].
In this study, we first report the preparation and characterisation of the GO-$MnO_2$ using XRD, FTIR, UV-Vis, Raman, TEM, FESEM and EDX. Next we report the synergic electrochemical properties of GO-$MnO_2$ as an electrode material for the development of asymmetric electrochemical capacitor.

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# Bubble over voltage modelling during two-phase electrolysis. Experimental Study

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During two-phase electrolysis processes, for example for hydrogen production, there are bubbles which are created at electrodes. This implies a great vertical motion source in the normal earth gravity field and then a quite important natural two-phase convection. All other fields are then affected. Heat, mass and electricity transfers are modified due to both bubbles screening (at surface and in volume) and to bubbles transport promotion.
Many numerical modeling for two-phase processes such as kerosene pulverization in engines or coal combustion sciences have shown the difficulties of these multi-physics processes. Both particles and reactor scales must be considered according with a strong coupling modeling. In these processes the particles injection is "in the flow". In boiling or electrolysis processes, a new difficulty is added: particles birth or injection is strongly coupled to the local flow properties and leads to a complex boundary condition at surfaces. Electrical and electrochemical properties and processes are disturbed. This disturbance can lead to the modification of the local current density and to anode effects for example.
The both experimental and numerical investigation is here presented. Experiments are performed in laboratory and in zero gravity (parabolic flights) on Na2SO4 systems. Numerical calculation are performed for both bubble and electrochemical reactor cell.

Key words: Two-phase electrolysis, hydrodynamic electrochemical processes

# Synthesis and Characterization of Graphene Foam Composite for Electrochemical Applications

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The increasing demand for renewable and sustainable energy resources has intensified research activities for the development of energy storage systems that can meet future power requirements. Graphene, a two-dimensional honeycomb lattice of $sp^2$-bonded carbon atoms, has emerged and is being considered an ideal additive material for improved electrochemical charge storage application. This is because of its theoretical high surface area ($2630 m^2g^{-1}$), high electrical conductivity, chemical stability and excellent mechanical properties. More recently, the development of supercapacitors electrode materials has been focused on nanostructures composite of graphene and metal oxides. In this work we present supercapacitor device based on composite of graphene foam (GF) and metal oxide nanostructures highlighting the synergistic effects between graphene and metal oxides for improved electrochemical performance.

Keywords: Graphene foam, supercapacitors.

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# Synthesis and Electrochemical Characterization of Nickel Nanoparticles and their Conjugates with Phthalocyanines

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Metal nanoparticles have generally been produced by both gas and liquid phase processes [1]. The chemical reduction method is generally considered to be the ideal due to the ease of synthesis and low cost [2]. In order to prevent agglomeration of the nanoparticles, protecting agents are used. The protecting agents bearing the amine or carboxy groups are of interest in this work because they allow for the formation of Ni nanoparticle (NiNPs)-phthalocyanine (Pc) conjugate (Fig. 1) through an amide bond. The Pcs synthesized include those substituted with carboxy and tetraamino groups. Electrode surfaces will be modified with the NiNPs, Pc, metal NiNP-Pc conjugate~~s~~ or simply a mixture of NiNP and Pc. The surfaces will be characterized by several techniques including X-Ray photoelectron and Raman spectroscopies, atomic force and transmission electron microscopies and voltammetry. The Pc alone or its conjugate with nickel nanoparticles will be used to catalyse the electrochemical detection of analytes such as 2-mercaptoethanol.

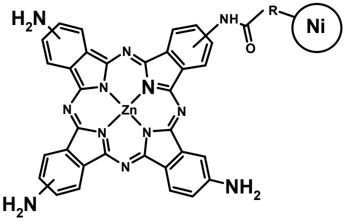

Figure 1. Structure of the nickel nanoparticle –phthalocyanine conjugate

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# Junction Electroanalysis

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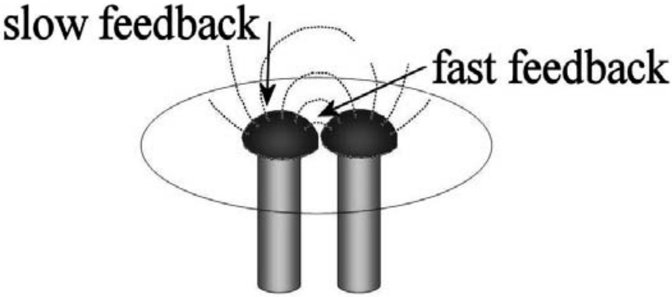
Electrochemical sensors based on two adjacent electrodes [1,2] with down to sub-micrometer separation provide an interesting alternative to conventional sensors based on a single electrode. The second electrode provides “feedback currents” in the case of chemically stable redox systems or even for the case of chemically reactive systems. Both sensitivity and selectivity can be enhanced.



The potential of the second electrode can be switched to remove unwanted background processes or stepped into the negative potential range to change the pH locally within the region between the two electrodes. Different types of new electrodes and electroanalytical processes will be discussed.

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# Bifunctional catalyst for electrocatalysis of oxygen reduction and water oxidation derived from manganese metalloporphyrins

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The development of low cost catalysts for oxygen reduction in fuel cells is a prerequisite for the development of commercially viable fuel cells. Large scale commercialization of fuel cells which rely on platinum would be hampered by cost and scarcity concerns. Catalysts obtained by pyrolysis of mixtures of a transition metal (M), nitrogen (N) and carbon (C) precursors (MNC catalysts) are a very promising class of non-precious metal based catalysts for oxygen reduction. Iron and cobalt are the most commonly used metals for synthesis of MNC catalysts. In this presentation, it will be shown that very active MNC catalysts which reduce oxygen nearly exclusively through the four electron pathway can also be obtained by pyrolysis of judiciously chosen manganese metalloporphyrins at mild temperatures. The manganese catalysts owe their high activity to the rich redox chemistry of manganese due to the multiple stable oxidation states of manganese compounds. We shall also show that besides their potential use in fuel cells, the catalysts can also be employed as dual purpose electrodes in metal-air batteries [1-3] for the reduction and evolution of oxygen when modified with manganese oxide.

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# Design and development of electrochemical biosensing systems for the detection of disease biomarkers for human and animal health

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The design and development of electrochemical biosensing systems for the detection of disease biomarkers is of paramount importance for monitoring animal and human health. Animal health in particular, is of interest to our research as 75% of human infectious diseases originate from animals (i.e. zoonotic diseases). Therefore, the design of early warning systems for the surveillance of disease outbreaks and to curb the spread of zoonotic diseases has become imperative.

Several systems are investigated at Mintek under the Nanotechnology Innovation Centre (NIC) – Electrochemistry Sensors Research and Development Group (Mintek NIC Sensors). The special focus for the group’s research has been on zoonotic diseases such as rift valley fever and several other diseases. The systems employed for the detection of such diseases include; electrochemical systems, enzyme linked-immunoassays (ELISA) and immunochromatographic lateral flow systems. The interest in these systems is their potential adaptability to detect multiple analytes simultaneously and they are very sensitive. The new generation of diagnostic combo systems with electrochemical component coupled with ELISA or lateral flow systems are investigated. The NIC Sensors Group has embarked on the research aiming at designing hybrid systems for application in remote areas or at point-of-care sites. This presentation will describe the development of electrochemical biosensor systems that will provide qualitative and quantitative analysis of infected serum or blood samples.

# Indigo dye incorporated Polyaniline composite's chemical and electrical properties

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Dye doped polymers (DCPs) has a wide application based on their optical and electrochemical properties. Polyaniline (PANI) has been widely researched due to its unique and controllable chemical and electrical properties. The chemically and electro synthesised of PANI in the presence of indigo/2, 2'-Bis (2, 3-dihydro-3-oxoindolyliden) (IND) composites were characterized by spectrophotometry and electrochemistry. The bluish green solids are slightly soluble in alcohols. The infrared spectra of PANI-IND has all the principal peaks of PANI (3250, 2667, 789 and below 700 $cm^{-1}$) as well as distinct peaks of IND (overtones between 1700 and 2000nm). Conventional cyclic voltammogram of PANI and PANI-IND had four distinct peaks and an addition peak at 600 mV in PANI-IND was observed. The intensities of these peaks increased with an increase in dye concentration. Therefore there is minimum interaction between the dye and the polymer. Morphological changes observable are smooth and orderly tubular PANI-IND. These observations are consistent with layer by layer arrangement. Fluorescence, UV-VIS and photoluminescence properties of PANI-IND indicates a wavelength red shift and increased intensity, thus indicating improved optical properties.

# 20 Years of Collaboration in the Middle Europe. Part II: (Bio)sensors Based on Screen-Printed Carbon Electrodes

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In this overview, scientific collaboration between the two electroanalytical groups, the Institute of (Analytical) Chemistry at the KFU Graz and the Department of Analytical Chemistry at the University of Pardubice, is presented. Having started in the early 1990s, the join research work was first focused on applicability of various types of carbon paste electrodes (CPEs) in inorganic and organic electroanalysis. The research work with this typical heterogeneous carbon material had logically stepped into another stage, when the individual developed concepts were tested and subsequently adapted for contemporarily progressive screen-printed carbon electrodes (SPCEs) [1].

Similarly as in case of CPEs, the printed heterogeneous carbon sensors could be modified by chemical or biological compounds in different ways. Direct admixing of bismuth(III) or antimony(III) oxides into printing ink served for electrochemical generation of corresponding metal film during accumulation of heavy metals in stripping analysis [2]. For the same purpose, the bismuth powder was incorporated as well. Such procedures eliminated the needs of addition of metal ions for formation of *in situ* bismuth or antimony film electrodes, which simplified the whole analytical procedure.

Joint research was also devoted to the preparation and characterization of SPCEs modified with various inorganic or organic compounds of metals, especially platinum group metals. From those particularly oxides and some organic complexes were tested for enhanced electrocatalytic detection of hydrogen peroxide and NADH in amperometric enzyme biosensors [3]. Different configurations of screen-printed biosensors comprising of mediator, oxidase or dehydrogenase, and protecting Nafion membrane were employed for the detection of glucose, biogenic amines, and ethanol in foodstuff using flow injection analysis. In recent years, the continuing work was in the sign of utilization of new progressive materials and approaches, e.g. conducting polymers and specially designed porous metal layers.

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# Electrodeposition of Pd on Carbon Paper and Ni Foam via Surface-Limited Redox-Replacement Reactions for Oxygen Reduction Reaction

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Fuel cells continue to be investigated as alternative energy source because of the worldwide increasing high energy demand. The electrocatalytic reduction of oxygen is of great importance in fuel cells and sensors. Noble metals have proved to be the best electrocatalysts for the oxygen reduction reaction (ORR). Among these electrocatalysts, Pd has attracted enormous attention since it is more abundant and cheaper than Pt. In the pursuit to improve reproducibility while overcoming the loss of catalytic activity during the catalyst preparation process, Pd nanosturctures are grown directly onto fuel cell gas diffusion layers and evaluated for the ORR. Pd nanostructures were synthesized via surface-limited redox replacement (SLRR) reaction employing the electrochemical atomic layer deposition (ECALD) technique. Pd was deposited on carbon paper and Ni foam substrates using Cu as a sacrificial metal following the procedure published by Mkwizu et al. [3]. The electrochemical activity of the prepared nanostructures towards ORR was investigated in both acidic and alkaline electrolytes at various flow rates. The morphology and particle size of the deposited nanostructures were characterised using microscopy techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). The nanoparticle composition on the substrate was estimated using energy dispersive X-ray spectroscopy (EDX) as illustrated in figure 1.

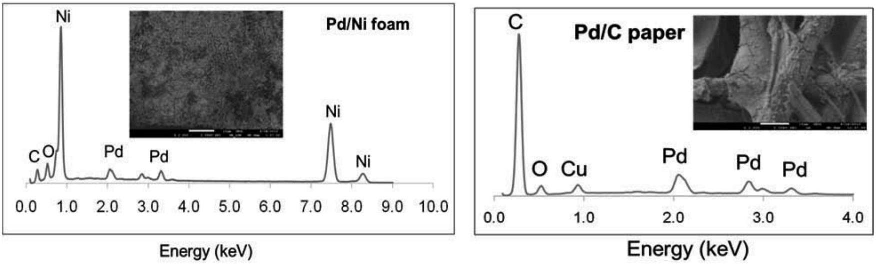

Figure 1: SEM micrographs and EDX profiles of Pd nanostructures on Ni foam and Carbon paper

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# Improved photoelectrochemical activity of $TiO_2$ nanotube arrays modified by deposited $Ag_2S$ nanoparticles

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Free-standing $TiO_2$ nanotube array (TNA) films were fabricated via two-step anodization of titanium sheet. The electrolyte consisted of DI water and ethylene glycol solution with volume ratio of 10:90, containing 0.1 M $NH_4F$ and $H_3PO_4$ (to reduce pH to about 5.7). The anodization process was carried out at optimized applied voltage of 60 V for 200 min. X-Ray diffraction (XRD) analysis indicated that TNAs are in anatase crystalline structure after annealing the films at 500 ºC in air producing well ordered and vertically oriented nanostructure with 122 nm in diameter, 28 nm in wall thickness and 4 μm in length based on their SEM observations (Fig. 1a). Surface modification of TNA was performed by using sequential-chemical bath deposition (S-CBD) method to fabricate $Ag_2S$ nanoparticles on the grown TNA forming $Ag_2S$/TNA nanostructure (Fig. 1b). Maximum photocurrent density of about 8.4 $A/m^2$ was measured for this system in visible light which shows 15 fold improvements as compared with the pure TNAs under similar conditions. The incident photon to current efficiency (IPCE) measurements determined that the visible photoresponse of the samples reached to its maximum value of ~18% at wavelength of 580 nm for the $Ag_2S$/TNA thin film system.

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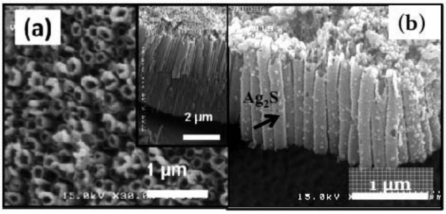

**Fig. 1.** SEM image of pure $TiO_2$ nanotube arrays after annealing in air at 500˚C for 80 min (a) and $Ag_2S$ modified TNAs (b). Inset: Cross sectional view of the corresponding system.

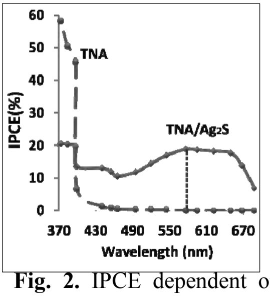

**Fig. 2.** IPCE dependent on irradiation wavelength for the both TNA and the $Ag_2S$/TNA thin film systems.

# Photoelectrochemistry of Metallophthalocyanines / Multi-walled carbon nanotube hybrid for the development of Dye Solar Cells

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Dye Solar Cells (DSCs) continue to be investigated as the next generation solar cell technology for their low cost compared to currently used solid state solar cells [1]. In these devices, photo-sensitizers are one of the main components for light-driven processes. A substantial amount of research work has been done towards the performance improvement of these devices by harvesting solar energy using the metallophthalocyanines (MPcs) as an alternative photo-sensitizer. Metallophthalocyanine (MPc) complexes, especially those containing diamagnetic metal centres (M = Zn, Ga, Si), are well established as efficient photo-sensitizers [2]. A significant effort has been made to enhance the photosensitization properties in DSCs by modifying MPc with carbon nanotubes (CNTs) [3]. Moreover, the use of MPc with CNTs in DSCs is rarely reported.

This presentation will describe the first MPc-based DSC in a single-cell (a real system for direct application) using $TiO_2$ film and also employing electrochemical impedance spectroscopy (EIS) to provide some insight into the observed transient photocurrent responses in respect of charge-transport and recombination dynamics. The microscopic and spectroscopic behavior of this hybrid will also be investigated.

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# Detection of Cholera Bacteria by an Electrochemical Immunosensor System Conjugated with Gold Nanoparticle-Enzyme for Amplification

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Cholera is a gastrointestinal infection caused by the bacterium *Vibrio Cholerae (1)*. It is commonly transmitted through the faecal-oral route via contaminated water or food. Cholera is the most feared of all diarrheal diseases in history. It remains a dreadful disease due to its rapid onset, severity to the extent of death if left untreated, and potential to cause outbreaks that easily break through the public health systems in impoverished settings *(2)*. The main symptoms of cholera are watery diarrheal, vomiting, rapid dehydration, metabolic acidosis, and hypovolemic shock (*3*).

Conventional methods for the detection and identification of bacteria from food and other samples depend on specific microbiological and biochemical interactions *(4)*. These methods are restricted in their usefulness due to the time it takes to make a full analysis. Therefore, due to the ease of miniaturization electrochemical transduction offer greater versatility for point-of-care usage. An electrochemical immunosensor based on amperometry for the detection of cholera bacteria utilizing the nanoparticle-enzyme amplification strategy is reported.

Lower detection limits and less cross-reactivity are envisaged due to the conjugated nanoparticle-enzyme modifications. The provision of a cheap, fast and accurate detection method for cholera will make it easier for routine testing of water, especially in rural remote areas.

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# Graphenated Transition Metal Oxides and Poly-(4-styrene sulphonic acid) Doped Polyaniline Nanocomposite Materials for the Development of Asymmetric Supercapacitors.

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Polymeric nanocomposite materials consisting of polyaniline, poly(4-styrene sulphonic acid) and nanocrystallite sized oxides of transition metals nickel, copper and chromium have been developed. The materials have been used in the design of electrodes for ultra-sensitive thin and flexible supercapacitors with graphene oxide being used as a platform. Development involved synthesis of the metal oxide nanoparticles by solution phase methods with calcinations set to control the size of the nanoparticles. These were then introduced during dispersive oxidative polymerization of aniline doped with poly(4-styrene sulphonic acid). The metal oxides and the polymeric nanocomposites were characterized using CV, SEM, HRTEM, EDX and optical techniques which includes UV-Vis and fluorescence spectroelectrochemistry and SNIFTIR-spectroelectrochemistry. Supercapacitive properties of these materials have been interrogated using galvanostatic charge-discharge cycling and found to possess superior charge storage and charge propagation characteristics with impedimetric studies showing that the stored energy of the composites can be accessible at high frequency.

# Design and characterisation of immunosensors developed on clathrate compound platforms

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Clathrate compounds or cage compounds are chemical substances consisting of a lattice of one type of molecule trapping or containing a second type of molecule. The name clathrate complex has been adopted for many weak composites which consist of a host molecule (forming the basic frame) and a guest molecule (held in the host molecule by inter-molecular interaction). Encapsulation of antibodies into porous matrices through physical entrapment is a popular approach in immunosensor design [1]. We have synthesised and characterised selected clathrate compounds as suitable platforms for parvalbumin immobilisation in the design of novel immunosensor systems and will present the results for the flourene derivative.

Flourene derivatives show unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at $C_9$ position of the flourene can improve the solubility and processability of materials containing flourene without significantly increasing steric interactions in the compounds backbone [2]. We have successfully synthesised 9, 9'-(ethyne1, 2-diyl)bis(flouren-9-ol) by reflux method. The product was characterised using spectroscopic methods and was found to be both UV/vis active ($\lambda_{max}$ = 400 nm) active and fluorescent (440nm and 467nm). The flourene derivative was drop coated onto commercial glassy carbon electrode (GCE) to produce thin films. Scan rate dependent cyclic voltammetry (CV) confirmed the electrodynamics of the thin films to be consistent with monolayer diffusion ($D_e = 8.9108 \times 10^{-6}\ cm^2/s$)

Parvalbumin is an important fish allergen with multiple isotypes within a single organism, which mediates cross – reactivity between fish species and plays a critical role in many physiological processes. Parvalbumin antibodies immobilised onto clathrate platform by incubation, was evaluated as immunosensors for fish species identification. The antibody-antigen binding event was evaluated using UV/vis spectroscopy, electrochemical impedance spectroscopy and atomic force microscopy (AFM). The biosensor response to parvalbuminin in real samples of hake and snoek (an indigenous fish species) will be discussed.

Keywords: Clathrates, electrochemistry, encapsulation, immunosensors, antibody – antigen binding.

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# Performance and Evaluation of Polysulfone/$TiO_2$ Nanocomposite for Alkaline Fuel Cell Applications

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In this present work, quaternary polysulfone/Titanium dioxide (QPSf/$TiO_2$) nanocomposite membranes were investigated for use in alkaline fuel cell (AFC) [1]. QPSf/$TiO_2$ membranes were prepared using the recasting procedure. The composite membranes were characterized by ionic conductivity measurements, TGA, SEM, XRD, and AFM. Thermal analysis results showed that the composite membranes have good thermal properties. The introduction of the inorganic filler supplies the composite membrane with a good thermal resistance. Performance and evaluation of fabricated membrane electrode assembly (MEA) will also be highlighted. The results obtained will indicate that QPSf/$TiO_2$ nano composite membranes have good prospects for use in AFC.

Keywords: Alkaline fuel cells; quaternized polysulfone; nanocomposite membrane; ionic conductivity; membrane electrode assembly

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# Towards Photoelectrochemical Technology for Water Treatment: The degradation of *p*-nitrophenol on an Exfoliated Graphite-$TiO_2$ Photoanode

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In the quest for more efficient photoanodes in the photoelectrochemical oxidation processes for organic pollutant degradation and mineralisation in water treatment, we present the synthesis, characterisation and photoelectrochemical application of exfoliated graphite - $TiO_2$ composite (EG-$TiO_2$) prepared using sol-gel method with organically modified silicate. Scanning electron microscopy, energy dispersive spectroscopy, X-ray diffractometry, Raman spectrometry and X-ray photoelectron spectroscopy were employed for the characterisation of the composites. The suitability of the EG-$TiO_2$ as a photoanode was investigated by its application in the photoelectrochemical degradation of *p*-nitrophenol water pollutant in 0.1 M $Na_2SO_4$ (pH 7) solution at a current density of 5 mA $cm^{-2}$. After optimising the $TiO_2$ loading, initial *p*-nitrophenol concentration, pH and current density, a removal efficiency of 62% with an apparent kinetic rate constant of 10.4 $x10^{-3}$ $min^{-1}$ was obtained for the photoelectrochemical process as compared to electrochemical oxidation and photolysis where removal efficiencies of 6% and 2.4% were obtained respectively after 90 min (see Figure). In addition, the EG-$TiO_2$ composite electrode was able to withstand high current density.

Keywords: photoelectrochemical oxidation, *p*-nitrophenol, Exfoliated graphite, titanium dioxide, photoanode, degradation kinetics

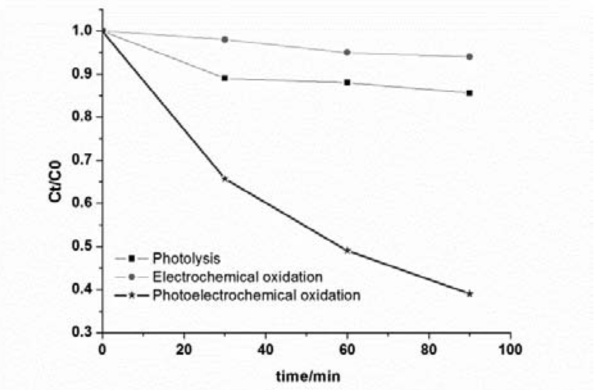

Figure: Normalized concentration decay with time of 0.4 mM *p*-nitrophenol in 0.1 M $Na_2SO_4$ solution (pH 7) at a current density of 5 mA $cm^{-2}$.

# Application of electrochemical techniques to the characterisation of nanofabricated surfaces for sensor development

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Significant progress has been made over the past few years in both quantitative (kinetic experiments) and qualitative (topographic imaging) applications of electrochemical techniques to studies of structures and electron transfer kinetic processes on the nano-scale **[1-5]**. In this work, electrochemical techniques (Cyclic voltametry, Chronoamperometry and Scanning electrochemical microscopy, SECM) are used to probe the information on surface topography and reactivity of carbon nanotubes-metallophthalocyanines (CNT-MPc) conjugate (Fig.1) on glassy carbon electrodes and glassy carbon plates in the presence of $Fe^{2+}$ / $Fe^{3+}$ redox mediator. The SECM constant-height mode is used to image both insulating and conducting CNT-MPc modified surfaces, and approach curves data obtained at high resolution using SECM feedback mode. This would give an insight into the possibility of the use of CNT-MPc conjugates in the development of sensors to overcome the emerging challenges for fast detection of analytes at low concentration levels.

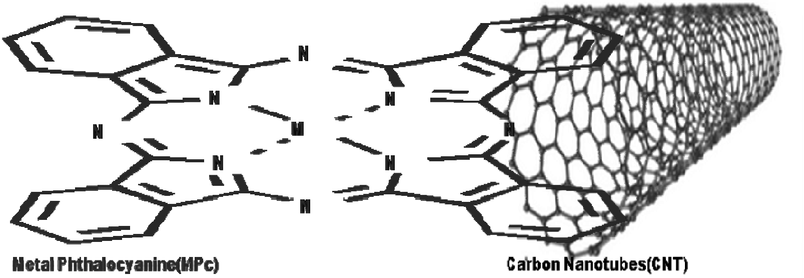

Fig.1: CNT-MPc conjugate

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# Electrochemical Sensor for the Monitoring of Values of Peak Current of Haemoglobins in the Presence of Anti-Sickling Agents and its Application in the Management of Sickle Cell Disease

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Human haemoglobin phenotypes have been shown to exhibit characteristic values of peak current in cyclic voltammetric studies using glassy carbon/Ag, AgCl/Pt electrode system at pH 5.0 in 0.2M acetate buffer. Sickle Cell Disease has a high mortality and cure is not within the reach of several patients. The presence of haemoglobin F has been found to reduce sickling of hemoglobin S significantly. Artificial mixtures of the two haemoglobins have been found to exhibit peak currents higher than those observed for HbS at various concentrations. Haemoglobin F has been found to exhibit the highest values of peak current among the common phenotypes thus the increase in the peak current is due to the addition of HbF. Some anti-sickling agents such as hydroxyurea and valproic acid induce HbF synthesis but clinical trials have shown undesirable side effects. However, if used at reduced concentrations in the presence of magnesium pidolate, another anti-stickling agent, promising results are expected with reduced side effects. Thus, the electrode system can be used as an electrochemical sensor to monitor the values of peak current of HbS on continuous addition of the mixtures of these anti-sickling agents and thus obtain desirable mixing ratios applicable in the management of Sickle Cell Disease.

Key Words: Sickle Cell Disease, Peak current, Anti-sickling agents.

# High-Aspect-Ratio Nanostructures of Semiconductors Fabricated by Chemical and Electrochemical Etchings

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Although conventional lithography techniques have been widely used to produce various ordered microstructures, it is still necessary to develop novel micromachining processes that can control the pattern precisely through a relatively easy process at a low cost [1]. We have reported the fabrication of ordered silicon microstructures such as silicon convex arrays and silicon nanopores patterns with regular periodicity of the order of micrometers by combining colloidal crystal templating and site-selective chemical etching using patterned noble-metal thin films as catalysts [2, 3].

In addition, sub-100 nm silicon nanohole arrays were fabricated by resist-free nonlithographic method, that is, a combination process involving site-selective electroless deposition of noble metals through anodic porous alumina and subsequent metal-assisted chemical etching. Under optimum conditions, the formation of deep straight holes with an ordered periodicity (e.g., 100 nm interval, 40 nm diameter, 2 μm depth, and high-aspect-ratio of 50) was successfully accomplished.

Micro pattering of GaAs and InP in the same manner was also performed [4, 5]. In the present study, we fabricated ordered microstructures of GaAs, with high-aspect-ratio of more than 350, such as triangular pillar arrays and hole arrays, as well as other semiconductors by combining isotropic anodic etching or metal assisted chemical etching and subsequent anisotropic chemical etching through a honeycomb photoresist mask prepared by sphere photolithography [6].

Furthermore, we fabricated self-organized porous anodic oxide nanotubes on GaAs by applying optimized anodization condition to attain the balance of oxide growth and dissolution. The detailed formation behavior and mechanism of anodic porous oxide nanotubes on GaAs will be reported.

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# Titanium Oxide Nanoparticles for High Power and Increased Capacity Anodes for Li-ion Batteries

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Oral

The development of Li-ion batteries for high power applications is especially needed for automotive powering (accelerations or regenerative breaking). Nanoparticles offer advantages for a use as active materials in high power Li-ion batteries, given the shortening of the transport pathways within the particles as well as the increased surface area in contact with the electrolyte. These advantages are especially obvious for active materials operating within the electrochemical stability windows of commonly used electrolytes.

$TiO_2$ anatase and $Li_4Ti_5O_{12}$ have higher operating potentials as compared to graphite and are thus good candidates for high power anodes based on nanomaterials [1], while being inherently safe (no direct reaction with the electrolyte in case of thermal runaway).

In this work, nanoparticles of $TiO_2$ (nanorods) and $Li_4Ti_5O_{12}$ (spherical) obtained, respectively, by solution synthesis in oleic acid and flame spray pyrolysis, were processed into high power electrodes. LTO showed capacities above 100 $mAh.g^{-1}$ at 50C with minimal processing and using a water-soluble binder, while $TiO_2$ nanorods, were first processed into $TiO_2$-carbon composites [2]. In the latter case, the processing has a large impact on the cell performance as aggregation, as well as the building of an efficient secondary electron conducting networks needs to be addressed for particles with diameters below 5 nm (much below the conductive carbon additives). In the case of $TiO_2$ nanorods, stable capacities of 230 mAh $g^{-1}$ after 100 cycles were obtained, whereas microsized $TiO_2$ only lead to capacities below 168 mAh $g^{-1}$.

Acknowledgement

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# Screen Printing Technology: Design and Development

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Screen printing is arguably the most versatile of all printing processes and consists of three elements: the screen which is the image carrier; the squeegee; and ink. It uses a woven mesh to support an ink-blocking stencil. The advantage of screen printing over other print processes is that it allows for printing on substrates of any shape, thickness and size. It can be used to print on paper, paperboard, plastics, glass, metals, fabrics and many other materials. A significant characteristic of screen printing is that a greater thickness of the ink can be applied to the substrate than is possible with other printing techniques. In this work we apply screen printer technology for the production of screen printed electrodes where we consider the sensor design and application techniques. We examine the printing technique and the printing parameters involved in the process.

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# The Use of Ultrasound in Fuel Cell Technologies – *An emerging research area*

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This presentation focuses on recent studies of ultrasonic, sonochemical and sonoelectrochemical production of noble metals and fuel cell materials (electrocatalysts, carbon supported electrocatalysts, fuel cell electrodes and membranes). Recently, it has been shown that ultrasound can be used as an effective method for producing nanosize mono- and bi-metallics (<10 nm) in the absence and presence of surfactants and alcohols. In most cases, the formation of nano-metallics is attributed to radical species (H• and OH•) generated by water sonolysis induced by cavitation whereby the nano-metallic size strongly depends upon the ultrasonic frequency and time, the type of surfactant, alcohol and atmospheric gas. It has also been demonstrated that the sonochemical production of carbon supported mono- and bi-metallic catalysts gives excellent electrochemical activity due to surface functionalisation of the support and better dispersion induced by ultrasound. These observations are mainly due to enhanced mass-transfer caused by asymmetrical collapse of cavitation bubbles at the surface support leading to the formation of high velocity jets of liquid being directed toward its surface. This jetting, together with acoustic streaming, is thought to lead to random punctuation and disruption of the mass-transfer at the surface [1,2].

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# Supercapacitors, Pseudocapacitors, and Flow Capacitors: Challenges and Advances of Polymer-Derived Nanoporous Carbons

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Porous carbons have always dominated applications such as gas and energy storage and catalysis. In particular, precise control over the porosity (i.e., pore volume, pore size, pore size distribution, and total specific surface area) with Angström accuracy is the prerequisite to obtain high performance carbon electrodes for electrochemical double layer capactiors, also known as supercapacitors. As energy storage devices move away from conventional powder films towards electrodes with complex 3D architectures, the ability to control and modify the shape of carbon particles has become another key design aspect. The latter applies specifically for the electrochemical flow capacitor which requires a flowable electrode slurry (*i.e.*, carbon particles + electrolyte). Preliminary data has shown that spherical nanoporous carbon beads exhibit superior rheological properties and monodispersity that has been shown to be mitigate clogging issues.

The use of polymer-derived ceramics makes it possible to synthesize hierarchical porous carbons with a large pore volume either with ordered or randomly arranged mesopores for supercapacitor and pseudocapacitor devices. Such hierarchic porous carbon materials can decrease transport limitations commonly encountered in microporous systems. However, a large pore volume associated with micropores is still required to obtain a high energy density; thus, comprehensive understanding and intelligent design of 3D nanoporous materials is the basis for improved electrochemical energy storage systems.

Starting with a polymer, complex shapes like foams, fibers, or beads can be achieved. After pyrolysis, complex-shaped carbides are obtained, which in turn can be transformed into extremely high surface area carbons. In particular, fibrous materials such as electrospun nanofelts have demonstrated excellent power handling ability leading to energy storage devices showing fast charge and discharge rates. At the same time, such fiber electrodes eliminate the need for conductive additives or organic binders used in conventional devices while remaining flexible and opening up novel applications, such as wearable electronics.

Pseudocapacitors utilize the synergistic combination of high surface area carbons with redox-reactive materials, such as metal oxides, and it is of particular importance to tailor and design the carbon porosity. Here, the challenge is to maintain a large ion-accessible pore volume after deposition of metal oxide particles and still achieve a high loading of pseudocapacitive additives.

# Electrodeposited 4-nitrobenzene diazonium as a powerful tool for the fine tuning of surface properties

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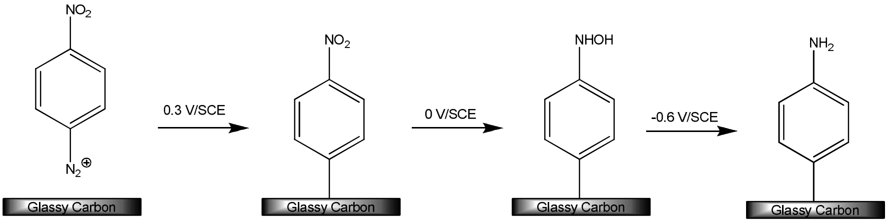
Diazonium grafting is one of the most promising strategies for carbon-based surface functionalization since it provides an easy way to covalently bind an organic layer to the electrode. The functional group borne by the aromatic moiety affords specific chemical and physicochemical properties to the surface which may be exploited in many application fields such as molecular electronics, energy conversion and chemical or biochemical sensing [1-2]. The immobilized chemical function can also be used for further modification using chemical reactions such as click chemistry or to directly interrogate the functionalized surface.

In this context, 4-nitrobenzene diazonium (NBD) is widely used because of its commercial availability and the presence of electroactive $NO_2$ moieties. However, despites many studies devoted to the influence of experimental parameters (solvent, substrate, grafting conditions…), the whole reduction mechanism of NBD remains unclear till yet.

Here we present electrochemical and spectroscopic experiments which definitively clarify NBD reduction mechanism. Experimental data proved that (i) NBD grafting and $NO_2$ reduction into NHOH occur at distinct potentials, as a two-step mechanism [3], and (ii) the formation of NHOH and/or $NH_2$ functions is mainly conditioned by the successive applied potentials. Spectroscopic data (XPS, AFM, and SFG-DFG) allow the determination of the thickness film and the identification of the nitrogen functions. The changes in the cyclic voltammograms of several redox probes as a function of the nitrogen form of the functional group grafted onto the surface will be also examined and rationalized.



Three-step reduction mechanism of 4-nitrobenzene diazonium

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# Improvement and Deeper Understanding of Electrical Performances of Molten Salts/Cerium Oxide Composite as Electrolytes for Intermediate Temperature Solid Oxide Fuel Cells

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Oral

New highly conductive electrolytes for intermediate-temperature solid oxide fuel cells (T<700°C) constitute a challenging field. Among them, composite materials based on mixtures of alkali carbonates and ceria-based compounds have attracted a growing interest in the last decade [1-4]. According to some authors, these materials, with enhanced ionic conductivity, are supposed to conduct both oxygen ion and protons. Oxide ions ensure the conductivity in the oxide phase and protons conduction would be predominant in the carbonate phase. Moreover, the carbonate eutectic being molten at intermediate temperature (>500°C) would create an interfacial conduction pathway, which may also involve protons. The hypothesis of significant proton conduction is far from being proven and the real mechanism paths are still controversial. Different approaches can be found in the recent literature, but they all outline a complex ionic transport at the interface between oxides and carbonates. A deeper view is required, in particular, on the understanding of the melt chemistry of carbonates with possible dissolved species as water and hydroxides.

We will give in this paper a critical panorama on molten carbonate/oxide composites, based on the literature and on the findings of our group. We will present the results of a systematic study performed by impedance spectroscopy as a function of the molten salt composition (carbonate mixture based on Li-K eutectic modified by alkali additions [5] as well as chloride based salts), the operating atmosphere (in air and as a function of hydrogen content in $H_2/N_2$ mixture), and temperature. Improved conductivities (> 0.1 $S.cm^{-1}$) and stability of the new composites will be discussed too, in order to give a future to these potential electrolytes for lower temperature solid oxide fuel cells (400-600°C).

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# Microwave-assisted Pechini Synthesis of Pd-Ni Nanocatalyst for Ethanol Electro-oxidation in Alkaline Medium

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Fuel cells provide a means for the direct conversion of fuels to electricity. Direct alcohol fuel cells (DAFCs) are particularly attractive because liquid fuels such as methanol or ethanol have a relatively low cost, a high volumetric energy density, and they are easily handled and stored [1]. Ethanol is not only less toxic than methanol, but can be produced from renewable resources, which makes it a promising fuel. Alkaline DAFCs also have the potential for better oxygen reduction kinetics than their acidic counterparts. For these reasons, electrocatalysts for the oxidation of ethanol in alkaline medium deserve special attention. Pd and its alloys, e.g. Pd-Ni, have been investigated widely as catalysts for ethanol electro-oxidation, and form the subject of this presentation.

Although Pd-Ni nanocatalysts have been well reported, there is no report on the use of the so-called Pechini method [2] to prepare them. The Pechini process is based on a sol-gel route whereby an aqueous solution of suitable oxides or salts is mixed with an alpha-hydroxycarboxylic acid such as citric acid and a polyhydroxy alcohol such as ethylene glycol. Upon heating, a polymer matrix forms and the metal is at least partially reduced. The result, after pyrolysis of the polymer, is a finely dispersed metal (or metal oxide), as is typically required for catalysis.

Microwave treatment has been used on a wide range of chemical reactions, including catalyst synthesis. However, no report could be found of its use in conjunction with the Pechini synthesis of Pd-Ni electrocatalysts for ethanol oxidation.

This presentation will describe the synthesis of a Pd-Ni nanocatalyst using a microwave-assisted Pechini method. Importantly, the enhancing effect of microwave irradiation on the electrochemical and electrocatalytic behaviour of the Pd-Ni nanocatalyst towards ethanol oxidation in alkaline medium will be discussed. Advanced microscopic and spectroscopic analyses are currently underway to elucidate possible microwave-induced structural or chemical changes, to corroborate the enhanced electrochemistry of the Pd-Ni nanocatalyst.

Oral

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# Conductivity Improvement of $LiFePO_4$ Cathode Material via Graphene-Coating and Aluminum-Doping

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The world at present faces a challenge of moving away from rapidly depleting fossil fuels towards renewable energy storage [1]. An example of these energy storage systems is the lithium-ion battery. Lithium-ion batteries (LIB) have proven to be a viable option to meet these demands due to their high energy density to weight ratio in comparison to other battery systems [2]. Some examples of the first rechargeable commercial LIB cathode material developed include the spinal $LiMn_2O_4$, the layered $LiCoO_2$ and the olivine $LiFePO_4$ (LFP). In order for cathode material to be viable in a lithium-ion cell, the material must accept and release Li-ions repeatedly and quickly. The material must also remain thermally stable; have oxidative stability and good conductivity. The olivine LFP is relatively oxidatively stable but is poorly conductive [3,4]. In order to improve this poor conductivity, coating with a carbon source or selective doping with metals such as aluminum can be done. When $LiAlFePO_4/C$ was synthesised, an improvement of the kinetics in terms of the capacity delivery, cycle life and rate capability was achieved [4]. An example of a carbon source that can be used to improve the conductivity of LFP involves reduction of graphene oxide to graphene.

LFP can be synthesised via several methods. In this work, we explore the integration of graphene-coating and aluminum-doping into the LFP cathode material via microwave-assisted synthesis. Below are some SEM pictures of synthesised LFP which showed a nanoflower-like morphology and layered graphene oxide prepared from graphite.

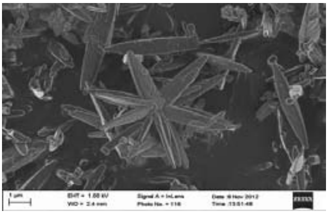

Figure 1: SEM picture of $LiFePO_4$

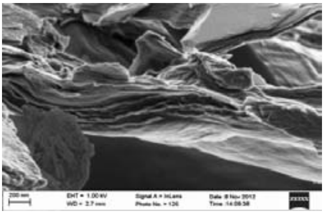

Figure 2: SEM picture of layered graphene oxide

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# PEM water electrolysis with reduced iridium oxide loadings : influence on kinetic parameters and electrolyser performances

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Oral

It is expected that PEM water electrolysis (PEMWE) will play a significant role in the hydrogen society as a key process for producing hydrogen from renewable energy sources. But before this, substantial cost reductions are still required. In a PEMWE cell, the oxygen evolution reaction (OER) occurs at high potential values and only few materials (usually platinum group metals) can be used as catalysts to avoid corrosion. In state-of-the-art, pure $IrO_2$ is generally used as catalyst (with typical loadings of a few mg.cm$^{-2}$). According to the literature, iridium loadings can be reduced either by dispersion of oxide nano-particles on conducting support materials[1]; or by addition of some inexpensive inert materials[2,3], in order to form Ir-based composite oxide catalysts. However, in addition to the instability of most of these supports in oxidizing environments, iridium loadings on such electrodes remain significantly high (1.5-2.0 mg.cm$^{-2}$). The purpose of our study was therefore to evaluate the influence of iridium oxide loadings on the overall performances PEMWE cells and on the kinetics of the OER. To the best of our knowledge, only few studies have been made to evaluate the effect of reduced catalyst loadings. Ma *et al.* were able to reduce the $IrO_2$ content down to the mg.cm$^{-2}$ scale but they reported significant losses of performances[4]. In order to gain more insights, several MEAs with different anodic catalyst loadings have been prepared and characterized using cyclic voltammetry and impedance spectroscopy, and by measuring polarization curves at different operating temperatures. MEAs with reduced metal loadings (0.25 mg.cm$^{-2}$ of Pt at the cathode and 0.5 mg.cm$^{-2}$ of $IrO_2$ at the anode) have been prepared. Typical cell voltages of 1.72 V have been recorded at a current density of 1 A cm$^{-2}$ (80 °C, atmospheric pressure, using a Nafion®115 membrane). Such performances are similar to those obtained with conventional loadings of several mg.cm$^{-2}$.

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# Measuring ppb Gas Concentrations in Air Quality Networks

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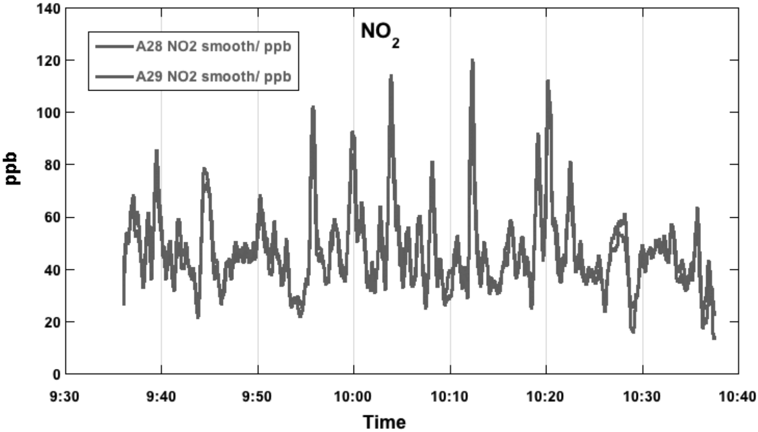
A collision of technologies has led to affordable air quality networks: GSM, GPS, lithium-ion batteries, low power radio links and affordable massive computing capability give us access to real time urban air quality networks. Until now, affordable ppb sensors have been missing, but this has now been solved.

Amperometric electrochemical gas sensors have been the workhorse of gas detectors in mines and confined spaces for decades, but it has been assumed they can not be used to measure concentrations below one ppm. Projects such as MESSAGE in the UK have shown that these low cost sensors can be used below one ppm. A combination of improvements in sensor technology, low noise electronics and new data manipulation algorithms give detection limits below 5 ppb for $O_3$, NO, $NO_2$, $SO_2$, CO and $H_2S$.

We will show laboratory test results for these sensors in the 0-200 ppb concentration range and discuss error sources including temperature, humidity, zero currents, interferents and long term stability. These results will be compared with field data from the Cambridge network of 50 motes in 2010 and the 50 mote Heathrow network which is operating now.



Comparison of adjacent air quality motes using amperometric electrochemical gas sensors

# Electrochemically Triggered Deposition of Porous ZnO: a Versatile Method to Realize Textile-Based Solar Cells

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Textiles are well known as flexible, mechanically rugged and lightweight materials. Electronics have been more and more integrated into textiles, mainly for sensing purposes. Textile-based photovoltaics are of interest as independent energy supply and can further be of interest for a number of medical and outdoor applications because of their attractive mechanical properties. Dye-sensitized solar cells represent a suitable photovoltaic cell technology since electrolytes are capable to bridge an insulating gap between the active electrodes of 10 - 100 µm typical even in very finely woven fabrics.
Electrochemical preparation of porous semiconductor films from precursor solutions represents a very promising approach to obtain a proper collecting semiconductor contact because of good compatibility of the processes to a low thermal stability of textiles and to the need of a three- dimensional coating process. More general, film preparation from aqueous solutions without thermal treatment steps and based on elements abundant in the earth crust represents an attractive approach to realize photovoltaics on a large scale as needed from a global perspective for a sustainable and affordable supply of energy for households, traffic and industry.
Thin porous films of ZnO were electrochemically deposited and the role of microelectrode effects, options of forced convection, deposition under pulsed potential, alternative deposition baths and different substrate metals were investigated [1]. Corrosion-resistive active electrode structures were realized on wires of tungsten or on thin metal fibres of stainless steel compatible to textile technologies and cells with conversion efficiency around 1 % under AM 1.5 conditions were obtained [2]. Present work focuses on increasing the efficiency by detailed control of injection and collection vs. recombination [3,4] and on the use of well-stabilized sensitizers on the surface [5].

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# On the influence of the electrolyte properties on the performance of Lithium-Ion Capacitors

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Lithium-ion capacitors (LICs) are devices containing both a Lithium-ion battery (LIB) and a Supercapacitor (SC) electrode. Thanks to this combination, LICs can display energy and power values in between those of LIBs and SCs, as well as a high cycling stability [1].

So far, most of the research on LIC has been focused on the active materials. Graphite and activated carbon have been the most used active materials for the realization of LIC [1-4]. More recently, also alternative materials, e.g. soft carbons or graphene, have been proposed for the realization of LICs. However, only a few works focused on the electrolytes of these devices. Nevertheless, the choice of the electrolyte strongly affects the performance as well as properties of a LIC. The electrolyte in a LIC faces three main challenges. Since a LIC is a high power device, the electrolyte needs to posses high ionic conductivity. Moreover, the electrolyte should show a good SEI forming ability to prevent irreversible reactions and capacity loss in the beginning and during cycling. Finally, in order to allow the realization of safe devices, it should be non-flammable and non-toxic.

In the present work we investigate the influence of several electrolytes on the performance of LICs containing soft carbon as anode and activated carbon as cathode. A mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with Lithium hexafluorophosphate ($LiPF_6$) was selected because it possesses a low viscosity and a high conductivity. This enables the use as electrolyte at rather high currents. In addition, thanks to the presence of EC, it also displays good film forming ability. To achieve higher safety, also gel polymer electrolytes were considered [5].

The results of this study indicated that a right selection of the electrolyte has a strong impact on the LIC performance. Using EC:DMC $LiPF_6$ as electrolyte, it is possible to realize LICs with high capacity and stable performance over 50,000 cycles carried out using current density up to 10 A/g. These LICs also display high values for the energy and power density.

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# Microstructure and morphology of electrodeposited Cu films

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Our research group has studied the surface morphology of Cu films electrodeposited from organic additive-free acid sulphate electrolytes for over a decade. We have shown through scaling analysis that the local roughness exponent, $\beta_{loc}$ which describes the evolution of the root-mean-square surface roughness at length-scales shorter than the surface correlation length, is especially sensitive to the electrodeposition conditions. We show its dependence on both the deposition potential and the anions present in the electrolyte and interpret this dependence in terms of the film microstructure. We also introduce slope analysis as a complementary approach to scaling analysis, and if time permits, will present new data for Cu-based multilayer films.

# Fabrication of High Capacity Lithium Alloy Electrodes For Lithium Ion Batteries With The Utilization of Electrodeposition

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The physical and subsequent electrochemical characteristics of lithium ion battery electrodes are heavily dependent on their fabrication technique. Higher capacity electrodes are required to improve upon and thrust lithium ion batteries into a broader span of applications. The current capabilities of the commercial negative electrode, graphite, have reached their maximum value of 372 mAh/g. A group of materials with capacities 3-5 times higher are lithium alloys. The major impediment withholding lithium alloys from replacing current negative electrodes is a lack of adaption to the substantial volumetric changes occurring during repetitive lithium intercalation and de-intercalation. Due to these volume changes in which some alloying materials undergo expansion up to 300%, the material degrades because of pulverization. A fabrication technique that has the ability to manage this disadvantage and is commercially viable is electrodeposition. Electrodeposition can accomplish this by the addition of a mechanically robust phase to form a composite electrode and by the confinement of the alloy particle size to nanoscale to increase the yield and fracture strength. This process is also advantageous because it allows the user to fine-tune the composition and microstructure of the composite electrodes, which will ultimately affect their functionality. This cost effective process is also unique because of its wide range of solution compositions while operating at ambient conditions. Herein, two methods will describe the formation of nanocomposite negative electrodes with a lithium alloy active material and the role electrodeposition plays in their production. Electrodeposition provides for the production of composite electrodes with promising cycling stability and with capacities in excess of 1000 mAh/cc and 1mAh/cm2 for the entire electrode. These electrodes' electrochemical properties dependence on the nanocomposite's microstructure and phase formation will be discussed in further detail.

# Preparation of $Li_2MSiO_4/C$ (M=Fe, Mn) Nanocomposites by a Novel Synthesis Method for Lithium Battery Cathode

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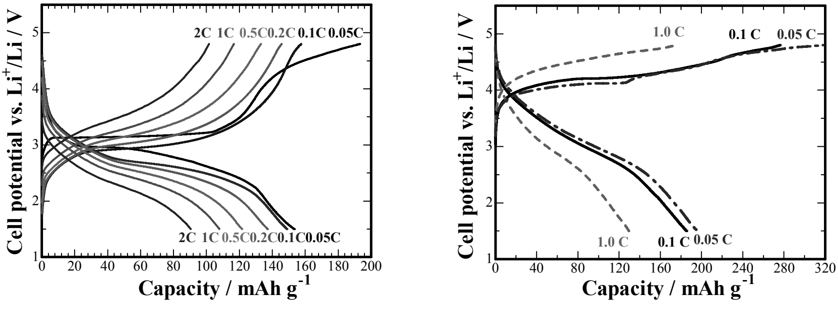
$Li_2MSiO_4/C$ (M=Fe, Mn) nanocomposites were successfully synthesized by a novel synthesis route, i.e., a combination of spray pyrolysis and ball-milling followed by annealing. The final samples were identified as $Li_2FeSiO_4$ with $P2_1$ monoclinic structure and $Li_2MnSiO_4$ with $Pmn2_1$ orthorhombic structure, respectively, by X-ray diffraction analysis. Field emission scan electron microscopy and transmission electron microscopy verified that the final samples were the agglomerates of primary particles less than 100 nm as a composite with carbon. $Li_2MSiO_4/C$ (M=Fe, Mn) nanocomposite samples were used as electrode materials for rechargeable lithium batteries, and then the electrochemical measurements were carried out by using Li|1 M $LiPF_6$ in EC: DMC = 1:1| $Li_2MSiO_4$ cells at room temperature.. The $Li_2FeSiO_4/C$ and $Li_2MnSiO_4/C$ nanocomposite electrodes delivered the first discharge capacities of 154 and 195 mAh $g^{-1}$ at 0.05 C, respectively, as shown in Figure 1.



(a) $Li_2FeSiO_4/C$ (b) $Li_2MnSiO_4/C$

Figure 1 Charge-discharge curves of (a) $Li_2FeSiO_4/C$ and (b) $Li_2MnSiO_4/C$ nanocomposite electrodes prepared by a combination of spray pyrolysis with ball milling at different C-rates.

# A New Method for Synthesis of Self-Doped Graphene as High-Performance Material for Lithium-Ion Batteries

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Graphene, having a structure of one layer $sp^2$-hybridized carbon, gets increasing interest from the researchers in recent years since its discovery in 2004 by Geim and co-workers [1]. Among the numerous research orientations, hetero-atom doping in graphene has become one of the most exciting topics of research. Hetero-atom doping in graphene can dramatically alter its electrical properties and modulate its band structure [2]. The new electrical properties and band structures can largely expand the applications of graphene. The doped graphene used in energy storage systems is one of the application examples [3]. Here, we report a new method to large-scale self-assembly growth of Nitrogen-doped graphene based on N-containing resin The N-containing resin exchanged with metal ions and heat treated to form N-doped graphene. Individual single layers N-doped graphene sheets have been confirmed by AFM (Fig 1a). The XPS verified the existence of nitrogen element. The electrochemical cycling result of N-doped graphene for lithium-ion battery electrode is shown in Fig 1b.

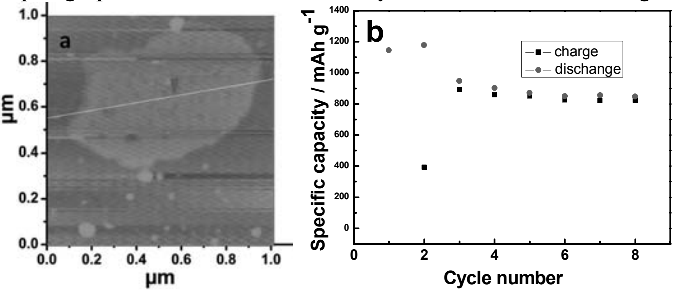

Fig. 1 (a) Tapping mode AFM image of N-doped graphene on new-delaminated mica, the section analysis displays the height is 0.37 nm and (b) electrochemical cycling results for N-doped graphene electrode.

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# Bismuth film coated SPCE for Electrochemical Stripping Measurement of Platinum Group Metals

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The increasing use of platinum group metals, PGMs (e.g. platinum, palladium and rhodium) in catalytic converters and the increasing mining activities for these metals in South Africa, has increased the presence of these metals in the aquatic environment. For this reason, the development of sensitive detection techniques for metal ions in environmental samples have been proposed [1,2]. The work reported in this paper describes the development of an adsorptive differential pulse stripping voltammetric procedure for the determination of palladium (Pd), platinum (Pt) and rhodium (Rh) in the presence of nickel (Ni) and cobalt (Co), using standards and environmental samples [3]. A screen-printed carbon electrode coated with a bismuth film, SPCE/BiFE was constructed. The optimisation of the experimental conditions performed, included an appropriate buffer solution for coating and the supporting electrolyte solution. The voltammetric procedure included pre-concentration of the metals using dimethylglyoxime (DMG) as chelating agent, followed by adsorptive differential pulse stripping voltammetry (AdDPSV) at appropriate deposition potentials for each of Pd, Pt and Rh. Other essential stripping voltammetric parameters optimised included the DMG concentration, composition of the supporting electrolyte, pH, deposition time, and deposition potential. Interference studies in the presence of Ni and Co have also been conducted and showed promising results. Application of the assay using the SPCE/BiFE sensor on standards and environmental samples has shown excellent linear behaviour in the concentration range from 0.01 to 0.1 μg/L, with good detection limits obtained after a 120 s deposition time. The voltammetric analysis has further been applied to the determination of Pd, Pt and Rh in river water and sediment samples.

Keywords: Adsorptive stripping voltammetry; platinum group metals; screen-printed carbon electrodes, dimethylglyoxime; environmental samples

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# Voltammetric Determination of Precious Metals in Environmental Samples

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The emission of heavy and precious metals from mining, smelters and other industrial activities in the South African environment has been receiving considerable attention, due to the potential threat to human health and the environment. These metals have the potential to accumulate in sediment and biota, posing a serious threat to aquatic ecosystem health. It is further known that some of these elements are toxic to living organisms even at quite low concentrations, whereas others are biologically essential and natural constituents of the aquatic ecosystems and only become toxic at very high concentrations. Studies conducted on the toxicity of platinum group metals (PGMs), its environmental bioavailability and increased concentrations in biologically relevant media have indicated that environmental exposures to PGMs may indeed pose a health risk, especially at sublevel concentrations [1-2]. Voltammetric stripping analysis is considered to be one of the most sensitive electro-analytical techniques that can be employed for the monitoring of toxic metals. This technique is very sensitive and it can be attributed to its pre-concentration step, in which trace metals are accumulated onto the working electrode surface. This is followed by a measurement step in which the metals are stripped away from the electrode during an appropriate potential scan [3-4]. The performance of stripping voltammetry is further affected by factors such as: i) composition of the supporting electrolyte; ii) pH of the solution; iii) deposition or pre-concentration time; iv) deposition potential; v) voltammetric mode; and vi) electrode surface characteristics that affects the limit of detection of the constructed sensor [5-6]. This paper describes current developments in the design and fabrication of electrochemical sensors for the determination of PGMs in environmental samples, with emphasis on sensor-fabrication methods, operating details and performance characteristics for selected applications.

Keywords: Stripping voltammetry; Platinum group metals; Optimisation; Environmental samples

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# Electrodeposited amorphous Al-Mn coatings on NdFeB magnet from an AlCl3-BMIC ionic liquid

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Al–Mn amorphs alloy coatings were electrodeposited in aluminum chloride (AlCl3)–1-butyl-3-methyl imidazolium chloride (BMIC) ionic liquid. The effects of current efficiency and temperature and manganese content on the structure and properties of alloy coating were discussed. The results show that Al-Mn coatings with Mn content ranging from 0 to 27.11 at.% exhibit a significant range of structures. For alloys with Mn content up to 14 at.% approximately, the Al–Mn amorphous coating can be obtained. Then the microstructure, composition and phase constituents of the coatings were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX), and X-ray diffraction (XRD). The corrosion resistance of the coatings was evaluated by potentiodynamic polarization measurements in 3.5% NaCl solution electrochemical and impedance spectroscopy (EIS). It was confirmed that the Al–Mn alloy coatings exhibited good corrosion resistance and remarkablely reduced corrosion current density at anodic potentiodynamic polarization.

# Facile Synthesis of Regioselectively Decorated Electrocatalytic Nanoparticles for Highly Sensitivity DNA Detection

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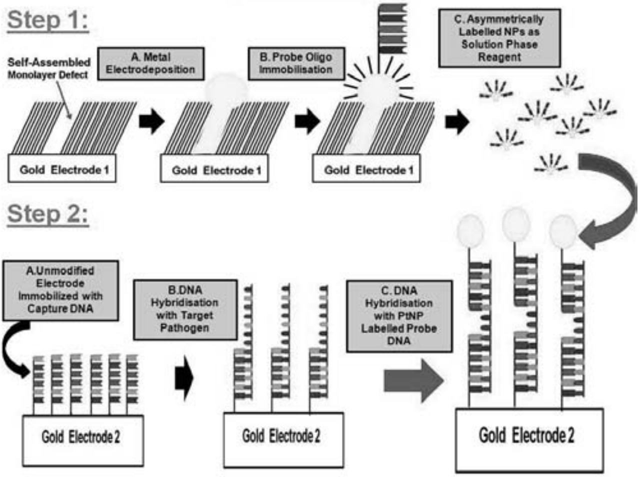
As illustrated in Scheme 1, an approach is described where electrodeposited nanoparticles within a dodecanethiol monolayer can be regio-selectively functionalized with thiol terminated probe strand DNA. A current step is applied to melt the nanowire connecting the hemispherical nanoparticle to the electrode causing rapid desorption of the DNA functionalized PtNPs electrode while retaining the functionality of the bound nucleic acid. These DNA labeled electrocatalytic particles are then used in a hybridization assay to determine the concentration of the target DNA sequence from the specific strain of *S. aureus* that causes mastitis (mammary gland inflammation) by measuring the faradaic current associated with reduction of peroxide in solution. Significantly, beyond the ability to successfully create regio selective functionalized platinum nanoparticles (upper surface only) with DNA while the remainder of the particles surface is unmodified allowing efficient electrocatalysis to occur, we have also demonstrated that these particles are capable of detecting DNA with high sensitivity and selectivity at atto molar concentrations. The assay is characterized by a wide dynamic range, high sensitivity, a low detection limit and an excellent ability to discriminate against interferences. This approach can easily be extended to reduction of water, which, in the case of biological samples, can come from the sample itself.



Scheme 1. Platinum nanoparticle formation and regio-selective DNA functionalisation.

# Electrochemical detection and quantification of commercial silver nanoparticles in seawater media

Emma J E Stuart, Neil V Rees, Yi-Ge Zhou, Kristina Tschulik, Jay T Cullen and
Richard G Compton

It is impossible for the risks associated with the incorporation of nanotechnology into everyday products to be established without an effective method for the detection and quantification of nanoparticles that have leached into the environment from consumer products.

The development of a unique technique used to detect silver nanoparticles known as anodic particle coulometry (APC) will be discussed. This electrochemical method involves the observation of nanoparticle collisions at a potentiostatted electrode surface allowing the user to detect, identify and size nanoparticles in a solution. Using an integrated form of the well known Shoup and Szabo expression it is also possible to determine unknown concentrations of nanoparticles in a sample from the data generated by APC1.

This novel method has been successfully applied to detect silver nanoparticles in authentic seawater media2 as well as nanoparticles contained in a commercially available disinfectant cleaning product3. These proof-of-concept measurements show that APC has the potential to be used for measuring unknown nanoparticle concentrations in the aquatic environment which is an important development in determining the risks posed by the inevitable leaching of nanoparticles into the environment.

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# Electrochemical Micromachining of Passive Electrodes – Application to Bulk Metallic Glasses

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Bulk metallic glasses (BMG) are very promising materials for the production of micro-devices. They exhibit outstanding mechanical properties and are therefore regarded as attractive structural materials in microelectromechanical systems (MEMS).

However, forming micro-parts from BMGs is still challenging. Therefore, a shaping technique operating at room temperature might open new possibilities for the utilization of glassy alloys.

Electrochemical micromachining (ECMM) is a method for micro-structuring of actively dissolving metallic materials exhibiting some unique advantages compared to other methods. A sub-micrometer precision can be achieved when nanosecond pulses are used. There is no tool wear and no induction of heat or stress into the material. The material removal is independent of the microstructure of the material and it is independent on the materials hardness. These benefits make the ECMM a promising technique for manufacturing micro-parts from BMG.

However, micromachining of passive BMG electrodes exploiting the transpassive dissolution regime – this appears to be difficult. According to available models, the resistance of the passive layer is expected to prevent the localization of the dissolution process. This is in contradiction with experimental results, i.e. there is obviously a gap between the experimental data and the model description of the machining process.

Here, two models describing the electrochemical micromachining (ECMM) of passive electrodes utilizing the transpassive dissolution are developed. Numerical simulations are performed on the machining model circuit with the use of measured electrochemical properties of the model system ‘tungsten tool electrode - 1 M $H_2SO_4$ electrolyte - stainless steel work piece electrode’. It is demonstrated, that in principle no conductivity through the passive layer is needed for the machining process. The findings from the model system are then adapted to Fe-based BMGs. For two different compositions two strategies for a successful machining were developed and verified experimentally.

# A Multi-Signal biocompatible Platform From $[Ru(Bpy)_3]^{2+}$ Ion Exchanged In *AuCuG*/Perfluorosulfonate Ionomer Composite Films And Its Potential Applications In Electrochemical Sensors.

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Gold-Copper bimetallic nanoparticles *(AuCu)* were synthesized on graphene *(G)* through facile one-pot environ-friendly chemical reaction, which could enhance the surface area and bio-compatibility. This nano-catalyst, denoted as *AuCuG* was successfully used to load large amount of Ruthenium 2,2-bipyridine chloride ($Ru(bpy)_3Cl_2$) and immobilized on Nafion coated glassy carbon electrode (*GCE/Naf/AuCuG@Ru*$^{2+}$). The nanocomposite exhibited an excellent mediation effect on oxidation/reduction of Ruthenium 2, 2-bipyridine $[Ru(bpy)_3]^{2+/3+}$. The sensitivity of this platform was ultimately dictated by the rate at which the $Ru^{3+}$ sites were regenerated within the film, which was reflected by the high charge transfer diffusion coefficient. This can be attributed to the electronic ligand effect at the bimetallic interface and the enlarged electro-active surface area which increased the quantity of excited state of $[Ru(bpy)_3]^{3+}$ per unit time under the electrochemical condition and benefits the contact between the signal probe and the transducer. This indicates that this material is a suitable electron transfer mediator and can be tailored to develop high-performance electrochemiluminescence, voltammetric, impedimetric and amperometric sensors.

# Micro-ultracapacitors based on Interdigitated Electrode

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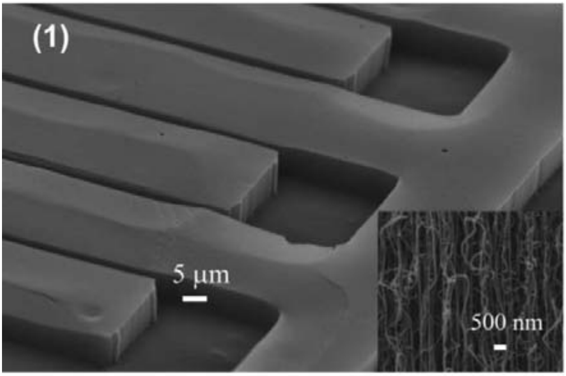
Microelectrodes of interdigital pattern have been widely employed in electrochemical devices. Decreasing the electrode dimensions and interelectrode gap enhance the device response and cycling efficiency, which are two critical attributes of ultracapacitor. We have developed operative skills to fabricate micro-ultracapacitors of MWCNT via photolithography, as shown in Figure 1. To eliminate its contact resistance, the comb-like CNT pattern has been gold sputtered and transferred onto a scotch tape, which can be attached to either rigid or flexible substrates. Several symmetric and asymmetric ultracapacitors have been made and analyzed with cyclic voltammetry, galvanostatic charge-discharge, cyclic stability experiments.

Ragone plots of most parallel-plate capacitors display a knee-shaped curve, such as the lower one shown in Figure 2 for a cell of activated carbon and $MnO_2$. But the micro-ultracapacitors of this work, either aqueous or organic electrolyte, demonstrate an opposite way of bending curve. Figure 2 presents the Ragone plot of CNT_h$RuO_2$ cell with aqueous 1.0 M $Na_2SO_4$ electrolyte. The Ragone plot of $LiPF_6$ organic electrolyte, Figure 3, shows the similar concave up and decreasing trend with increasing energy. This unique shape is thought to result from a significant reduction in resistance.



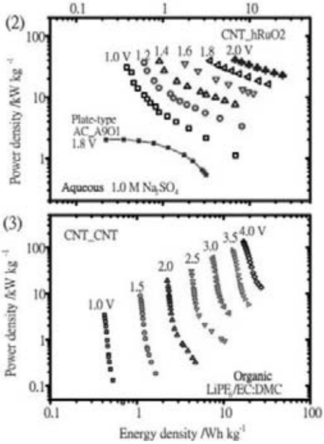


Figure 1 An image of a comb-like CNT pattern on scotch tape and a magnified image of nanotubes. Figure 2 Ragone plots of micro-capacitors in an aqueous electrolyte. Figure 3 Ragone plots of micro-capacitors in an organic electrolyte.

# Electropolymerization and Electrochromism of Poly(4,7-dithien-2-yl-2,1,3-benzothiadiazole) in 1-butyl-3-methylimmidazolium Ionic Liquids

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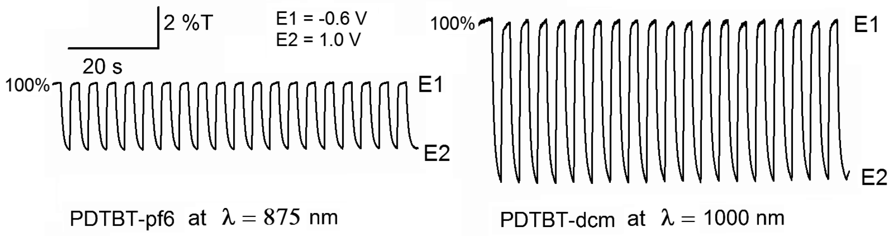
The electropolymerization and electrochromic properties of poly(4,7-dithien-2-yl-2,1,3-benzothiadiazole) (PDTBT), a donor – acceptor polymer, was investigated in 1-butyl-3-methylimidazolium ionic liquid (IL) compounds of terafluroborate (bmimbf4), hexafluorophosphate (bmimpf6), and bis(trifluoromethylsulfonyl)imide (bmimtf2n) using Pt, Au, GC, and indium tin oxide (ITO) electrodes. PDTBT-bf4, PDTBT-pf6, PDTBT-tf2n, and PDTBT-dcm represent the PDTBT films produced in bmimbf4, bmimpf6, bmimtf2n, and 0.1 M tetrabuthylammonimm perchlorate/ dichloromethane (dcm). Compared to previously reported onset oxidation potentials, the monomer oxidized at a lower potential (0.55 V - 0.69 V vs Ferrocene's redox potential). A well defined electrochemical activity was observed during p- and n-doping of the polymer. Spectro-electrochemical spectra of the PDTBT-bf4, PDTBT-pf6, PDTBT- tf2n, and PDTBT-dcm films formed on ITO electrodes exhibited two absorption bands in the visible range, both attributed to $\pi$- $\pi^*$ transitions, and the respective dominant peaks having $\lambda_{max}$ = 540 nm, 579 nm, 578 nm, and 560 nm. A slight red shift observed for PTBT-pf6 and PDTBT- tf2n indicated increased conjugation length of the polymer in the hydrophobic ILs (bmimpf6 and bmim-tf$_2$n). PDTBTs thin film was blue-black color in the reduced state and turned to transparent upon complete oxidation. The visible absorption bands disappeared during oxidation and bipolar bands appeared in the near infrared region around 850 nm for PDTBT-bf4, 875 nm for both PDTBT-pf6 and PDTBT-tf$_2$n and 1000 nm for PDTBT-dcm. The band gaps were estimated as 1.5 eV for PDTBT-bf4 and 1.3 eV for the others. From simultaneous double potential-step (E1 = -0.6 V, E2 = 1.0 V) chronoamperometry and fixed-wavelength transmittance (*T*) measurements, the switching times and maximum optical contrasts (%$\Delta T$) were 14-17% and 1.8-2 s for PDTBTs formed in the ILs ($\lambda$ = 875 nm) and 39% and 2.6 s for PDTBT-dcm ($\lambda$ = 1000 nm). The switching ability and optical contrast of the polymer demonstrates its potential for electrochromic device applications.



PDTBT-pf6 at $\lambda = 875$ nm

PDTBT-dcm at $\lambda = 1000$ nm

# Electrochemical microsensor for detection of pollutants

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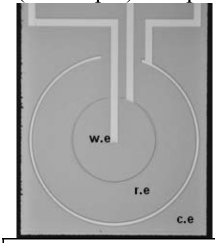
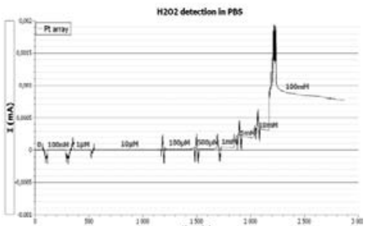
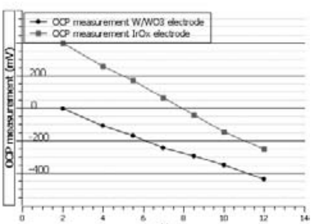
Assessment of water quality has become an increasingly important environmental issue in the past few years triggering the need for the development of fast, portable, reliable and highly sensitive sensors such as electrochemical sensors that provide useful information on water pollution by detecting wide range of chemical species [1]. Moreover, algae are also often used in biochemistry as indicators for the detection of toxic compounds [2]. In this study, using micro fabrication technology, integrated electrochemical microcells were fabricated on silicon chip to detect water toxicants by measuring the variations in metabolic activities of algae. Therefore, an autonomous micro-electrochemical system was developed with three electrodes integrated on same chip (Fig.1). Different working electrode configurations were patterned, both single µ-electrodes and µ-electrode arrays. Electrode materials were determined according to the species to be detected, taking part in algal metabolic activities. Pt working electrodes were fabricated for the detection of $H_2O_2$ and dissolved $O_2$ whereas $W/WO_3$ and $IrO_x$ metal oxide electrodes were used for pH monitoring. In order to attain high sensitivity of Pt working electrodes, porosity and surface area were enhanced by forming black Pt electrodes. The autonomous, miniaturized electrochemical cell was completed by integrating a Pt counter electrode and an Ag electrode in the structure. The Ag electrode was further oxidized to form the Ag/AgCl reference electrode. Calibration curves for $H_2O_2$ and dissolved $O_2$ ultra microsensors were then obtained by current measurements over a wide concentration range (Fig.2). As expected, black Pt electrode arrays exhibited the greatest sensitivity for $H_2O_2$ detection with a slope of 107.3nA/mM and a LOD of 100µM. Moreover, they even showed a good performance in terms of $O_2$ detection, with signal variation between saturated and zero oxygen solution of approx. 600nA at 22°C. Additionally, pH measurements (OCP) were conducted for calibration of both $W/WO_3$ and $IrO_x$ electrodes (Fig.3). The electrodes demonstrated an almost linear response over a wide pH range (2.0-12.0). The sensitivity of the $IrO_x$ electrode (66mV/pH) is superior compared to that of the $W/WO_3$ electrode (42.3mV/pH).







| | | |
|---|---|---|
| **F.1**: Integrated three electrode system | **F.2**: Current response to different concentrations for a Pt electrode | **F.3**: pH monitoring with OCP measurement |

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# Scanning Electrochemical Microscopy Study of PEFC Cathode Catalyst after Long –Term Endurance Test

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To investigate a degradation mechanism of a polymer electrolyte fuel cell (PEFC) after a long-term endurance test is indispensable to realize a lasting-longer fuel cell. This report describes a research result in which the cathode catalyst after a 9,000 h operation was taken out to evaluate the $O_2$ reduction reaction (ORR) and $H_2O_2$ generation amount during the ORR. A small amount of the catalyst was packed in the tip of a porous miroelectrode (PME), which was served as a generator electrode of a scanning electrochemical microscopy (SECM). $H_2O_2$ generation during the ORR was observed at a detector of the SECM.

On both surface of a perfluorosulfonic acid membrane, Pt-Ru/C and Pt-Co/C-based layers were prepared as an anode and a cathode, respectively. The thus prepared membrane electrode assembly was installed in a PEFC single cell. Then, a long-term durability test was conducted at 80°C under a current density of 200 mA $cm^{-2}$. After the 9,000 h cell operation, a part of the cathode was cut off, ground, and then packed into a tip cavity of the PME (□50 μm), which was used as a generator of the SECM. ORR at the generator was measured in 0.5 mol $dm^{-3}$ $H_2SO_4$ at a scan rate of 1 mV $s^{-1}$. At the same time, the $H_2O_2$ as a by-product was observed at a detector (□2 μm Pt) of the SECM.

Figure 1 (lower) shows ORR voltammograms at the generator containing the cathode catalysts before and after the 9,000 h operation. The onset potential of the ORR is known to shift toward cathodic direction by the long-time operation. The graphs in Fig. 1 (upper) demonstrate the $H_2O_2$ detection current. The $H_2O_2$ detection current after the long-time operation exceeds that before the operation. Consequently, the long-time operation degrades the cathode catalyst in terms of the ORR onset potential shift and the $H_2O_2$ generation increase.

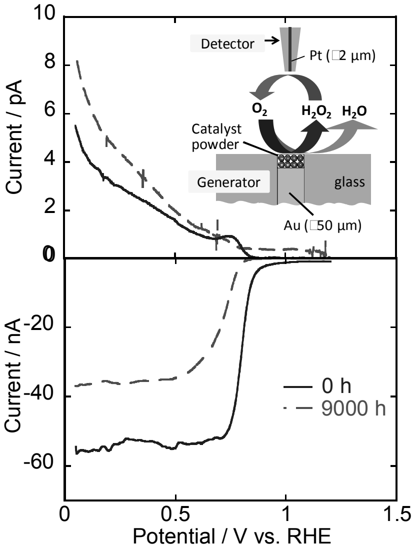

Fig. 1 Lower: Oxygen reduction *i-E* curves at cathode-catalyst-packed PME in $O_2$-saturated 0.5 mol $dm^{-3}$ $H_2SO_4$ at a sweep rate of 1 mV $s^{-1}$. Upper: $H_2O_2$ detection current at 1.3 V vs. RHE.

# Fundamental understanding of PEM electrolyser operation: characterisation tools development

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The proton exchange membrane (PEM) electrolysis of water is a promising technology to generate hydrogen for variety of applications including fuel cells. Special characterisation tools are required for fundamental understanding of the PEM electrolyser functioning and features such as failure modes, break down of performance losses, improved durability and efficiency, etc. The development of characterisation tools not only provides fundamental understanding of PEM electrolyers but also provides benchmark-quality data for research.

The electrochemical nature of PEM water electrolysis includes several interfacial processes within the components (membrane electrode assembly (MEA), catalyst layer (CL), gas diffusion layers (GDL) and flow fields (FF)). Suitable selection of characterisation tools can unlock fundamental details of the different processes, components and conditions of the PEM electrolyser, such as, for example, high-current density (HCD) conditions. Table 1 indicates the capabilities of the characterisation tools to diagnose the processes, components or conditions. The characterisation tools will be extended as the technology improves and future work is included. The important aspect of affordability of the equipment is also indicated which is dependent on the power rating of the electrolyser.

Electrochemical impedance spectroscopy (EIS), current interrupt (CI), current mapping (CM) and visualization tools (VT) are among those required and will be discussed. Experimental data using EIS and CI will also be provided.

**Table 1: Capabilities of the characterisation tools**

| Tools | Processes or conditions | Components | Future work | Cost |
|---|---|---|---|---|
| **EIS** | Ohmic resistance, activation potential and mass transfer phenomena. | MEA, GDL, boundary layers, catalyst layers | Stack analysis. Ohmic resistance breakdown. HCD. | High |
| **CI** | Membrane resistance, high current densities | Membrane, catalyst layer | Define suitable ranges. HCD. | Low to medium |
| **CM** | Current distribution | Flow fields and current collectors | Stack analysis | Low to medium |
| **VT** | Flow and heat distribution | Single cell | Stacks | Custom made |

Reference:

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# Electrodeposited $Cu_2ZnSnS_4$ thin films

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$Cu_2ZnSnS_4$ (CZTS) is a quaternary semiconductor compound that has recently emerged as one of the promising candidates for thin film photovoltaic devices. The advantages involve its direct band gap (1.45-1.50 eV) and high absorption coefficient (above $10^4$ $cm^{-1}$). Besides, all the constitutive elements in CZTS are abundant and environmentally friendly. Among the methods to produce CZTS thin films, electrochemical approaches present important features: they are cost-effective (mainly because they do not require high vacuum o high temperatures), they can be used in large and flexible substrates (even in intricate geometries) and they can be scaled-up into industrial production.

In this work $Cu_2ZnSnS_4$ (CZTS) thin films have been prepared using Electrochemical Atomic Layer Deposition (E-ALD) and compared to one-step conventional constant potential electrodeposition. E-ALD is the electrochemical analog of atomic layer deposition and it is based on the alternating underpotential deposition (UPD) of the elements to form the compound semiconductor in a cycle. UPD is a surface limited phenomenon; the resulting deposit is generally limited to an atomic layer. When the UPD range is changed, the driving force is not sufficient to grow atoms on top of the underlying atoms; thus, each deposition cycle can form only a monolayer of heterogeneous elements, and the thickness of the deposit is controlled by the number of deposition cycles.

Optimal deposition conditions were investigated using cyclic voltammetry (CV) on TCO, Au and Au/S covered electrodes. Then, based on CVs results, CZTS films were growth employing different E-ALD deposition cycles like Au/S/Cu/S/Zn/S/Sn/S to form the desired quaternary compound. The results were compared to those of conventional one-step electrodeposition performed at -1.1 V vs. Ag/AgCl during 1 hour. Other deposition parameters were also investigated in an attempt to optimize the stoichiometry.

The crystal structure of the films was characterized by XRD and micro Raman spectroscopy, while the morphology, thickness, topography and elemental composition were addressed using FI-SEM, AFM and EDS.

# Electron conducting glasses as electrode materials

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Investigations concerning the application of electron conducting glasses instead of metal electrodes in order to avoid drawbacks are presented. These contain iron or titanium oxides. For a practicable subsequent treatment of the membrane materials their composition was optimised related to the electrochemical functionality and to their processability, especially with regard to thick film technology.

The few up to now proposed glass based redox electrodes[1] have sensor designs known from pH glass electrodes. Here it is necessary that the thermal expansion coefficients $\alpha$ of the redox glasses and of the shaft glasses are nearly identical. A high content of metal oxides like $Fe_2O_3$, $Fe_3O_4$ or $Ti_2O_3$ effect an electronic conduction. But additionally, they lead to $\Delta\alpha$ values causing a fast cracking at the glass fusion region. Furthermore, the glass-blowing processability for these special materials becomes worse. Therefore, the motivation of the presented work is the development of new highly sensetive redox active glasses as well as the realisation of a cost efficient reproducible processing technology for the production of large quantities.

A number of glasses was prepared for the fabrication of thick film redox electrodes. The characterisation in terms of important physicochemical and physical glass properties of the iron oxide containing redox electrodes is already described elsewhere[2]. The glasses molten in platinum crucibles were further processed to thick film compatible pastes. These pastes were applied on planar alumina substrates with Pt conducting paths, dried and stoved. Resulting electrodes were measured in standard redox systems. The values obtained were compared to those measured with platinum electrodes and validated. Fig. 1 shows results from measurements with a titanium oxide containing redox glass electrode. It was found that a pH dependency of the measured values observed for Pt based sensors could be reduced, significantly. The functionality of the novel sensors can be explained by electron-hopping processes within the transition metal oxides.

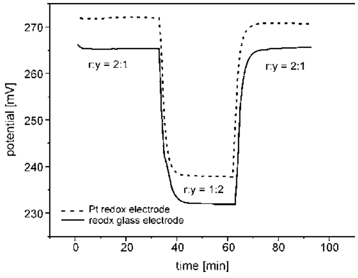

Figure 1: Electrode function of a redox glass electrode in thick film technology compared to that of a commercial Pt redox electrode in mixtures of red (r) and yellow (y) prussiate of potash

# The role of spinel phase $LiPtAu_{0.02}Mn_{1.98}O_4$ nano-materials in the enhancement of the current discharge density of lithium-ion batteries

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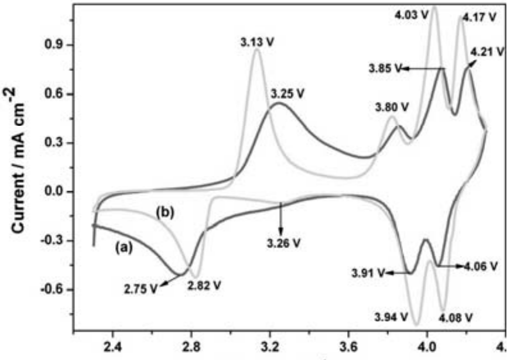
This study involves the synthesis of $LiMn_2O_4$ and bimetallic (Au-Pt) nanoparticle and exploiting their synergistic and catalytic properties to improve on the energy storage capacity of lithium ion battery (LIB). Spinel phase $LiMn_2O_4$ was coated with the bimetallic Pt-Au(1:1) nanoparticles to form nano-$LiPtAu_xMn_{2-x}O_4$, with concomitant oxidation of the $Mn^{3+}$ ions (responsible for LIB capacity loss) to $Mn^{4+}$. This novel nano-composite architecture accommodates the structural transformation that occurs during $Li^+$ ion charge and discharge, and also increases the discharge currents densities. Ultra-low scan rate (0.1 mV $s^{-1}$) cyclic voltammetry of the cathode material in 1 M $LiPF_6$ (in 1:1 EC:DMC ), showed four sets of redox peaks, which reflect the typical redox process of the active material in the spinel structure due to lithium intercalation and deintercalation**(Fig.1)**. The Li/$LiPtAu_{0.02}Mn_{1.98}O_4$ cell has a smaller difference between its voltage plateaus, i.e. smaller polarization. The electrochemical impedance spectroscopy (EIS) results verified that coating of $LiMn_2O_4$ spinel with PtAu alloy decreased the overall charge transfer resistance. The exchange current density, $i_{0,}$ for $LiPtAu_{0.02}Mn_{1.98}O_4$ was 2.8 x $10^{-4}$ A $cm^{-2}$, which suggests increase in the rate of electron transfer compared to $LiMn_2O_4$ (1.8 x $10^{-4}$ A $cm^{-2}$).This allows faster charge transportation at high current rates and prevents the pronounced pile-up of $Li^+$ ions and undesired $Mn^{3+}$ ions on the surfaces during high-rate discharge. The $^7$Li-NMR spectrum (**Fig.2**) shows two different types of lithium sites for both samples. The isotropic resonances of $LiPtAu_{0.02}Mn_{1.98}O_4$ spreads over a higher frequency region indicating the lithium atoms are less shielded and a higher $Mn^{4+}/Mn^{3+}$ ratio exist.



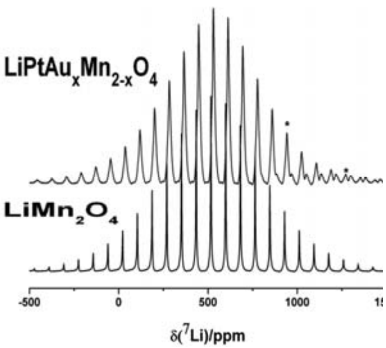


**Fig.1. Cyclic voltammograms for $LiMn_2O_4$ (a) and $LiPtAu_{0.02}Mn_{1.98}O_4$ (b) cycled at 0.1 mV $s^{-1}$.**
**Fig.2. $^7$Li MAS NMR spectra of $LiMn_2O_4$ and $LiPtAu_{0.02}Mn_{1.98}O_4$ acquired at 16 kHz.**

# Chemical synthesis of $C_{60}$-Pd polymer spherical nanoparticles - morphology and electrochemical properties

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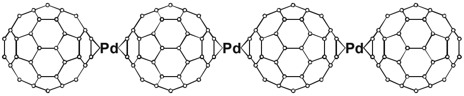
Two-component films of fullerene and palladium, $C_{60}$-Pd, can be synthesized chemically and electrochemically. In opposite to the most of conducting polymers, such as polypyrrole, polyaniline and their derivatives, $C_{60}$-Pd polymer exhibits *n*-doped properties. In these materials, palladium atoms are coordinated directly to the fullerenes in $\eta^2$ fashion to form a polymeric network:



So far studies were focused on the process of formation and properties of electrochemically synthesized materials. Electrochemical polymerization is suitable for formation of thin, uniform, and relatively smooth polymeric layer directly at the electrode surface. In the case of mass production, chemical polymerization can be applied. This method is simple, cheap, fast, and can easily be scaled-up. $C_{60}$-Pd synthesized that way forms cubic crystalline superficial structures which are composed of small spherical nanoparticles (Fig. 1). This crystalline structures can be easily disintegrated to spherical nanoparticles with high energy ultrasound.

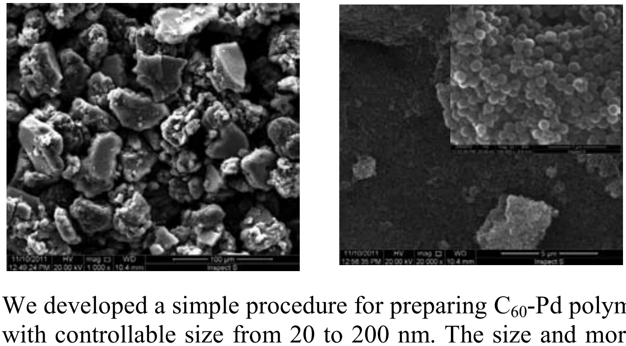


**Fig. 1.** SEM images of film formed from chemically synthe-sized $C_{60}$-Pd in solutions containing 1:3 ratio of $C_{60}$ to Pd.

We developed a simple procedure for preparing $C_{60}$-Pd polymer spherical nanoparticles with controllable size from 20 to 200 nm. The size and morphology of these particles depend on different parameters of polymerization process, such us precursors concentrations, temperature, and time of polymerization. This films of these particles deposited at the electrode surface exhibit electrochemical activity at negative potentials due to the fullerene moieties reduction. Charge transfer processes of such films are very fast. A relatively high pseudocapacitance of about 100 F/g has been also found for these materials.

# Carbon Dioxide Reduction by N-heterocycles: Mechanistic investigations

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Carbon dioxide reduction is a critical method for storing energy from renewable sources as well as for production of fuels for the transportation sector. N-heterocycles such as pyridinium have been used as catalysts to produce fuels such as methanol from $CO_{2.}$ The proposed mechanism begins with one-electron reduction of the catalyst, followed by $CO_2$ binding to form a carbamate intermediate and subsequent reduction of the carbon dioxide, with the process iterating to form the six-electron reduced species of methanol. The proposed carbamate intermediate has not been observed spectroscopically in the electrochemical cell, however. In addition, substituted pyridinium catalysts, such as 4,4'-bipyridinium, have been shown to produce multicarbon products including isopropanol, however, the mechanistic details of carbon-carbon bond formation are not well understood. Cyclic voltammetry with electrochemical modeling and bulk electrolysis with product detection were used to characterize the mechanism of $CO_2$ reduction to multicarbon alcohols. Electrochemically, these catalysts appear similar to pyridinium, indicating the first steps in the mechanism may be the same. In order to further investigate the mechanism of $CO_2$ reduction to multicarbon fuels by N-heterocycles, UV-Vis spectroelectrochemistry and EPR spectroscopy were used to observe catalyst kinetics and to identify intermediates in the catalytic cycle. Catalysts with different $\pi$-orbital energies were investigated to determine the effect on reduction potential as well as product distribution, and to attempt to stabilize catalytic intermediates.

# Adsorption and determination of dichromate in aqueous solution based on pine needle powder modified carbon paste electrode by potentiometry

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Cr (VI), as one of important environmental pollutants, can induce mutations and cause cancer.Compare to Cr (III), Cr (VI) is a more harmful toxic species to the human, so that one of the removal methods of Cr (VI) from environment was reported as the reduction of Cr (VI) to Cr(III) with chemical agents. Recently, the transformation from Cr(VI) to Cr(III) with low-cost natural biomaterials has been investigated. Among the many natural biomaterials, pine needle was reported as a more powerful natural polymer material with microporous structure containing reducing group, such as phenolic, hydroxyl, amino groups. The adsorption and transformation efficiency of pine needle for Cr (VI) is several hundreds times than other natural biomaterials, and reduce the content of Cr (VI) pollutants effectively in the aqueous solutions.

The electrochemical behavor, adsorption and preconcentration of $Cr_2O_7^{2-}$ on pine needle powder modified carbon paste electrode were studied by open circuit potential. The adsorption and preconcentration of $Cr_2O_7^{2-}$ followed logarithmic adsorption model. The experimental conditions were optimized as proportion of modifier as 0.3% and pH as 2.4.Under the optimal conditions, the method was used in the determination of $Cr_2O_7^{2-}$ in the concentration range of $1.0\times10^{-6}$M～$1.0\times10^{-2}$M in aqueous solution with a detection limit of $1.0\times10^{-7}$M (Signal to Noise Ratio:3). The experimental results showed that the interference of $Cr^{3+}$,$Cu^{2+}$,$SO_4^{2-}$ ions to the determination of $Cr_2O_7^{2-}$ were small and $CrO_4^{2-}$,$Pb^{2+}$ were great. The waste water additional recoveries were in the range of 94.70%-103.5% with RSD of 3.44%.The satisfied result was obtained.

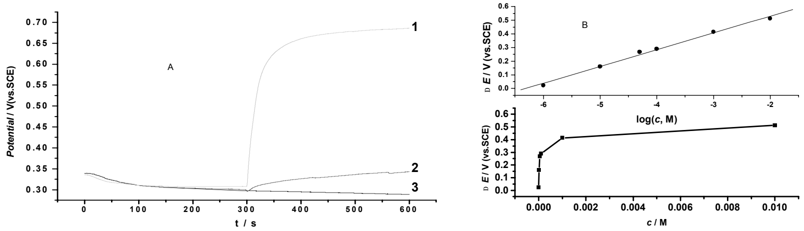

Fig. 1. A the open circuit potential changed with time; B. open circuit potential difference changed with concentration of dicharomate.

# Compact $TiO_2$ Films Prepared by Sol-Gel Dip-Coating for Dye Sensitized Solar Cells and Other Applications

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$TiO_2$ films attract attention because of their interesting mechanical, chemical, electrical and optical properties, which find various applications particularly in photocatalysis and dye sensitized solar cells[1] (DSCs). Among others, the performances of DSCs are limited by the charge recombination taking place mainly at the FTO/$TiO_2$ interface[2]. Due to the porous structure of $TiO_2$ films the electrolyte easy percolates to the FTO. The physical contact between the electrolyte and the FTO surface causes the charge recombination resulting in a considerable loss of photoelectron conversion efficiency in DSCs. Therefore, the recapture of the photoinjected electrons with the $I_3^-$ions should be avoided. FTO coverage with a thin compact $TiO_2$ underlayer was found to be the effective way to reduce the contact surface area for the bare FTO substrate and the redox electrolyte (so-called blocking effect). Besides the blocking effect, the compact layer can improve the adhesion of the FTO/$TiO_2$ interface as well and creates more electron pathways from the porous layer to FTO and subsequently increases the electron transfer efficiency. Exceptionally dense $TiO_2$ films can be prepared via dip-coating from a sol containing poly(hexafluorobutyl methacrylate) as the structure directing agent[3]. The films were grown on glass, F-doped $SnO_2$ and crystalline silicon (111) face, either pure or covered with a thin layer of $SiO_2$. The $TiO_2$ films cover perfectly even rough surfaces of the substrates, which was ascribed to thixotropic properties of the precursor gel. The films are mechanically and chemically stable, scratch-resistant and they provide antireflection function to crystalline Si wafers for photovoltaic applications. The optical reflectance in visible to NIR light is considerably smaller for Si wafers covered by $TiO_2/SiO_2$ double-layer film compared to that of $SiO_2$/Si. The dense $TiO_2$ films are amorphous with small amount of anatase and monoclinic $TiO_2$(B). These two phases withstand calcination at 900°C in films deposited on Si, and no recrystallization to rutile occurs. To the best of our knowledge no other organic additives except poly(hexafluorobutyl methacrylate) in the sol precursor promote formation of such compact films.

**Acknowledgement:** This work was supported by the Grant agency of the Czech Republic (Contract No. P108/12/0814) and by the FP7-Energy-2010-FET project Molesol (Contract No. 256617).

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# Abstracts of Poster Presentations

s1-001

# Design, synthesis and photo physical and electrochemical studies of some Ru(II) complexes for application in DSSCs

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Solar radiation is the most abundant and accessible energy on Earth, providing 178,000TW/year. To harvest this energy, convectional photovoltaic (PV) cells were developed in the 1950s using solid-state semiconductors. In recent years, the dye-sensitized solar cells provide technically and economically credible alternative concept for present day p-n junction photovoltaic devices has been widely studied. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Thus, the ruthenium complexes have become a paradigm of heterogeneous charge transfer sensitizer for mesoporous solar cells. The ruthenium complexes widely used at present as sensitizer absorb strongly in the visible region of the solar spectrum but not in the near IR region where significant amount of solar energy reaches the Earth. There is a need for improved photo sensitizers to enable the absorption of the PV cell to be more closely matched to the solar energy spectrum in order to improve cell efficiency. In continuation of our efforts [1-4] to develop Ru(II) complexes for possible applications as sensitizer for DSSCs, we present design, synthesis and photo physical and electrochemical studies of some ruthenium(II) complexes of pyrazolyl based ligands.

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s1-002

# Gas diffusion electrodes for high temperature PEMFCs

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Current industry trends are looking at the commercialisation of domestic fuel cell cogeneration systems and because higher temperatures result in a higher cell voltage, a stumbling block to the commercialisation of combined heat and power (CHP) systems is the inherent need to humidify low temperature polymer electrolyte membrane fuel cells (LT-PEMFCs), as a result the focus has shifted to high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) which do not require humidification and have improved operational efficiency [1].

Operation at elevated temperatures (120-200 °C) comes with its own set of challenges for HT-PEMFCs which include; the high corrosion rate of the amorphous carbon catalyst support, the dissolution and sintering of catalyst particles at high temperature and the accelerated degradation of the membrane electrode assembly (MEA) due to the OCV in the zero-load state [2]. Novel materials which provide high performance and high durability under HT-PEMFC operating conditions are therefore a prerequisite. This study aims to address the above issues by developing the gas diffusion electrode, both the gas diffusion layer and the catalyst layer. Commercial GDLs (Elat, Freudenberg, SGL) were hand-sprayed with a catalyst layer and the prepared GDEs were tested in MEAs for durability and reproducibility. The best commercial GDL was coated with a catalyst layer using both the hand spraying technique, with the hand-sprayed GDEs exhibiting better performance. The PTFE binder in the catalyst layer was replaced with proton conductors such as $CsHSO_4$ and tested for its suitability in HT-PEMFCs. Toray carbon paper was coated with a microporous layer (Carbon Black, Vulcan XC 72) and a catalyst layer. The produced MEAs were electrochemically evaluated by polarisation studies in a HT-PEMFC test- bench as well as undergoing EIS and CV. The MEAs were physically characterised using SEM and mercury intrusion porosimetry.

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s1-003

# Non-Covalent Functionalized Graphene Foam as Electrode for Supercapacitors

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We describe a simple and scalable technique to synthesize graphene foam using chemical vapour deposition (CVD) and nickel foam as the template for the growth of graphene. Non covalent functionalization of the graphene foam (GF) was performed using 1-pyrene carboxylic acid. This method of functionalization prevents the distortion of the $sp^2$ honey comb lattice of the graphene, resulting in good quality crystalline samples (defect free). Morphological characterization reveals that the functionalized sample consists of densely packed honey comb flower structures. Symmetric electrochemical double layer capacitor of the functionalized foam was fabricated and found to demonstrate a good capacitive performance.

Keywords: Graphene foam, pyrene carboxylic acid, supercapacitors.

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s1-004

# Investigation of electrodeposited polymer by optical and EPR measurements during doping process

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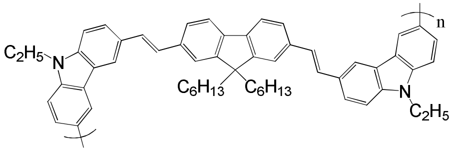
Conjugated polymers attract significant interest among scientist because of their interesting physicochemical properties, such as ability to change optical spectra upon electrochemical oxidation (often referred as electrochemical doping). This phenomenon is widely studied because of its potential applications, which include smart windows, antiglare coatings and reflective type displays. As change of polymer optical spectra is connected with creation of charge carriers possessing a non-zero spin (polarons), it is advisable to examine doping process with method, which enables both UV-Vis-NIR and EPR spectra recording at the same time. Such technique can be realized when optical EPR cavity is used in conjunction with waveguide optical spectrometer.

In this work, we had examined the doping process of two carbazole polymers (shown in the figure below), using simultaneous EPR-UV-Vis-NIR spectroelectrochemistry. Polymers change their optical spectra upon doping, showing increase of absorbance both in UV-Vis and NIR region. This observation is rather unusual, as doping of conjugated polymer commonly leads to decrease of absorbance of some bands. Optical data is compared with EPR spectra, showing generation of spins during the doping.



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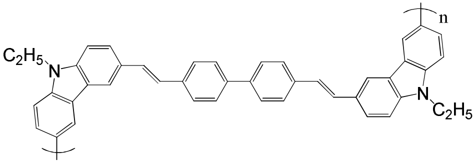

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s1-005

# Preparation, Photophysical, Electrochemical and Sensing Properties of Luminescent Tetraaminophthalocyanine-grafted Silica Nanoparticles

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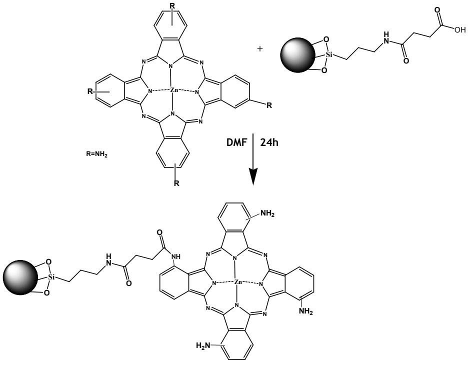
The interest in luminescent silica nanoparticles is due to their distinct features which include, ease of particle separation, surface modification, biocompatibility and low toxicity. As a result of these advantages, the hybrid nanoparticles have found convenient use as fluorescent probes for applications ranging from biosensing to drug delivery[1-2].

Luminescent silica nanoparticles have been developed in this work for potential use as chemosensors. We present our work on the synthetic protocols, characterization, photophysical and electrochemical properties of the hybrid silica particles.



Synthetic route for Phthalocyanine- Silica nanoparticles conjugate

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s1-006

# Electrosynthesis of Dimethyl Carbonate from CH3OH and CO with [Cu(2,2′-Bipy)Cl2] Catalyst

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A two-compartment electrolytic cell with a volume of 20cm3 for each part was fabricated, and with which we had demonstrated that the electrocatalytic carbonylation of methanol to DMC can be achieved at atmospheric pressure and room temperature with a catalytic system based on CuCl2-2,2′-bipyridyl complexes. And for this electrosynthesis reaction, there were no other species but CH3OH and DMC were found by GC in the distilled anolyte after reaction.

Furthermore, we also did some research about the reaction mechanism and influence factors. The information we got from the research was that only the formation of complex Cu2+(bipy) was active towards the oxidative carbonylation of methanol to DMC at room temperature and atmospheric pressure, and the stronger the basicity of the supporting electrolyte was, the more favorable to the formation of DMC, besides, anode potential, the concentration of KOH and CuCl2-bipy also had significant influences on the formation of DMC.

The reaction mechanism was: in the reaction solution, firstly, CH3OH was dissociated into H+ and CH3O-, and the complex Cu2+(bipy) formed “in situ”, and then CO was oxidized to carbonyl by Cu2+(bipy), and two CH3O- attacked to the carbonyl to occur nucleophilic addition reaction, then formed a DMC in the anolyte. The reduced Cu2+(bipy) was oxidized to Cu2+(bipy) in the surface of anode electrode, and then diffused to the anolyte anew to oxidize CO again.

Finally, we obtained the proper conditions for the electrosynthesis of DMC: anode potential 0.3V vs (Ag/Ag2O), the concentration of CuCl2-bipy 0.07molL-1, the concentration of KOH 0.1molL-1, and under this conditions, the content and CE of DMC were 0.1279% and 76.4%, respectively, and the amount of DMC was 0.3161mmol.

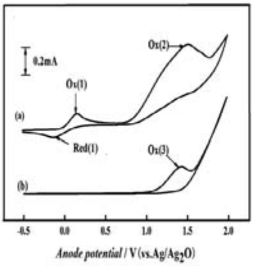

Figure 1. Cyclic voltammograms over the glassy carbon electrode. Voltage scan rate=100 mVs-1; electrolyte, KOH (0.1molL-1)/CH3OH under nitrogen atmosphere. (a) CuCl2 (0.07molL-1) +2,2′-bipyridyl (0.07molL-1), (b) CaCl2 (0.07molL-1) +2,2′-bipyridyl (0.07molL-1).

s1-007

# Electrochemical synthesis of CdSe/CdS nanowires for hybrid photovoltaic structures

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We demonstrate a electrochemical method to fabricate metal chalcogenide nanotube and nanowire structures. CdS and ZnS nanowires and nanotubes with diameter 40-200 nm have been synthesized by direct electrodeposition on ITO/CdSe substrate from acidic solution. Effect of addition of small $SeO_2$ and $TeO_2$ amount in solution on the processes of electrodeposition of metal sulfide films has been studied.

Different treatments of nanowires are applied and the influence on resulting hybrid solar cell. The scanning electron microscopy (SEM) study of nanowire structures reveals the change of the morphology from nanowires to pearl chain - like nanostructures after thermal treatment at 250°C.

photoelectrochemical, structural and optical properties ot the obtained films were characterized by electrochemical characterization, UV–vis absorption spectroscopy, photoluminescence (PL) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The spin casting of poly (3-octylthiophene) (P3OT) in nitrobenzol solvent was used for coating of CdSe/CdS nanowires and formation polymer films for hybrid photovoltaic structures. We have studied obtained CdSe/CdS nanowires/P3OT hybrid photovoltaic structures and optimized them by additional post deposition treatments.

s1-008

# Electrodeposition of Gadolinium-Doped Ceria Nanostructured Thin Layers

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Ceria-based can find many applications but one of those is as an electrolyte for solid electrolyte fuel cells, [1]. High performance of ceria is largely based on the ease of reducing $Ce^{4+}$ to $Ce^{3+}$, high oxygen storage capacity, and high oxygen ion conductivity. This last properties is enhanced by doping to form $Ce_{1-x}Gd_xO_{2-0.5x}$. Chemical methods are recognized as a promising route to the fabrication of a variety of ceria nanostructures, although often requiring long or harsh experimental conditions. For this reason, a cost-effective and tunable technique, electrodeposition appears as a promising way to fabricate such components, which provides an easy way to monitor process parameters and tailor coating characteristics.

Electrodeposition is an interesting cheap method which can be done at ambient pressure and rather low temperature (less than 100°C). Moreover, it allows the control (in-situ) of the film thickness, in situ. Electrodeposition of ceria is based on the reduction of an oxygen precursor to form hydroxide ions nearby the electrode. Consecutively higher is the pH in the vicinity of the electrode. In the presence of Ce(III) ions in the solution, cerium oxide is thus directly formed on the electrode by precipitation with hydroxide ions [2,.

The current study reports on the possibility of obtaining nanostructured ceria and gadolinia doped ceria in one electrochemical step. Cubic fluorite type ceria nanostructured films of, as confirmed by X-ray diffraction. Other characterizations such as Raman spectroscopy and SEM analysis have been carried out. We focus on the possibility to obtain a specific composition of the doped film from a specific composition of the electrolytic solution.

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s1-009

# Spectroelectrochemical Properties of Pyrrole Naphthalimide Derivatives and Their Polymers

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We report an electrochemical and spectral properties of new class of pyrrole monomers with 1,8-naphthalimide as substituent. Pyrrole is used as electron donor and 1,8-naphthalimide as electron acceptor. The monomers were synthesized via Paal Knorr condensation reaction. All monomers (Fig. 1) are electroactive. Polymers were polymerized by electrochemical route. Poly(2) and poly(3) present reversible oxidation and reduction whilst poly(1) is not stable even in the polymerization potential. The cyclic voltammetry was used to determine HOMO and LUMO energy levels of investigated monomers and polymers. The value of electrochemical band gap is 1.24 eV for poly(3) and 1.28 eV for poly(2). The large difference between energy gap estimated from electrochemical and optical measurements is observed. The TDDFT calculations explain this. The HOMO to LUMO transition is much weaker than HOMO-2 to LUMO transition. The cyclic voltammetry, spectroelectrochemical UV-vis and EPR measurements prove that the p and n doping processes are independent. The oxidation occurs at polypyrrole chain and the reduction at naphthalimide units.

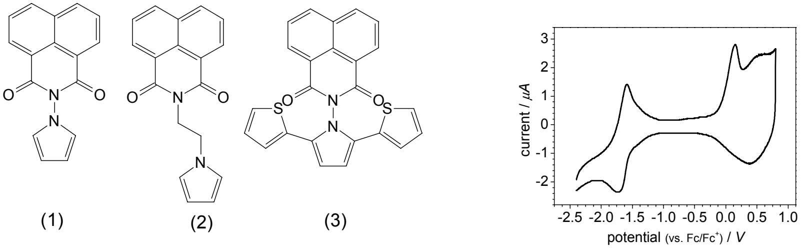

**Figure 1**. The structure of monomers (left) and cyclic voltammetric curve of poly(2) on ITO electrode; $Bu_4NBF_4/CH_2Cl_2$; 100 mV·s$^{-1}$ (right).

s1-010

# Electrochromic properties of nanostructured $WO_3$ films in acid and protic ionic liquid electrolytes

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Electrochromic materials are materials capable to induce reversible optical coloration through ion–electron insertion, and are currently attracting much interest in academia and industry for both their fascinating spectroelectrochemical properties and their commercial applications. Tungsten oxide ($WO_3$) is the most studied electrochromic material, its applications in electrochromic, photocatalitic, photoluminescent, field emission and gas sensing materials[1]. $WO_3$ can display from colorless to blue color by applying positive and negative voltages, inducing reversible optical coloration through ion–electron insertion, for example $H^+$, $Li^+$ and $K^+$. $WO_3$ nanoparticles were synthesized in just few minutes by reacting the precursor transition metal chloride ($WCl_6$) in non-aqueous solvent benzyl alcohol using a one-step process ultrasonic irradiation[2]. To investigate the structure of the nanoparticles powder X-ray Diffraction (XRD), Raman Spectroscopy, transmission electron microscopy (TEM) were performed. Spectroelectrochemical experiments were carried out comparatively using $H_2SO_4$ and a novel Protic Ionic Liquid (PIL) N-propyl-pyrrolidinium tetrafluoroborate $[C_3mpyr][BF_4]$ electrolytes. The nanostructured films were deposited by a unique Electrophoretic Deposition (EPD) process onto ITO glass substrates. Different voltages range, from 100 to 400V were applied between the electrodes for different times, resulting in the formation of the thin films onto the working electrode. Cyclic voltammograms (CVs) were investigated for all deposited films, during each scan, the films undergo typical reversible color change from colorless to blue. The integrated cathodic current to the amount of $H^+$ intercalation/desintercalation was used to calculate the coloration efficiency (CE) of films, values varied from 23.55 to 44.32 $cm^2C^{-1}$, in good accordance with nanostructured $WO_3$ films reported[3]. The *in situ* coloration time for a 90% transmittance change was investigated at 623nm with potential being stepped from -0.5V to 1.0V for 60s, the coloration/bleaching responses showed (tc~1s and Tb~9s).The films showed good color efficiency, fast coloration time and optical contrast in acid electrolytes. The relationship between the CE performance and EPD conditions were systematically investigated. The results using PIL as electrolyte, instead of $H_2SO_4$, show that all electrochromic parameters were improved, including, the cyclic durability that was higher 4-fold using PIL, this performance can be attributed to the slowly $WO_3$ film dissolution in organic electrolyte. Therefore, the use of PIL enables proton intercalation suggesting PIL as a good electrolyte for electrochromic devices.

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### s1-011

# Synthesis and surface modification of non-spherical gold nanoparticles for optical sensing

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Metal nanoparticles have attracted a lot of attention in sensor based applications due of their unique optical properties [1-3]. The optical properties of gold nanoparticles depend on their size and shape and their surface plasmon absorption can be tuned to longer wavelengths in the UV-Vis spectrum. Plasmon resonance properties of gold nanoparticles can be adjusted by the change in the morphology, therefore shape directed synthesis is very important. The surface chemistry of nanoparticles is very crucial for their applications. Therefore the surface of gold nanoparticles in this work is modified with binding ligands which allows for plasmon coupling. These unique properties can be used in optical sensors for detection of chemical species.

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### s1-012

# High-throughput combinatorial synthesis and parallel screening of electrocatalysts for oxygen reduction

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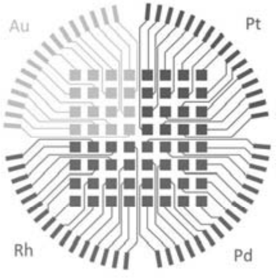
The oxygen reduction reaction (ORR) is at the moment one of the biggest challenges for fuel cell technology to take off due to the sluggish electrochemical kinetics on the platinum cathode. This, together with the high cost of platinum prevents the fuel cell from becoming a widely used power source. Despite this platinum has remained the most practical cathode material, but there is a great focus in finding new materials capable of lowering the overpotential and reducing cost [1]. Materials research benefits today from the development of novel combinatorial techniques for the synthesis and high-throughput screening of new electrocatalysts.

We present here a new combinatorial sputtering and screening setup that is able to deposit from single to quaternary thin films. The setup includes a multichannel potentiostat for parallel electrochemical testing of 64 electrodes. As a validation procedure, the setup was used for the simultaneous deposition of single thin films of gold, platinum, palladium and rhodium on a silicon support. The thin films were subjected to a rapid thermal annealing process, subsequent to which the crystallinity and chemical purity of the deposited thin films were verified with X-ray diffraction and energy-dispersive X-ray spectrometry. The influence annealing has on the catalysts' activity for ORR was tested in both alkaline and acidic oxygen saturated electrolytes. The activity of these sputtered thin films was compared with single-cell studies performed on equivalent polycrystalline electrodes. Future studies will investigate the activity of binary thin film electrocatalysts obtained by this combinatorial sputtering approach using different ratios of the four metals and the results compared with other works. This setup will allow for the rapid screening of a large number of new binary, ternary and quaternary catalysts which are of interest for different electrochemical reactions.



Single thin films of Au, Pt, Pd and Rh sputtered on a 64-electrode silicon support.

s1-013

# Electrochemical synthesis and characterization of multi-component nanocomposite of polypyrrole and carbon-based materials

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Electrode materials based on polypyrrole (PPY) doped with carbon nanotubes (CNTs) were synthesized by one-step electropolimerization both in galvanostatic mode and potentiostatic one. CNTs dispersion was improved with the help of graphene oxide (GO). The electrochemical properties of the nanocomposites were investigated as a function of GO oxygen functionalities upon different graphite oxidation conditions. Ultraviolet-visible absorption spectroscopy, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, X-ray diffraction, conductivity measurements and cyclic voltammetry were employed to characterize the multi-component nanocomposites revealing distinct properties with respect to single PPY film and improved electrochemical performance for energy storage applications.

s1-014

# Multi Stimuli Electro Conductive Hydrogel and its Application in Controlled Drug Delivery

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Electro conductive hydrogels are recognized as composites or blends obtained by the mixture of conducting polymers with hydrogels, resulting in a unique polymeric material that combines special properties of their constituents as high swelling ability in water, *in vivo* and *in vitro* biocompatibility and high electrical conductivity. These materials have been already studied in drug delivery systems[1].

In this work, pyrrole was electropolymerized in a matrix of poly(acrilic acid) hydrogel (PPy-AA). The presence of carboxylic groups in the hydrogel ensured a great swelling change driven by changes in pH and ionic strength. The swelling degree of the hydrogel and PPy-AA were done in differents pHs (3.8, 6.8 and 13) and in different ionic strength (maintaining the same pH). It was observed that the presence of the polypyrrole decreased the water absorption due the hydrophobicity of the conducting polymer. At the same pH and changing the ionic strength, the swelling of the hydrogel decreased with the increase of the salt solution concentration. The same outline was observed with the hydrogel filled with polypyrrole. Keeping constant ionic strength and changing the pH, the swelling degree of the hydrogel increased with increasing the pH. In this case, when the hydrogel is immersed in a solution with pH above the hydrogel´s pKa (4.25), carboxylate groups are formed and to neutralize the charge, water and protons penetrate the hydrogel. The same result was observed for the PPy-AA, but in pH 13 the swelling degree was twice compared with the observed for the hydrogel in the same pH. Above the polypyrrole´s pKa, an electrostatic repulsion between the polyacrylate and polypyrrole chains is expected due to the unpaired electrons on the nitrogens, since the polypyrrole is deprotonated.

The i/E potentiodynamic profiles of the PPy-AA were obtained and the characteristic voltammetric profile of polypyrrole was maintained on PPy-AA. Due the PPy-AA capacity of water absorption and conductivity, this material can be considered a electro conductive hydrogel.

As the PPy-AA has a multi stimuli responsive behavior (pH sensitive and conductor), the safranin delivery was monitored combining the pH and potentials. For the best of our knowledge, this work describes for the first time, a multi stimuli responsive electro conductive hydrogels that can display differents release patterns (based on Fick´s Law), i.e., zero-order or others, only as a function of external parameters.

Posters

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s1-015

# Preparation of $LiMPO_4/C$(M=Fe,Co) Nanocomposites by a Combination of Emulsion Drip Combustion and Ball Milling with Heat Treatment

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A novel preparation method was developed to synthesize $LiMPO_4/C$(M=Fe,Co) nanocomposites through a combination of emulsion drip combustion and ball milling with heat treatment. The emulsion was prepared by addition of an aqueous solution with stoichiometric amounts of $LiNO_3$, $H_3PO_4$, $Co(NO_3)_3{\cdot}6H_2O$ or $Fe(NO_3)_3{\cdot}6H_2O$ into organic solvents(heptane, kerosene or 50vol./50vol.-heptan/kerosene) vigorously stirred by a homogenizer. The details of experimental apparatus were described in our previous paper [1]. The synthesis was carried out at reactor temperatures of $T$ = 400 – 800 °C and a fluidization number of $U_0$(superficial velocity) / $U_{mf}$(minimum fluidized velocity) = 5. The as-prepared samples were milled and then annealed in a tubular furnace at 700 °C for 4 h in a $N_2$ + 3 % $H_2$ atmosphere.

Figure 1 shows the XRD patterns of the $LiCoPO_4/C$ samples synthesized by the present method from different organic solvent in emulsion: heptane, kerosene and a mixture of kerosene and heptane with the volume ratio - 50/50. The diffraction peaks of all samples can be assigned to an ordered olivine structure($LiCoPO_4$) indexed by orthorhombic *Pnma*.

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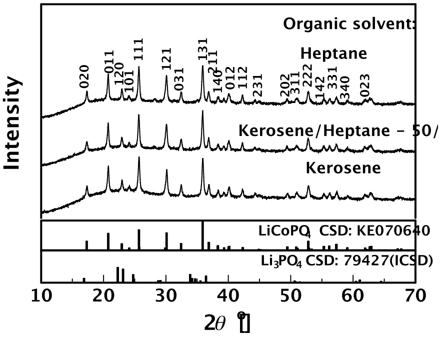

Figure 1 XRD patterns of $LiCoPO_4/C$ sample.

s1-016

# Synthesis and Characterization of $Li_2MnP_2O_7$ Cathode Materials for Lithium Batteries

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$Li_2MnP_2O_7$ were synthesized by spray pyrolysis(SP) with heat treatment. The precursor solution was prepared by dissolving the required amounts of $LiNO_3$ (98 % purity), $H_3PO_4$ (85 % purity) and $Mn(NO_3)_2 \cdot 6H_2O$ (98 % purity) in distilled water in a stoichiometric ratio. The total concentration of Li, Mn and P was 1.0 mol $dm^{-3}$. The preparation was carried out for various SP and annealing temperatures from 600 to 800°C in a $N_2$ atmosphere and the annealing time was fixed at 4 h. The details of the spray pyrolysis equipment were described in our previous paper [1].

Figure 1 shows the X-ray diffraction(XRD) patterns of the samples prepared by SP at various temperatures from 600 to 800°C with heat treatment at 600°C. Although a small impurity peak were detected in the sample synthesized at a SP temperature of 600°C, the XRD peaks of the present sample prepared by SP at 800 °C could be identified as the desired $Li_2MnP_2O_7$ phase without impurity.

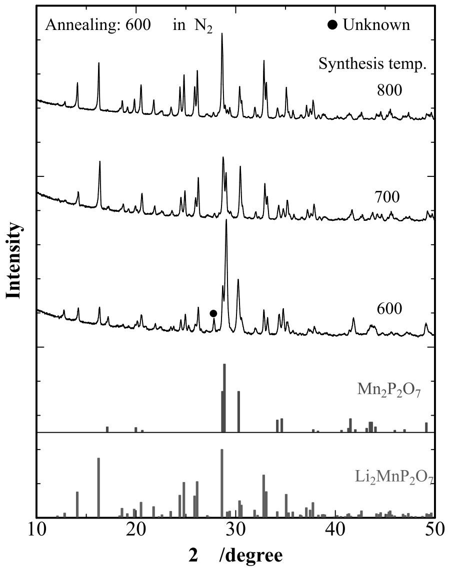

Figure 1 XRD patterns of the samples prepared by SP with heat treatment.

References
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s1-017

# The Development and Scale-Up of Enhanced Oxygen Reduction Reaction (ORR) Catalysts for Hydrogen Fuelled Low Temperature PEMFCs

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The South African government has set in motion an aspiring National Hydrogen and Fuel Cell Technologies Flagship project, branded as Hydrogen South Africa, HySA. One of the key goals of the programme is the development of high performance electrocatalysts that will be required in the near future by the ever-growing PEMFC industry. As a result of the mentioned key goal, a study on high performance catalyst material commenced at *HySA/Catalysis* [Mintek] in January 2012.

In the last decades Pt bimetallic nanoparticle catalysts (PtM with M = Co, Cr, Ni, etc.) have become more significant due to the improved ORR activity, the decrease of Pt loading and therefore the resulting reduced material cost. Consequently, the ability to engineer the composition and structure of nanoalloy catalysts is significant for developing active, robust and low-cost catalysts for PEM Fuel Cell applications. The aim and focus of the current project was, therefore, the rational design of Pt bimetallic fuel cell nano particle catalysts with improved electrocatalytic properties.

Presented in this work are thin-film RDE results for the development and laboratory scale-up of $PtM/C_{Vulcan}$ catalyst. In brief, several Pt alloy catalysts were synthesized by means of a wet impregnation method using in-house developed 20wt% Pt/C material. The $Pt_{1-x}/Co_x$ alloy catalysts showed significantly higher specific and mass activities than the Pt-only catalysts, with a $Pt_{0.25}Co_{0.75}$/Vulcan sample showing approximately 2.5 times the specific activity and 70% higher mass activity than Mintek's Pt/Vulcan catalyst.

Another goal of *HySA/Catalysis* [Mintek] is the fabrication of MEAs using in-house produced catalysts and to benchmark these MEAs against commercially available counterparts. To this regard, both CCM and CCS assortments of MEAs were fabricated by means of spray coating as the main technique for electrode preparation. The platinum-cobalt alloy catalyst materials have displayed high levels of potential for the application of in-house MEA fabrication and single cell testing results of 25cm$^2$ MEAs are furthermore reported on.

s1-018

# Oxy/ Hydroxy Manganese Electrodeposition on 1-Methyl-3-octylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid - Carbon Paste Electrode

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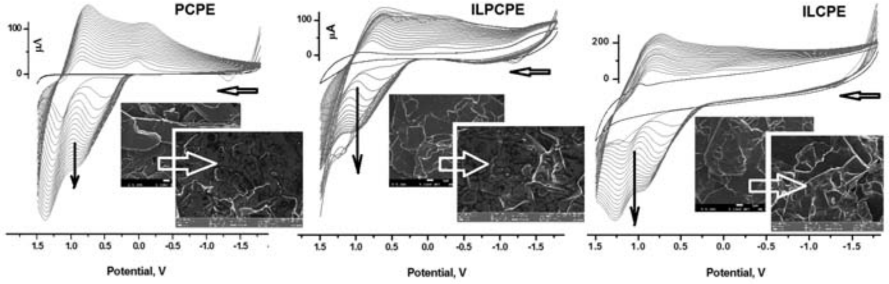
A study on carbon paste electrode (CPE) materials containing 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl) imide ($MOImTf_2N$) – a hydrophobic room temperature ionic liquid (IL) - is reported. CPEs with (a) the IL as the only binder (ILCPE) and (b) 1:1 (v/v) IL: paraffin mixture as the binder (ILPCPE) were prepared, characterized, and applied to the electrodeposition hydroxy/ oxy manganese ($Mn_xO_y$) using $Mn^{2+}$ as the precursor ion in aq. KCl. Cyclic voltammetry (CV) exhibited a potential window of +1.5 V to -1.8 V regardless of the electrode type, including the traditional paraffin CP electrode (PCPE). However, the IL increased the background current by 100-folds relative to paraffin. The electrochemical impedance spectroscopy (EIS) of ILPCPE in aq. KCl (0.1M) revealed two phase angle maxima in contrast with the single maxima for PCPE and ILCP in the frequency range 0.1 Hz – 100 kHz. The formation of $Mn_xO_y$ films onto the electrodes was confirmed by the observation of new and stable cathodic and anodic peaks in a fresh precursor ion – free medium. CVs of $H_2O_2$ as a redox probe as well as the ATR-FTIR spectra and SEM images of surface samples supported the above conclusion. This study demonstrated that the use of this hydrophobic IL alone or in combination with paraffin as a binder gives viable alternative CPE materials with better performance for the electrodeposition of $Mn_xO_y$ films than the paraffin CPE. Thus, in combination with the easy preparation methods and physical “morpheability” in to any shape, these CPEs are potentially more useful in electrochemical technologies based on high rough-ness factor $Mn_xO_y$-films, such as rechargeable batteries, super capacitors, and sensors.



s2-001

# Wines of the world. Their antioxidant capacity estimated by means of DPPH radical scavenging assay and electrochemical index.

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Considering the importance of phenolic compounds in wines for the health promoting properties, two different methods capable of measuring wine's antioxidant activity were used here (1). The DPPH (1,1-diphenyl-2-picrylhydrazine) assayand a novel electroanalytical approach (Differential Pulse Voltammetry - DPV) have been performed in order to compare the antioxidant activity of different grape beverages (2). A total of forty-five wine samples from different regions were analyzed. Red wines presented higher antioxidant capacity than rose or white ones and than red juices, evidencing the influence of the overall process of fabrication in phenolic extraction from the skin of grapes (3) (Figure 1A).

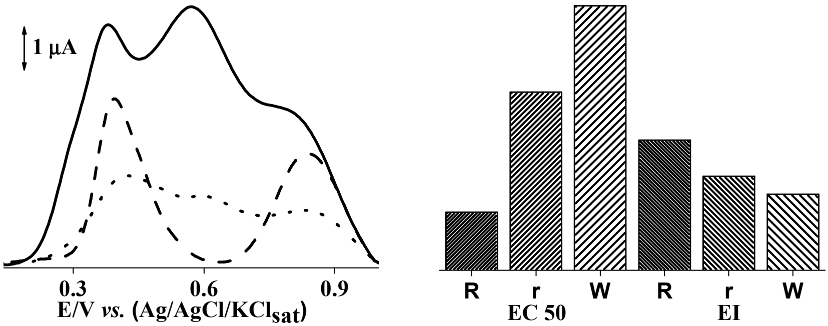

Figure 1. A) Red wine (---) white wine (---) and red juice (¨) voltammograms. **B)** Histogram representing EC50 and EI of red (R), rose (r) and white (W) wines.

The antioxidant activity of the different amount of wine required to produce amount of wine required to produce 50% of decolorization of DPPH• relative to the blank control ($EC_{50}$) and as an electrochemical index (EI) (Figure 1B). The EI was calculated following the formula: EI = $I_{pa1}/E_{pa1} + I_{pa2}/E_{pa2} + \ldots I_{pan}/E_{pan}$. A negative Pearson's correlation was found (-0.99458) and this result is consistent with what was expected due to the different principles inherent to these methods.

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s2-002

# Synthesis and Characterization of ZnO-CdO Composite Thin Film by chemical methods

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We use simple and economical chemical methods such as successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition for the deposition of nanocrystalline zinc cadmium oxide (ZnO-CdO) films. The deposition of ZnO-CdO films were on non-conducting glass and steel substrates. Paramount on the deposition were the optimisation of bath deposition parameters such as the pH of bath, deposition temperature and dipping cycles and annealing temperatures. After the deposition, post deposition treatments, such as annealing in air to improve the film properties were carried. The films were characterised using physico-chemical techniques such as SEM, FT-Raman, two point probe and spectrophotometers. We studied the hydrophilicity of ZnO-CdO thin films using contact angle measurement.

s2-003

# Palladium Telluride Quantum dots Electrochemical Biosensor for Protease Inhibitor Anti-retroviral Drug: Indinavir

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The project will involve the fabrication of a 3-mercaptopropionic acid (MPA)-capped and palladium telluride (PdTe) quantum dots-cytochrome P450 3A4 (CYP3A4) enzyme electrochemical biosensor for the detection of indinavir, a protease inhibitor antiretroviral drug. The indinavir biosensor is very crucial in monitoring drug toxicology and a patient's response to treatment due to genetic polymorphism which causes inter-individual variability in the rate of drug clearance from human systems after administration. The biosensor combined the electrochemical properties of MPA-capped PdTe quantum dots and the oxo-ferrylmonoxygenation cycle of the CYP3A4 haemolytic enzyme in the determination of indinavir. The approach taken in the development of the biosensor involved the incorporation of PdTe quantum dots capped with MPA onto a gold electrode that was previously modified with self-assembled cysteamine. CYP3A4 enzyme was then self-assemble onto the modified gold electrode by reacting with n-3-(dimethylaminopropyl)-n-ethyl carbodiimide hydrochroride. Fourier transform infrared (FTIR) spectra of the biosensor at 2956 $cm^{-1}$ confirmed the formation of a secondary amide bond from free carboxylic groups on the MPA-capped PdTe quantum dots surface and amine groups on the CYP3A4. The nanobiosensor's voltammetric response was studied by amperometry and electrochemical impedance spectroscopy.

s2-004

# Organic Isocyanide-Adsorbed Gold Nanostructure: A SERS Sensory Device to Detect Volatile Organics

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Volatile organic compounds (VOCs) are numerous, varied, and ubiquitous. A major source of manmade VOCs is solvents, especially paints and protective coatings. Allergic, respiratory, or immune effects in infants or children are largely associated with these man-made VOCs. The ability of VOCs to affect health varies greatly from those that are highly toxic, to those with no known health effect. At present, not much is known about what health effects occur from the levels of organics usually found in homes, although many VOCs are known to cause cancer in animals. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed.

The early detection of VOCs is a challenging task. In principle, VOCs in the environment or certain atmospheres can be detected based on the specific interactions between the organic compounds and the sensor components. There are a lot of VOC sensing materials, including metal oxide, conducting polymers, carbon nanotubes, carbon-polymer composites and functionalized gold nanoparticles to detect a wide range of VOCs. In fact, metal oxide materials such as SnO2 and ZnO and conducting polymers have been used in commercial sensors to detect even ppm concentrations. However, so far, the direct VOC sensing devices using vibrational spectroscopy such as Raman scattering have rarely been developed.

Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the Raman scattering cross sections are dramatically enhanced for the molecules adsorbed thereon. Very recently, Fan and coworkers reported a direct detection of 2,4-dinitrotoluene vapor using photo-chemically synthesized Au nanoparticles as the SERS substrate [1]. It was possible due to the high affinity of 2,4-dinitrotoluene vapor towards Au nanoparticles. However, to detect VOCs similarly via SERS, but whose adsorption strength to Au or Ag is very weak, it would be mandatory to cool down the SERS substrate.

When a molecule is adsorbed on the SERS-active surface, its electronic structure changes noticeably, resulting in the shifting and splitting of spectral lines. Further spectral change can also occur by the application of an external electric field. Thereby, the peak position of the NC stretching band in the potential-dependent SERS spectrum of 2,6-dimethylphenylisocyanide (2,6-DMPI), for instance, is sensitive to the electrode potential [2]. We illustrate in this work that the isocyanide-adsorbed noble metal nanostructures can be used as a platform for a VOC sensor operating via SERS, though indirect, without a thermoelectric cooler: not only various VOCs including carbon tetrachloride, methanol, ammonia, and butylamine but also their concentration dependent behaviours have been investigated in detail.

Posters

s2-005

# Voltammetry in Complex Microbiological Growth Media: Challenges and Recommendations

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Industrial bioprocess control is necessary to determine essential growth parameters such as pH, temperature, feedstock levels and dissolved oxygen concentrations of the microbial growth media [1]. These measurements allow reactive measures to be taken, thereby improving the efficiency of the process [2]. Similarly, the yield of the target product needs to be determined. Due to the lack of appropriate on-line sensors for product yield determination directly in complex microbial growth media, these analyses are often performed on samples taken from the reaction vessel and termed off-line measurements. While the use of off-line analysis (often by HPLC) offers accurate results, the time delay incurred can prevent effective feedback process control [3,4].

The use of voltammetry as a rapid detection method for fermentation reaction metabolites was thus probed. This study aimed to determine the possible interferents likely to be encountered in different complex microbiological growth media and their effect on the sensitivity and accuracy of voltammetric measurements. This was done through the use of cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS).

The study revealed the presence of several electrochemically active components in both commercially purchased and laboratory prepared microbiological growth media and identified key reagents which might limit direct electroanalysis. Through the use of voltammetric and impedimetric studies, this work outlines certain challenges associated with voltammetry in complex microbial growth media and makes recommendations towards improving detection accuracy.

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s2-006

# Electrochemical evaluation of ambroxol at a boron-doped diamond electrode and its adsorptive stripping voltammetric determination enhanced by anionic surfactant

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Ambroxol (AMB) is an expectorant agent which leads to bronchial secretion due to its mucolytic properties. It has also been reported to have antioxidative properties.
Although AMB is an electrochemically active compound, however, a limited number of studies on its voltammetric characteristics have been carried out which involves the use of hanging mercury drop [1], carbon paste [2] and glassy carbon [3] electrodes.

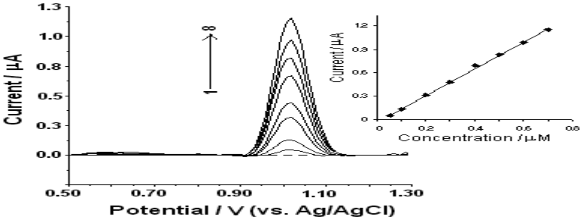

Figure 1: The stripping voltammograms for AMB levels of (1) 0.05, (2) 0.07, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5, (7) 0.6 and (7) 0.7 µM in phosphate buffer pH 2.5 containing 4x10-4 M SDS. Inset depicts a corresponding calibration plot for the quantitation of AMB.

Its electrochemical oxidation was first investigated in aqueous and aqueous/surfactant solutions by cyclic voltammetry using BDD and also glassy carbon electrode for comparison. The compound was irreversibly oxidized in one/two steps at high positive potentials, resulting in the formation of a couple with a reduction and re-oxidation wave at less positive potentials. The oxidation process was irreversible and adsorption-controlled. Special attention was given to the use of adsorptive stripping voltammetry on BDD in aqueous solutions over the pH range of 1.0-10.0. Addition of anionic surfactant (sodium dodecylsulfate, SDS) to the AMB-containing electrolyte enhanced the stripping current signal. The process could be used to determine AMB in the concentration range of 0.05 to 0.7 µM (21-290 ng mL$^{-1}$), with a detection limit of 0.012 µM (5 ng mL$^{-1}$). The suggested method was also applied to the determination of AMB in different drug formulations and spiked human urine samples.

s2-007

# Electrochemical investigations of testosterone hormone using various electrode

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Testosterone is a potent androgen that is primarily secreted By Leydig cells in men and thecal cells in women. Secretion is regulated by luteinizing hormone derived from the pituitary Gland. Lesser amounts of testosterone are secreted by the Adrenal cortex. Testosterone plays critical roles in spermatogenesis, the development and maintenance of the internal and external genitalia and secondary sex characteristics in men, and the control of libido in both genders[1]

In this study, glassy carbon electrode, boron-doped diamond electrode and bismuth-film electrode were investigated at different supporting solutions (acetate, phosphate and Britton-Robinson). Testosterone yielded a well-defined voltammetric response in acetate buffer, pH 4.8 at -1.45 V (vs. Ag/AgCl) (figure1). Electroanalytical application of this work is continuing in our laboratory.

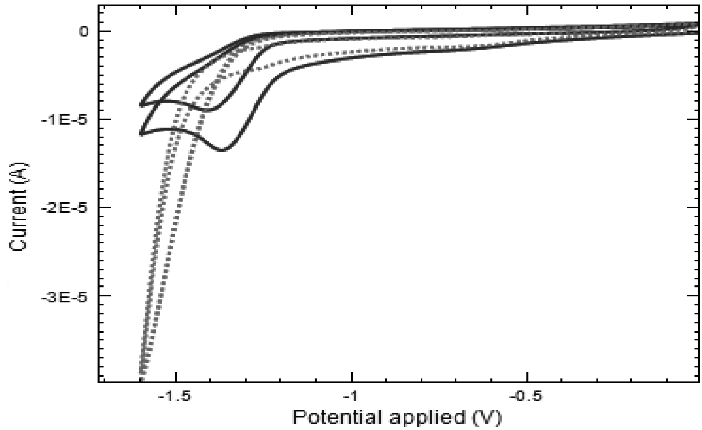

Figure 1. The repetitive CVs of 1.0x10$^{-3}$ M testosterone solutions in 0.1 M acetate buffer, pH 4.8 for glassy carbon electrode. Scan rate, 100 mV/s. The blue line represents the first scan, and the blue line the second one, while dashed line represents background current.

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s2-008

# Nanocomposite Based Immunosensors for Active Tuberculosis

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Tuberculosis (TB) is well recognized as one of the most life-threatening infectious diseases in the world with about 2 million deaths and 8 million new cases per year [1]. It is also the major cause of death in Human Immunodeficiency Virus/ Acquired Immune Deficiency Syndrome (HIV/AIDS) co-infected individuals, for whom no fast, affordable accurate TB test is available [2]. It has been estimated that a delay in the diagnosis and treatment of TB of more than three weeks after it presentation accounts for 45 to 85% deaths of TB/HIV co-infected patients [3]. There is therefore an urgent need for the rapid diagnosis of TB especially in Sub-Saharan Africa where the population is most burdened by the HIV/AIDS pandemic.

In my MSc studies, it was shown that self-assembled monolayer (SAM) platforms could be used for an electrochemical impedimetric immunoassay of TB in the sera of patients co-infected with human immunodeficiency virus (HIV) [4-5].

In my current study (PhD studies), I have continued the work of the MSc programme. However, the main objective this time is to explore the use of nanocomposite electrode platforms rather than the use of thiol-based SAM electrode.

In summary, the presentation will discuss the following:

- The impact of different immobilization strategies with carbon nanotubes (CNT's) with different functional groups.
- The impact of different stabilizers / binders, and
- The impact of different redox probes (e.g. ruthenium and iron based).

The insight gained from these studies could provide a useful basis for the design and development of a potential impedimetric immunosensor for active TB.

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s2-009

# Real-Time Electrochemical Monitoring of the Polymerase Chain Reaction by Conducting Polymers

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Described is a label-free oligonucleotide sensor that can monitor real-time PCR amplification of DNA, by using voltammetry and electrochemical impedance spectroscopy to detect the amplified DNA product generated in the PCR reaction solution, after each PCR cycle. The polymer was grown on the surface of a glassy carbon working electrode, and then functionalized with a specially-designed DNA strand, consisting of the forward primer required in PCR amplification, modified at the 5' end with a 10 mer thymidine bridge and again modified at the new 5' end with an amino group. To measure the DNA amplification, after each PCR cycle, voltammetry experiments were carried out in situ, using the potassium chloride and magnesium chloride present in the PCR buffer as the supporting electrolyte, in a 3 electrode micro-electrochemical cell, contained in the PCR machine. As the forward primer, which is tethered onto the electrode, is complementary to part of the DNA sequence that is being amplified, the measurements were obtained during the annealing stage of the PCR cycles; this meant that there were partial ds-DNA on the electrode surface, which allowed the exponential increase of DNA in the cell to be seen, by the decrease of the electronic readout from the potentiostat.

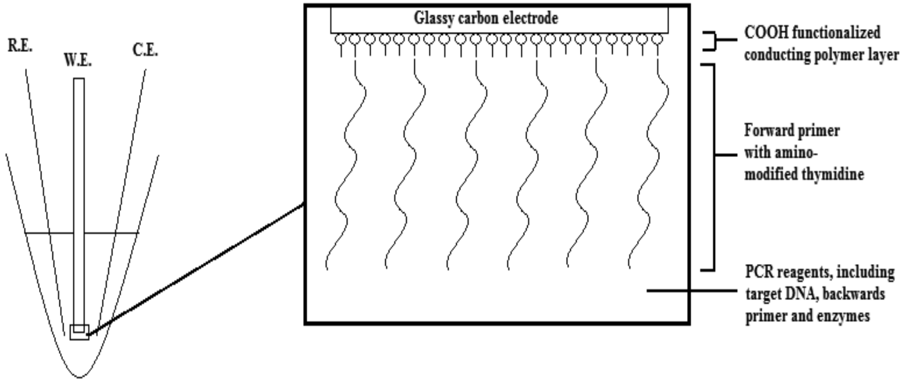

Figure 1: Schematic of the 3-electrode micro-electrochemical cell (R.E. is palladium hydride, W.E. is glassy carbon, C.E. is platinum) and the DNA modification to the surface of the electrode.

s2-010

# Protein Phosphatase immunosensor for the detection of cyanotoxins associated with algal bloom

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The toxicity of microcystins is associated with the inhibition of serine/threonine protein phosphatases 1 and 2A, which can lead to hepatocyte necrosis and hemorrhage. Analysis of microcystins is most commonly carried out using reversed-phase high performance liquid chromatographic methods (HPLC) combined with ultra-violet (UV) detection .The ability of these techniques to identify unknown microcystins in environmental samples is also restricted by the lack of standard reference materials for the toxins. Highly specific recognition molecules such as antibodies and molecularly imprinted polymers (MIPs) have been employed in the pre-concentration of trace levels of microcystins from water and show great potential for the clean-up of complex samples for subsequent analysis. New biosensor technologies are also becoming available, with sufficient sensitivity and specificity to enable rapid 'on-site' screening without the need for sample processing .We have constructed a novel immunosensor for microcystinLR in aqueous medium, incorporating the unique properties of nanoscale materials electrochemically synthesised in our laboratory and the sensitivity of protein phosphatase 2A inhibition. Conductive polymers are stable and highly conductive mediator platforms and have been used in many biosensor systems for various applications, without loss of biomolecule reactivity after immobilisation. The electrochemistry of the immunosensor was evaluated using cyclic voltammetry and square wave voltammetry. The affinity binding of the microcystinLR to protein phosphatase 2A was investigated using electrochemical impedance spectroscopy which is a highly sensitive method for measuring interfacial kinetics of biosensor systems.

s2-011

# Development of electroactive polymer platforms for evaluation of halocarbon adsorption

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A novel polypyrrole derivate, phenazine 2,3-diimino(pyrole-2-yl, was electrochemically polymerised to produce thin films of the polymer at glassy carbon screen printed electrodes (GCSPE). The actuator molecule poly (Phenazine 2,3-diimino(pyrole-2-yl)) doped with PVSA (PPDA), was studied under conditions of doping and de-doping to evaluate the conformational changes within the molecule, resulting in large space volume required for actuation. Evaluation of the surface morphology of the PPDA by scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirmed the homogenous distribution of porosity and high surface roughness of the material, which identified is as a good platform for adsorptive analysis of selected halocarbons dichloromethane and dibromopropane.

Dichloromethane adsorption was observed as an irreversible peak at 1200mv (acetonitrile, vs Ag/AgCl) which was clearly separated from the dibromopropane reduction peak at -1000mV. The PPDA sensor showed showed linear concentration dependence for both analytes in the milli to micro-molar range. This was confirmed by electrochemical impedance spectroscopy as a change in total impedance of 83Ω for dibromopropane and 7233Ω for dichloromethane for high frequency measurements. The mechanism of dibromopropane reduction involved the evolution of bromine gas which could account for the smaller total impedance change observed.

Atmospheric samples were collected by time dependent adsorption of air samples onto activated charcoal (4-8 mesh). The adsorbed materials were released by solid phase extraction (SPE) into pentane. Compositional analysis of the adsorbed material was done by high performance liquid chromatography (HPLC) and the PPDA sensors were applied for the detection of dichloromethane and dibromopropane.

Keywords: sensors, electrochemistry, adsorption, halocarbons, air samples

s2-012

# Spectro-electrochemical interrogation of novel biocompatible nano-platforms for mycotoxin immunosensors

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Quantum dots and metal nanoparticulate platforms for application in electrochemical mycotoxin immunosensor will be developed. Mycotoxins are toxic metabolites of fungi that contaminate a variety of food (e.g. cereals and roasted coffee) and animal feed stored under temperate and humid conditions favourable to mould growth. They are very potent toxins that exhibit cytotoxic, nephrotoxic, neurotoxic, immunosuppressive and estrogenic effects. Generally FAO permissible level for mycotoxins is ~25 ppb in food and ~300 ppb in feed. The testing of crops, food and animal feeds for mycotoxin contamination is very important in South Africa that permissible levels are controlled by two sets of legislations: (i) Department of Agriculture Acts No. 36 of1947 and No. R1087 of 3 Nov 2006 dealing with regulations relating to animal feeds. (ii) Department of Health No. 54 of 1972 and No. Acts R1145 of 8 Oct2004 that stipulates regulations governing tolerance for fungus-produced toxinsin foodstuffs. In this study impedimetric immunosensors will be developed with biocompartible gold nanoparticles (AuNP) and quantum dots functionalised with glycydoxypropyltrimethoxysilane oraminopropyltrimethoxysilane or mercaptopionic acid for easy linkage to, and labelling of, anti-mycotoxin antibody. The immunosensing process was studied by electrochemical impedance spectroscopy, fluorescence and FTIR/UV-Vis spectroelectrochemistry. The economic benefit of this study is that it will reduce the cost of testing foods and feeds for mycotoxins. Currently, 29 laboratories in South Africa (information from National Institute of Metrologyof South Africa –NIMSA- 2009) determine mycotoxins using chromatographic/spectroscopic techniques which are expensive, requires extensive sample pre-treatment and expertise. The immunosensor techniques being proposed in this study are relatively cheap, easy to use, do not require extensive sample pretreatment and are suitable for on-site deployment. The target mycotoxins will be zearalenone and trichothecenes.

s2-013

# 3-Mercaptopropionic acid capped $Ga_2Se_3$ nanocrystal-cyp3a4 biosensor for the determination of 17-alpha-ethinyl estradiol in water

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Water soluble and biocompatible 3-mercaptopropionic acid capped gallium selenide nanocrystals, were synthesized from hydrated gallium (III) perchlorate and selenide ions. The 3-Mercaptopropionic acid capped gallium selenide nanocrystals, was non-fluorescent but showed a sharp UV-vis absorption maximum at 250 nm. The synthesized nanoparticles were used to develop an electrochemical biosensor for the detection of 17-alpha-ethinyl estradiol, an estrogenic endocrine disrupting compound (e-EDC). The biosensor was fabricated by potentiostatic deposition of novel gallium selenide nanocrystals on a L-cystine modified gold electrode, followed by covalent coupling of genetically engineered cytochrome P450-3A4 (CYP3A4), a Heme containing enzyme. The biosensor gave an electrochemical response at about -220 mV. The results revealed that 3- Mercaptopropionic acid capped Gallium Selenide nanocrystals can be used in conjunction with CYP3A4 as an electrode modifier for the detection of 17-alpha ethinyl estradiol. The 3- Mercaptopropionic acid capped Gallium Selenide nanoparticles exhibited a semiconductor like behaviour.

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s2-014

# Metal nanoparticles modified polysulfone membrane materials for water treatment.

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Membrane separation processes have been widely applied in the treatment of wastewater with polysulfone polymer membrane being the most frequently used in ultrafiltration of wastewater due to its chemical and structural stability and mechanical robustness (Castro Vidaurre E. and Achete C.*et al, 2002)*. A disadvantage to these membranes is their hydrophobicity and their membrane fouling caused by organic pollutants in water. Many studies have been conducted to increase the hydrophilic properties of the polysulfone membrane surface (Asatekin A. and Kangb S, *et al,2005*). Recently metal nanoparticles have been added to the polymer matrix in order to reduce membrane fouling and increase its hydrophilicity.

For this research work three organic acids (Humic Acid, Tannic Acid and Alginic Acid) were selected to test the fouling behavior of nanometallic synthesised polysulfone membranes. Metallic nanoparticles of silver, cobalt and nickel were chemically synthesized and integrated within the polysulfone polymer matrix to form the polymeric polysulfone nanocomposites. The metallic nanoparticles and the nanocomposites were characterized using UV-visible, FTIR, HR-TEM, SEM, EDX, AFM, CV, SWV, EIS, contact angle. The fouling behaviour of the composite was tested.

Keywords: Fouling, Hydrophilicity, Polysulfone (PSF), Electrochemical Impedance Spectroscopy (EIS), Organic Acids, Metal Nanoparticles.

s2-015

# An investigation of graphene-modified pencil graphite electrodes for the determination of trace metals by anodic stripping voltammetry

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Pencil graphite has been previously used as an electrode substrate material in different applications of stripping analysis due to its good conductivity, little pretreatment, low cost, ease of availibility and low background current [1]. Nafion has shown to increase the detection sensitivity and alleviate the interference from the surfactants of bismuth film electrodes [2]. The study reports the synthesis of graphene by the oxidation of commercialy bought graphite to graphite oxide using $KMnO_4$ and reducing the graphene oxide to graphene using $NaBH_4$. The graphene produced was characterised using FT-IR, SEM, TEM, AFM, XRD, Raman spectroscopy and solid state NMR and showed good quality graphene with flake sizes in the nanometer range [3]. The inexpensive pencil graphite substrate, which is a good alternative to the commonly used expensive glassy carbon electrode, was modified with graphene nanomaterials by dipcoating and electrodeposition methods to yield the graphene and modified-graphene pencil graphite electrodes (GPLE). Graphene, the 2D allotrope of carbon with $sp^2$ hybridisation, has been applied to many areas of research including chemical sensing, due to its high surface area and improved electron conductivity for enhanced sensing [3]. The GPLEs produced was used as voltammetric sensor for determining heavy metals ($Cd^{2+}$, $Pb^{2+}$ and $Zn^{2+}$) by square wave anodic stripping voltammetry (SWASV) in 0.1 M acetate buffer solution (ABS), pH 4.7 and applied as voltammetric sensor to real samples containing traces of these metals and compared to Inductively coupled plasma (ICP) techniques. The modified sensing platform resulted in enhanced sensitivities, well-defined and reproducible peaks and improved limits of detection at a prescribed preconcentration time. The detection limits ranged from 0.07-0.15 $\mu g.L^{-1}$ for the various modified electrodes.

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s2-016

# Development of Rapid Test Systems of Enzyme and Aptamer Nanobiosensors for Water Estrogens

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Current water treatment technologies do not remove many endocrine disruptor compounds (such as 17betaestradiol and17alphaestradiol) in its entirety. New technologies including ozonolysis and activated carbon are being used to increase to enhance the efficiency of treatment plant for the removal of estrogens from wastewater. However, the amount of estrogens that continues to enter the aquatic environment through wastewater effluents is still capable of causing harmful health effects. An objective of this study is to develop a biosensor method for real-time determination of low levels of estrogens in municipal wastewater effluents, which is mainly the state that interacts with aquatic environment. We report DNA aptamer and enzyme electrochemical nanobiosensors for 17-betaestradiol and 17-alphaestradiol developed using poly(glutaraldehyde-co-aniline) electrically conductive entrapment agent for the DNA aptamer or for the enzyme (cytochrome P450 or laccase) in the presence of gold nanoparticle. The biosensor are applied to a synthetic real sample and compared with standard HPLC and ELISA techniques.

s2-017

# Application of *in situ* coupled Glucose Oxidase and Poly (propylene imine) Dendrimer for the Amperometric Detection of Glucose

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Dendrimers are an interesting group of polymers owing to their reactivity, biocompatibility and chemical tunability. Coupling such dendrimers to enzyme may yield better enzyme activity and stability. In this light, an amperometric biosensor for glucose was developed using *in situ* coupled glucose oxidase (GOx) and poly (propylene imine) dendrimer (PPI) (with EDC/NHS linker) bioreceptor. The GOx-PPI couple was characterised with UV and FTIR. A biosensor was then prepared by drop coating the GOx-PPI on a glassy carbon electrode and used for the amperometric detection of glucose. The biosensor showed a linear current response to glucose concentration from 20 to 200 μM with a detection limit of 15 μM. The coupled enzyme showed improved stability and higher metabolic activity towards glucose in comparison to the pristine GOx. Thus, this simple coupling chemistry can be applied to myriads of enzyme with the aim of enhancing enzyme activity and increasing enzyme shelf life at room temperature for various applications.

Keywords: glucose oxidase, poly (propylene imine) dendrimer, amperometric biosensor, glucose, enzyme.

s2-018

# Development of methacrylate hydrogel nanobiosensor for phenolic endocrine disrupting compound, Bisphenol A

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The study involved the synthesis of new hydrogellic methacrylate co-polymers and their application as biocompatible platforms for the construction of nanobiosensors for phenolic endocrine disruptor compound, Bisphenol A (BPA). Bisphenol A (BPA) is a hormone-disrupting chemical considered to be potentially harmful to human health and the environment. BPA based polycarbonates are used as a plastic coating for children's teeth to prevent cavities, as a coating in metal cans to prevent food contamination, as plastic in food containers, refrigerator shelving, baby bottles, water bottles, and eating utensils. It is now widely known that BPA can leach out of plastic during normal use and cause health effects such as cancer or disrupt the endocrine system. Therefore, developing a sensitive and selective biosensor for BPA has become a very important issue in the past decade. Poly(glycidyl methacrylate-aniline or pyrrole), poly(3-thienylmethylmethacrylate-aniline or pyrrole), and poly(glycidyl methacrylate-3-thienylmethylmethacrylate) nanocomposites were synthesised and doped with titanium nanocomposites. The biosensor was prepared by incorporating manganese peroxidase into the above mentioned hydrogels either by electropolymerisation or by chemical immobilisation. Electrochemical characterisation of the biosensor and its components was achieved using voltammetry and electrochemical impedance spectroscopy (EIS); while size, structural and morphological characterisation was studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Ultra violet–visible (UV-Vis) spectroscopy and Brauner-Emmett-Teller (BET).

s2-019

# HRP Inhibition Based Amperometric Biosensor for the Detection of Heavy Metals

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Horseradish peroxidase (HRP) based biosensors are important in many fields of analyses such as pharmaceutical and food industries, and environmental applications. In general a biosensor is constructed so that it consists of a base electrode coated with a mediator and immobilized biomolecules [1]. In this study an amperometric biosensor based on the inhibitory effects of horseradish peroxidise (HRP) activity towards the reduction of hydrogen peroxide ($H_2O_2$ substrate) by selected heavy metals (Hg, Cd, and Pb) has been investigated. The polymers of PANI and PANI-co-PDTDA were used as mediators since they provide a suitable platform for the immobilisation of HRP on the platinum electrode surface and it also mediate in electron transfer between HRP and the electrode [2]. A 0.1 M buffer solution (pH = 6.8) was used throughout the study for Pt/PANI/HRP biosensor, while a pH = 7.2 solution was used for the Pt/PANI-co-PDTDA/HRP biosensor. The apparent Michaelis – Menten parameters ($K_m^{app}$) and $I_{max}$ values, which provide an indication of catalytic activity of an enzyme were calculated to be 0.6 mM and 1.7 µA for the Pt/PANI/HRP biosensor, and 0.7 mM and 0.27 µA for the Pt/PANI-co-PDTDA/HRP biosensor in 1 mM $H_2O_2$ substrate solution. Comparison and evaluation of the inhibition results for $Cd^{2+}$, $Pb^{2+}$ and $Hg^{2+}$ analysis have indicated that the best sensitivity has been obtained for $Cd^{2+}$ analysis, while the highest inhibition was obtained for $Hg^{2+}$ analysis. Each of the biosensor systems evaluated has shown different results for the inhibition analysis towards $Cd^{2+}$, $Pb^{2+}$ and $Hg^{2+}$. The detection limit obtained for each sensor for the analysis of $Cd^{2+}$, $Pb^{2+}$ and $Hg^{2+}$ respectively has been determined. The linear range for the Pt/PANI/HRP biosensor was established to be 0 – 0.75 mM ($r^2 = 0.997$). For the Pt/PANI-co-PDTDA/HRP biosensor the linear range was found to be 0 – 0.67 mM ($r^2 = 0.993$).

Keywords: HRP biosensor; amperometric; inhibition; heavy metals

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s2-020

# 20 Years of Collaboration in the Middle Europe. Part I: Electroanalysis with Carbon Paste-Based Electrodes

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In this presentation, scientific collaboration between the two electroanalytical groups, the Institute of (Analytical) Chemistry at the KFU Graz and the Department of Analytical Chemistry at the UPa, is summarised. Having started in 1993, the join research work with carbon paste electrodes (CPEs) and related sensors covers the series of new methods proposed for the determination of selected inorganic ions ($Ag^I$, $Tl^{III}$, $Hg^{II}$, $As^{III} + As^V$, $I^-$ and $IO_3^-$); in some cases, achieving remarkable results (see figure below and ref. [**1**] ). Furthermore, special characterisation of carbon pastes with the aid of modern microscopic techniques (e.g. SEM) was also of continuing interest.

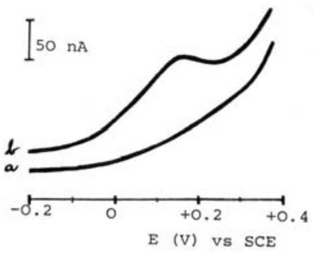

**Fig.**: *Determination of $Ag^I$ at the ultratrace level at chemically modified CPE employing synergistic preconcentration: Estimating the limit of detection.*
Legend: ***a*** ... base-line (blank), ***b*** ... c(Ag) = $7\times10^{-13}$ mol·L$^{-1}$. Experimental conditions: DPASV, tricresyl phosphate-based CPE, acetate buffer, accumulation time: 120 min. (For further details, go to [**1**])

In the early 2000s, another important research within our groups had been started, reflecting still more intensive orientation towards the "green analytical chemistry". Namely, our groups belonged to the pioneers in the development and testing of non-mercury metallic electrodes, bismuth and antimony modified CPEs, including some new configurations (see [**2**] and refs. therein). Recent years were then in the sign of work on some reviews and book chapters, culminating by the release of the very first monograph in the field [**3**].

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s2-021

# Graphenated–polyaniline Nanocomposite for Real Time Determination of Polyaromatic Hydrocarbons

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A graphenated – polyaniline nanocomposite electrode was prepared chemically by in situ polymerization of aniline in a suspension of graphene oxide through the chemical oxidation of aniline with APS in an acidic medium. The synthesised nanocomposite was characterized with scanning electron microscopy (SEM), transition electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and using electrochemical techniques. The graphenated polyaniline nanocomposite was then used to construct a sensor for the determination of anthracene. The direct electro-oxidation behaviour of anthracene on the graphene – polyaniline modified glassy carbon electrode was carefully investigated by cyclic voltammetry. The results indicated that there was an increase in the anthracene oxidation peak current with shift of the oxidation peak potential in contrast to that on the bare glassy carbon electrode The nanocomposite formed exhibited a remarkable electroactive activity towards oxidation of anthracene. A detection limit of $4.39 \times 10^{-7}$ M was established. The sensor exhibited high sensitivity, good reproducibility and long-term stability.

s2-022

# A Dendrimer-Gold Nanocomposite based Immunosensor for the Detection of Cholera Toxin in Water

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Cholera, a water borne disease, continues to be a major public health concern in developing countries and accounts for considerably high cases of illnesses. Most recently, cholera outbreaks have been reported in many countries including Haiti, Zimbabwe, Mozambique, Liberia, Iraq, the Democratic Republic of the Congo, India and South Africa. These sudden outbreaks could have been mitigated if there were faster, cheaper, and on-site cholera detection devices that do not need much expertise to operate. Such a devise will be useful for prompt cholera alert in rural areas were challenges in water sanitation and laboratory facilities are common. This work presents the development of an electrochemical cholera immunosensor based on a generation 2 poly(propylene imine) dendrimer-gold nanocomposite platform. The nanocomposite was prepared on a glassy carbon electrode by electro-co-deposition using cyclic voltammetry in a potential range of -300 mV to +1000 mV and characterised using electron microspcopy. The modified electrodes were electrochemically characterised in phosphate buffer saline and ferrocyanide electrolytes. The immunosensor was prepared by the immobilisation of anti-cholera toxin antibody on the nano-platform by drop coating for 2 hr at a temperature of 38 $^{o}$C. For the detection of cholera toxin, the immunosensor was incubated in water containing different concentrations of cholera toxin for one hour. The antibody-toxin bio-recognition event was monitored by square wave voltammetry and electrochemical impedance spectroscopy (EIS). A linear detection range of $10^{-7}$ mg $L^{-1}$ to $1 \times 10^{-11}$ mg $L^{-1}$ and a detection limit of $5 \times 10^{-12}$ mg $L^{-1}$ were obtained with good antibody stability.

Keywords: Cholera, immunosensor, nanocomposite, dendrimer, water, electrochemical impedance spectroscopy.

s2-023

# Synthesis and characterisation of bismuth-silver amalgam nanoparticles for electrochemical sensor applications

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Heavy and platinum group metal contaminations at trace levels in water resources presents a major current environmental threat, so the detection and monitoring of these metal contaminants results in an ever-increasing demand. Due to the toxicity of mercury, its difficulties in handling, storage and disposal has restricted its use in electro-analytical techniques. Nowadays, many researchers request alternative working electrodes for the determination of heavy and platinum group metals. The search for new electrode materials such as metal nanoparticles (silver, bismuth and bismuth/silver, etc.) for the determination of heavy metal analysis has increased. These metal nanoparticles (NPs) have received much attention due to their potential application in microelectronics, catalytic and optical properties, magnetic devices, electronics and chemical and biosensors nanomaterials. Silver has been widely studied because of its characteristic spectroscopic, optical and catalytic properties. The size, shape and surface morphology play pivotal roles in controlling the electronic, chemical, optical and physical properties of silver nanoscopic materials [1-3]. The individual silver, bismuth and a bismuth-silver amalgam nanoparticles were compared and characterised by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), ultraviolet-visible (UV-VIS) spectroscopy, atomic force microscopy (AFM), Fourier-transformed infrared (FTIR) spectroscopy, Raman spectroscopy, transmission electron microscopy (TEM) analysis and scanning electron microscopy (SEM) analysis to interrogate the structural and morphological properties of the compounds synthesised. The results reported in this study demonstrate that the synthesised nanoparticles of silver, bismuth and bismuth/silver can be used to construct an electrochemical sensor for the determination of platinum group metals (PGMs) in environmental samples.

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s2-024

# Impedimetry and microscopy of electrosynthetic poly(propylene imine)-co-polypyrrole dendritic star copolymer

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The electrochemical impedance spectroscopy of generation 2 poly(propylene imine)-co-polypyrrole conducting dendritic star copolymer (G2PPI-co-PPy) film was studied in lithium perchlorate (LiClO4) solution. The G2PPI-co-PPy was synthesised electrochemically, electrochemical oxidative copolymerization of pyrrole on a platinum electrode coated with PPI-2Py using cyclic voltammetry in LiClO4, resulting conducting dendritic star copolymer. The results show that the electrochemical deposition of G2PPI-co-PPy on platinum electrode decreased the electrochemical charge transfer resistance when compared to electrodeposited polypyrrole (PPy) on platinum electrode as well as the bare Pt. The dendritic star copolymer was characterized using Fourier transform infrared spectroscopy (FT-IR), and electrochemical impedance spectroscopy (EIS). NMR of G2PPI-2Py gave a new chemical shift at 8.1 ppm for N=CH, which confirmed the incorporation of 2-pyrrole aldehyde into the PPI dendrimer structure. Strong FT-IR bands appeared at 1630 $cm^{-1}$ for N=C in the dendrimer moiety, and at 729 $cm^{-1}$ for C-H at the α-position of the PPy ring. The decrease in charge transfer resistance may attribute to an increase in the conjugation length of the polymer as result of the linking of the highly conjugated PPy to the PPI dendrimer. Bode impedimetric analysis indicates that Pt|G2PPI-co-PPI is a semiconductor with a maximum phase angle shift of 45.3° at 100 mHz. The star copolymer exhibited a 2-electron electrochemistry and a surface coverage of 99%. The morphology of the dendritic star copolymer was investigated by scanning electron microscopy.

s3-001

# Oxalatophosphates: Novel Inorganic-Organic Hybrid Cathode Materials for Lithium Ion Batteries

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Lithium ion batteries (LIBs) have been the most attractive among the rechargeable battery technologies due to large energy density. Extensive research is being carried out globally to develop greener, cheaper and safer battery materials. Olivine structured $LiFePO_4$ is recently developed as the next generation cathode material, a commercial replacement for $LiCoO_2$. However, its poor electronic and ionic conductivity together with its slightly lesser operating voltage, provoke the need for innovative generation of different materials with good rate capability and high energy density. In the process of generation of materials with high energy density, vanadium based materials are of interest due to their higher operating potential. The different vanadium based materials such as $LiVOPO_4$, $LiVPO_4F$, $Li_3V_2(PO_4)_3$, etc., have been studied as cathode materials. In our study, a new class of hybrid inorganic-organic open framework materials (oxalatophosphates) have been synthesized and studied as cathode materials for the first time. Syntheses of $A_2[(VO)_2(HPO_4)_2(C_2O_4)]$; (A=Li/Na/K) were carried out at low temperatures of 120°C by hydrothermal method. Electrochemical characterization of these materials reveals that these materials exhibit reversible lithium storage properties at ~4V with good cycling stability.

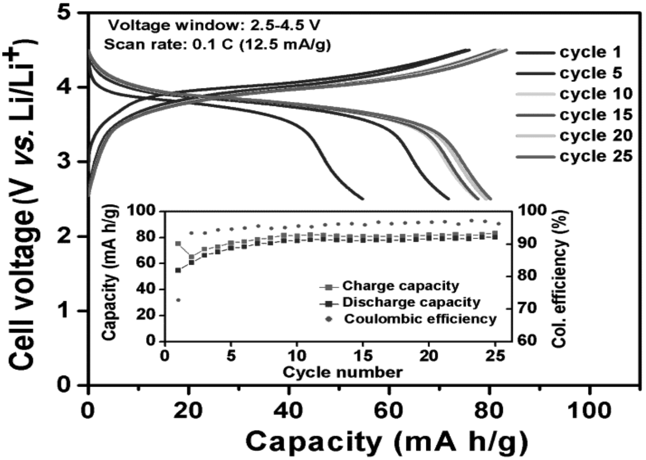

Figure: Galvanostatic charge-discharge profiles of $Li_2(VO)_2(HPO_4)_2(C_2O_4)$ at a current density of 12.5 mA $g^{-1}$ (0.1 C)

s3-002

# Investigation of a Composite Anode Catalyst in Direct Methanol Fuel Cells

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Direct Methanol Fuel Cells (DMFCs) are very actractive nowadays as power sources for portable applications [1,2]. In this regard, increasing interest is devoted towards the miniaturisation of these fuel cell devices in order to replace the current Li-ion batteries. Theoretically, methanol has a superior specific energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. Another significant advantage of the DMFC over the rechargeable battery is its potential for instantaneous re-fuelling. These significant advantages make DMFCs an exciting development in the portable electronic devices market [1].

Unfortunately, DMFC operation at low temperatures requires a high noble metal loading to enhance the kinetics of the methanol electro-oxidation reaction and counteract the poisoning effects at the cathode due to the methanol cross-over [1].

In this work, an 85% Pt-Ru (1:1 a/o) alloy supported on Vulcan XC-72 was in-house prepared by using a sulphite complex route [3] and utilised in DMFCs as the anode catalyst. In order to enhance the activity of this catalyst, in particular when low Pt loading is used, high surface area $TiO_2$ nanoparticles were added to the catalyst. An electrochemical investigation in a DMFC of the bare anode catalyst compared to the composite one was carried out in the temperature range 30-70°C.

Acknowledgements

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s3-003

# Hydrogenation and Corrosion Behavior of $LaNi_5$ Based Alloys with Nickel partly Substituted by Zinc

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The galvanostatic $-i/+i$ charge/discharge curves are the most convenient dependencies to determine ability of intermetallic materials to cathodic hydrogenation in terms of their capacity and kinetics of hydrogen absorption/desorption process [1,2]. In our recent papers we also indicated a usefulness of charge curves to evaluate corrosion susceptibility (formation of oxide phases) of the mono- or multiphase alloys based on $LaNi_5$ compound [2,3].

Partial substitution of nickel by zinc in $LaNi_5$ compound ensures monophase structure up to ca 10 at.%. For greater concentrations of Zn the alloy becomes multiphase [4].

The $La(Ni,Zn)_5$ powdered materials (particle size 50-100 μm) bonded with epoxy resin were used to prepare the working composite electrodes. The electrochemical tests were carried out in argon saturated 6M KOH at 23°C. The plots of charge curves allow to distinguish processes of atomic hydrogen absorption and evolution of molecular $H_2$ for the tested alloys [2,3]. To determine hydrogen diffusivity in powder composite material we applied chronoammetric- and cyclic voltammetry methods, according to [5].

For $La(Ni,Zn)_5$ alloys the alloy hydride discharge capacity clearly increases compared to $LaNi_5$ reference, increases the exchange current density of $H_2O/H_2$ system and increases the atomic hydrogen diffusion coefficient. It should be mentioned that Zn substitution for nickel evidently decreases the equilibrium pressure of $H_2$ [4].

During electrode discharging process nickel partially undergoes oxidation with formation of NiO but the NiO/Ni equilibrium is reversible and nickel oxide phases undergo reduction during charging. However, electrode cycling causes degradation of the electrode material and its corrosion. It is shown in our paper that presence of Zn in the alloy is also advantageous from material corrosion point of view.

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s3-004

# Transient Electrochemical Gas Permeability Measurements for PEM Fuel Cells and Electrolysers

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An advanced hydrogen-based fuel cell power train system for the automotive industry must meet a number of demanding requirements to become commercially attractive. These include requirements of fuel cell vehicles, such as improvements in fuel economy, power efficiency, and durability to provide suitable vehicle range and costs [1]. One of the key challenges that is directly associated with MEA components include relatively high gas permeability of the perfluorosulfonic acid SPE membranes [2]. In modern high-pressure PEM water electrolysers, excessive gas cross-over (permeability) of oxygen may limit the purity of discharged hydrogen, as well as excessive gas cross-over of hydrogen may present safety issues.

If a depolarised gaseous component, e.g., SO2 gas, is used in the electrolysis process for hydrogen generation, cross-over of the SO2 may be detrimental to the operation of a PEM electrolyser. Permeability of gases in membranes under operation conditions existing in a PEM fuel cell and PEM electrolysers has thus become one of the key properties that require comprehensive research. In order to gain a fundamental understanding of gas transport phenomena in membranes and to design new membrane materials with set permeation properties, one needs to understand the values and nature of kinetic transport parameters such as diffusion coefficients [3].

In this paper, we discuss fundamentals of electrochemical transient gas permeability measurements that allow determination of a critical kinetic parameter of membrane gas permeation, i.e., diffusion coefficient [4].

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s3-005

# Electrochemical Performance of co-doped $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Mn, Ni, Co) Cathode Materials

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The composite material has a $xLi_2MnO_3 \cdot (1\text{-}x)LiMO_2$ (M = Mn, Co, Ni) structure has been considered as one of the most promising cathode materials for advanced lithium-ion batteries due to their low-cost and high capacity (> 200 mAh g−1) between 4.8 V and 2 V [1, 2].

However, these $Li_2MnO_3$-like composite cathode materials have three major disadvantages: high initial irreversible capacity, poor cycling stability and poor high rate capability. The development of the $Li_2MnO_3$-like composite cathode materials for lithium ion battery still is a challenge for meeting current and future energy storage requirements.

The cation doping is considered as an effective way to modify the intrinsic properties of electrode materials [3]. The magnesium-doping can be an effective way to improve the performance of this $Li_2MnO_3$ like materials. Sun et al reported that by magnesium substitution for Ni, the structural stability and cycling behavior of $Li[Li_{0.15}Ni_{0.235}Mg._{0.04}Mn_{0.575}]O_2$ material was better than that of non-doped material [4]. In this study, the $xLi_2MnO_3 \bullet (1\text{-}x)LiMO_2$ cathode materials were prepared by a co-magnesium-doping. It was found that the co-doping can further improve the structural stability and the electrochemical properties of $xLi_2MnO_3 \cdot (1\text{-}x)LiMO_2$. The influence of co-doping on the electrochemical properties of $xLi_2MnO_3 \cdot (1\text{-}x)LiMO_2$ was investigated in detail.

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s3-006

# Binding Modes of $CO_2$ on Indium Metal and Native Indium Oxide and The Implications for Heterogeneous Electrochemical Reduction of $CO_2$

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$CO_2$ fixation into usable fuels has garnered much attention recently due to its potential to provide transportable energy that can be generated from renewable sources. Several avenues of $CO_2$ reduction have been explored, including molecular, homogeneous electrochemical, heterogeneous electrochemical and photelectrochemical reduction, among others. Of these, heterogeneous catalysis currently promises to be the most scalable technique due to high efficiency, low overpotentials and high current densities. Recent investigation has shown that the efficiency of heterogeneously reducing $CO_2$ at various transition metal and sp metal surfaces depends strongly on the oxidation state and morphology of the substrate. A metal that shows this oxide/morpholgy dependence is indium, however, there is neither consensus on the mechanistic role of the metal in formate production, nor insight into how the oxide influences the reduction pathway. In this study in-situ ATR-IR was employed to observe the indium substrate in order to determine binding modes and affinities of $CO_2$ at indium with indium oxides. Ex-situ ultra-high vacuum techniques (including XPS, TPD and HREELS) were also performed in order to gain insight into the interaction of $CO_2$ and $H_2O$ with indium and how oxidation of the substrate affects substrate-adsorbate relations. The results of the in-situ and ex-situ spectroscopic studies will be presented and discussed in the context of how electrochemical $CO_2$ reduction pathways to formate may be influenced by the metal oxide moieties present.

s3-007

# Novel Poly(propylene thiophenoimine)-co-Poly(ethylenedioxythiophene) Composites of Naphthalene Diimide for Applications in Organic Photovoltaic Cells.

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Solar energy is generated upon absorption of photons by a semiconducting material; electrons are then ejected and taken up by the electric field to produce charges. This energy is stored in a battery. In a solar panel the semi-conducting material is sandwiched between two electrodes, this component is what is known as a cell. These cells are connected together to form what is called the modules. These modules in turn, are connected together to form an array, which is referred to as a solar panel. One of the challenges for the development of solar energy is the cost of the materials since the most commercially used material (C-Si) is very expensive. In this study, generations 1-3 poly(propylene thiophenoimine)-co-poly(ethylenedioxythiophene), G2PPT-co-PEDOT, dendritic star polymers was synthesized and doped with naphthalene diimide. Bilayer, hybrid and bulk heterojunction techniques were used. These heterojunctions use the donor/acceptor concept, with a few tenths of electonvolt (eV) energy difference between the lowest unoccupied molecular level (LUMO) of the polymer and the LUMO of the acceptor which allows efficiently dissociated excitons into separated electrons and holes. Optical band gaps measurements were used to determine their potentials for light harvesting and exciton generation. The material was then deposited on substrates by spin-coating, spray-coating or thermal evaporation. The characterization of the polymeric semiconductors was done by TEM and EDX, X-ray diffraction, UV/Visible spectroscopy and Fluorescence spectroscopy.

Key Words: organic photovoltaic cells, polymeric semiconductors, electrochemical energy, solar panel, solar energy.

s3-008

# PGM based $SO_2$ electrocatalysts for electrolytic hydrogen production

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PtM (M = Ir or Ru) binary electrocatalysts supported on $TiO_2C$ were prepared by employing two synthesis routes, namely, photochemical and direct chemical reduction methods. The morphological properties of the as-prepared electrocatalysts were investigated by carrying out SEM, HRTEM and XRD analysis. The effects of the reaction intermediates and possible adsorbents such as sulphur and sulphoxygenated species originating from $SO_2$ and $H_2SO_4$ disproportionation reactions on the electrocatalytic activity were investigated by carrying out electrochemical characterization tests employing cyclic voltammetry, chronoamperometry, linear polarization techniques.

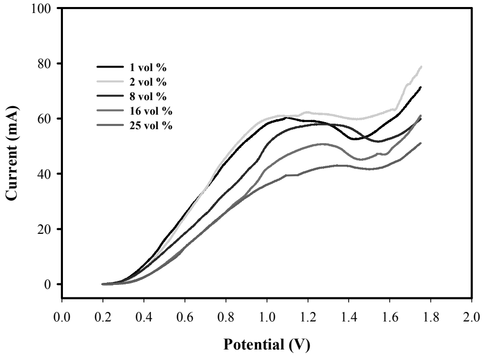

Figure 1: Effect of binder concentration studied in $SO_2$ saturated 4 M $H_2SO_4$ at 100 rpm

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s3-009

# Cross-linked polybenzimidazole / $Sn_{0.9}In_{0.1}P_2O_7$ composite membrane for high temperature PEMFCs

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High temperature proton exchange membrane fuel cells (HT-PEMFCs), which are able to operate at temperature above 100°C under non-humidified conditions, have been extensively studied for their commercialization.

Phosphoric acid (PA) doped polybenzimidazole (PBI) membrane is regarded as one of promising electrolyte membranes for HT-PEMFCs due to its thermal stability and high proton conductivity at around 150°C. Recently, new membrane which was not soluble in highly acidic solution was developed by cross-linking of polybenzoxazine into the PBI [1].

Also it has been reported that some inorganic proton conductors such as Tin pyrophosphate ($Sn_{0.9}In_{0.1}P_2O_7$) showed high proton conductivities above $10^{-2}$ $Scm^{-1}$ at the temperature range of 100~200°C under non-humidified conditions [2].

In this study, organic-inorganic composite membrane which is cross-linked PBI / $Sn_{0.9}In_{0.1}P_2O_7$ membrane showing higher proton conductivity and improved mechanical properties will be discussed.

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s3-010

# Synthesis of high capacity performing 1D-$SnO_2$ anode materials for Li-ion battery

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Tin oxide ($SnO_2$) is n-type semiconductor oxide with a wide band gap of 3.6 eV. SnO2 has been extensively researched for different applications such as optoelectronics, solar cells, gas sensors and lithium ion batteries. Since 1997, $SnO_2$ first identified as a potential candidate as anode material for lithium ion battery (LIB) [1]. $SnO_2$ has large theoretical capacity (782 mAh g-1), which is more than twice the theoretical capacity of currently used graphite (372 mAh g-1). However, the practical use of $SnO_2$ based anodes is challenged by their capacity fading due to the large volume change during repeated charge-discharge cycling process. Such volume variation causes cracking and result in electrical disconnection from the current collector, and eventually limit the cycling capability of electrodes. Hollow or porous nanostructured $SnO_2$ anode materials can solve this capacity fading problem by accommodating the large volume change within the local empty spaces thereby retain their high capacities.

The objective of this work is to synthesize a high capacity, good cycle performance, and good rate capacity anode materials for LIB applications. Accordingly, 1D-$SnO_2$ anode materials were synthesized using electrospinning methods. The morphology, structural and electrochemical properties of the synthesized anode materials were characterized by means of SEM, X-ray diffraction (XRD), TEM and charge/discharge cycle battery tester.

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s3-011

# Application of Heteropolyacids in Bifunctional Air Electrodes

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Heteropolyacids (HPAs) are a subgroup of a wider class of chemicals called polyoxometalates. HPAs exhibit high acidity, great solubility in polar solvents, great thermal stability and redox behaviour. The most important aspect of HPAs is their ability to be chemically adjusted by simple modification of their structure.

HPAs have so far only been investigated in acid media for their ability to enhance the kinetics of the oxygen reduction reaction (ORR) [1]. Data is presented which shows that HPAs can also be used to enhance both the oxygen evolution reaction (OER) and the oxygen reduction reaction in an alkaline environment.

Electrodes that contained only nickel (Ni) and nickel with HPA (Ni/HPA) as the catalyst were manufactured. The HPA chosen for preliminary investigations was molybdophosphoric acid ($H_3PMo_{12}O_{40}$). The catalyst was distributed within a supporting ink containing a Nafion® binder and was manually printed onto a Toray carbon paper based gas diffusion substrate [2].

Cyclic voltammetry and constant current cycling between OER and ORR were used to characterise the electrodes. The use of $H_3PMo_{12}O_{40}$ in combination with nano-powder nickel showed enhanced performance when compared to nano-nickel alone.

The overpotential associated with the OER, when HPA is mixed with nickel in the catalyst ink, is reduced when compared to the catalyst ink that includes only nickel. A slight reduction in overpotential for the ORR is also observed with the HPA containing electrodes. The voltage difference between OER and ORR for the Ni/HPA electrode is still relatively high for fuel cell and battery applications, however, it may be suitable for water electrolysers, since only oxygen evolution is required in these devices [3].

During the constant current experiments for OER and ORR, the Ni/HPA electrode shows stable performance over many hours.

Further investigation on the catalyst ink composition, i.e. component concentration, HPA choice, is ongoing to optimise the performance further.

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s3-012

# Evaluation of novel PBI based membranes for $H_2$ production through $SO_2$ electrolysis.

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The Hybrid Sulfur (HyS) thermochemical process has been identified as one of the possible alternative hydrogen production methods for the future. This sulfur based cyclic process uses a thermal decomposition step wherein concentrated $H_2SO_4$ is decomposed to $SO_2$, $O_2$ and water. After $O_2$ is separated as a by-product, the $SO_2$ and water is sent to a sulfur depolarized electrolyzer (SDE) to produce $H_2$ and $H_2SO_4$ of which the $H_2SO_4$ is sent back to the decomposition step. The Pt on C based catalyst deposited on a proton exchange membrane (PEM) within the electrolyzer chemically converts the $SO_2$ and water at the anode to protons, electrons and sulfuric acid. $H_2$ is produced by recombining the protons and electrons at the cathode. The theoretical potential needed for this reaction is 0.158V, which has a significant advantage over traditional water electrolysis having a theoretical potential of 1.23V.

PBI membranes are favored above commercial Nafion® due to their higher operating temperatures and their ability to transport proton without being hydrated (as is needed for Nafion®. To increase the $SO_2$ electrolyser efficiency PBI based membranes were evaluated at higher operating temperatures (>80°C). A concern for the $SO_2$ electrolyser is $SO_2$ gas loss from the anode to the cathode due to transport. The $SO_2$ gas transport was measured by the Electrochemical Monitoring Technique to determine both the diffusion and solubility coefficient for each membrane.

The membranes were tested using a commercial 25cm$^2$ DMFC test cell from Fuel Cell Technologies®. The SO2 gas to the anode was kept at a higher stoichiometry than theoretically needed using a thermal mass flow controller (Brooks) and was humidified before entering the cell. The cell was operated under constant current mode using a power supply (Accutronics) while the voltages were recorded. A custom Labview® program was used to operate the system. The $SO_2$ diffusion and solubility measurements were performed on the same setup by reversing the anode and cathode and running the cell at constant 0.7V while measuring the current.

All membranes were characterized using polarization curves, AC Resistance and $SO_2$ cross over at various operating temperatures.

Initial results show that PBI membranes have comparable performance at 80°C to that of N117.

s3-013

# Synthesis of High Energy Density Spinel $LiMn_2O_4$ Cathode for Lithium Ion Battery

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Pristine $LiMn_2O_4$ and cation substituted lithium manganese oxide $LiM_xMn_{2-x}O_4$ (M=Ni and/ or Al) spinel cathode materials were synthesized by an aqueous reduction method for use in lithium ion batteries [1]. Structural and electrochemical properties of synthesized Ni and Al doped lithium manganese oxide ($LiM_xMn_{2-x}O_4$) spinel cathode material were characterized using scanning electron microscopy, X-ray diffraction and charge/discharge testing. The objective of this work is to examine the effect of nickel and/or aluminium doping on the voltage and discharge capacity retention of $LiMn_2O_4$ with different concentration (x= 0, 0.05, 0.1, 0.2, and 0.3) of substitution cations. The effect of Ni/Al substitution on the cyclability of the $LiMn_2O_4$ will be reported [2].

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s3-014

# Synthesis of Quaternary Ammonium Polysulfone-based $TiO_2$ Nanocomposite Anion-Exchange Membrane

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A considerable amount of work has been dedicated to understanding and improvement, through chemical modification of polysulfone as an anion-exchange membrane for alkaline fuel cells [1]. High performance quaternary ammonium polysulfone-based $TiO_2$ nanocomposite membranes were synthesized through three steps: (1) chloromethylation, (2) quaternization and (3) alkylation. Characterization by $H^1$-NMR and FT-IR was done on the chloromethylated polysulfone. Optimization of the synthesis to obtain high performance was done through comparison studies of chloromethylating agents, temperature and time of chloromethylation reaction and quaternization reaction nucleophiles. Membranes were tested for ion-exchange capacity, water uptake, thermal stability and ionic conductivity.

Keywords: Alkaline fuel cells; polysulfone; quaternary ammonium; nanocomposite membrane; ionic conductivity

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s3-015

# The Impact of Multi-walled Carbon Nanotubes on the Electrochemical and Electrocatalytic Properties of Iron(II)tetrakis(diaquaplatinum) octacarboxyphthalocyanine

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Metallophthalocyanine (MPc) complexes represents a class of $N_4$-macrocyclic metal compounds with unique physico-chemical properties and a wide range of technological applications such as sensors, photocatalysts, electrocatalysts, [1] and supercapacitors [2]. Reports have shown that MPc complexes integrated or supported on carbon nanotubes greatly enhance the electrocatalytic performance of the electrode [3]. One of the means of tuning the electrocatalytic properties of transition MPc complexes is by introducing substituents at the peripheral positions of the phthalocyanine rings. Thus, this work describes for the first time, the impact of co-ordinating platinum to the peripheral position of an iron(II)octacarboxyphthalocyanine (FeOCPc) forming an iron(II)tetrakis(diaquaplatinum)octacarboxyphthalocyanine (abbreviated as PtFeOCPc, Fig.1). We show that the modification of the PtFeOCPc with MWCNTs leads to an enhanced electron transfer behaviour and electrocatalytic performance for oxygen reduction reaction (ORR) and formic acid oxidation, making it a potential candidate as a catalyst in energy conversion devices.

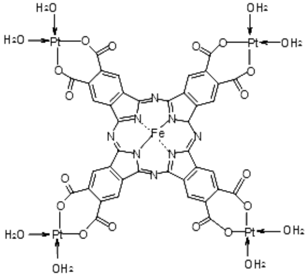

Fig. 1: Structure of PtFeOCPc

s3-016

# Developing Current Switching Method to Evaluate Electrochemical Characteristics of a PEM Electrolyser

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Hydrogen can be used as an energy carrier in renewable energy systems, fuel cell vehicles and other various applications. A promising technology is generating hydrogen through proton exchange membrane (PEM) water electrolysers. A PEM electrolyser consists of various components like the PEM, catalyst layer, diffusion media and flow fields. Their interfaces require advanced diagnostic tools for a better fundamental understanding. Characterisation tools are required to indicate the relationship between the performance and functional properties of the PEM electrolyser components.

The current switching method, also known as the current interrupt method, is conventionally used for estimation of the ohmic losses of an electrochemical system. The current switching method was implemented on other electrochemical cells like batteries and fuel cells. In this instance, the current switching method is used to indicate the electrochemical characteristics of the PEM electrolyser through an equivalent electric circuit. The electrochemical characteristics include the activation losses, ohmic losses and the concentration losses.

The current switching method, consisting of the natural voltage response method and system identification, is used to develop the Randles-Warburg cell of the PEM electrolyser. A depiction of the Randles-Warburg cell is presented in Figure 1. The Randles-Warburg cell consists of the following components, the membrane resistance ($R_m$), the double layer capacitance ($C_{dbl}$), the charge transfer resistance ($R_{ct}$) and the Warburg impedance ($Z_w$). The membrane resistance relates to the ohmic losses, the charge transfer resistance relates to the activation losses and the Warburg impedance relates to the concentration losses.

A simulation model and a practical implementation of the current switching method will be discussed.

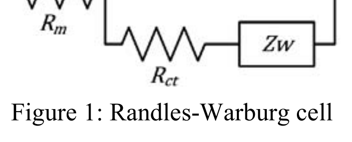

Figure 1: Randles-Warburg cell

s3-017

# Development of Platino-Iridium/Ruthenium Telluride Nanoalloy Electrode Systems for High Performance Ammonia Fuel Cell

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Hydrogen is the main fuel source for power generation with fuel cell, but its storage and transportation are still major issues. To overcome these problems, hydrogen has been stored and transported via chemical compounds such as alcohol, hydrocarbons, ammonia, etc. in many ways ammonia is an excellent hydrogen carrier [1,2]. Since ammonia is easy to handle and to transport as liquid or as concentrated aqueous solution. Its equilibrium potential is low and the theoretical charge for oxidation to $N_2$ is 4.75 $Ahg^{-1}$ that compared very well with the theoretical charge of methanol in its oxidation to $CO_2$ 5.02 $Ahg^{-1}$[3,4]. This study is of national importance and in line with the alternative energy strategy of the country. Since ammonia is in abundance and has very high hydrogen density compared to its competitors in the hydrogen economy, it will be useful to develop fuel cell technology based on ammonia as the source of hydrogen [5]. The main aim of the project is to develop telluride (Te) with alloys of platinum group metals which contain platinum, iridium and ruthenium. The platinum group nanoalloys with telluride were used as electrocatalysts in ammonium fuel cell. Techniques were developed for the synthesis of the platino-iridium (Pt-Ir) and platino-ruthenium (Pt-Ru) telluric nanoalloys. The properties of the platinum group telluric nanoalloys electrodes was interrogated electrochemically by voltammetry, electrochemical impedimetry, Hall effects, as well as by high resolution scanning, transmission and atomic force microscopy. Electroanalysis of nanoalloys was included the determination of charge transfer characteristics, redox potentials, Randel Sevcik distribution, standard current densities and conductivities. Impedimetric studies that included Nyquist modelling of cell responses in the presence and absence ammonia, to suitable equivalent circle; and also the determination of the Bode electronic profile and frequency modulation of the reactivities of the electrode systems.

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s3-018

# Improved Electrochemical Properties of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ by $LiCoPO_4$ Surface Treatment

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The lithium ion batteries mainly used LiCoO2 as cathode materials and are now well used as the rechargeable power source for applications ranging from consumer electronics to hybrid electric vehicles. Spinel $LiMn_2O_4$ is the first alternative cathode material to $LiCoO_2$ because of the low material cost, abundant material supply and better environmental compatibility compared to other cathode materials. However, it only delivers 100-120mAhg$^{-1}$ electrochemical capacity at sufficiently discharge rates. Thackeray et al. reported that the structurally integrated $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Mn, Ni, Co) can deliver a high discharge capacity more than 200mAhg$^{-1}$ as a promising cathode material with low-cost for lithium ion batteries[1-3].

The integrated $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ cathode materials suffer from three major disadvantages: high initial irreversible capacity, poor cycling stability and poor high rate capability. The development of this integrated cathode materials for lithium ion battery is still the challenge for meeting current and future energy storage requirements. Modifying the surface of the materials is an effective way to overcome those disadvantages according to many work have been reported. In this work, we report that the electrochemical performances could be significantly improved though our strategy of using surface treatments by coating $LiCoPO_4$.

Posters

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s3-019

# Ti-oxide Based Catalyst Supports for Low Temperature Fuel Cells

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The catalyst support activity concerning with a selection of stable materials characterized by suitable properties was carried out. The activity essentially regarded the development of non-carbonaceous supports alternative to benchmark carbon blacks, such as Ketjenblack, Vulcan, etc. The basic approach was to prepare and characterize ex-situ Ti-oxides and doped Ti oxides as well as other alternative supports with targeted properties relevant to fuel cell applications. In this regard, screening of non-carbonaceous support has essentially concerned the BET surface area and electrochemical stability characteristics. Moreover, the work was also focused on the study of chemical, structural, surface and morphology properties of the catalyst supports.

Acknowledgment
The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2011-2014) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement DURAMET n°278054.

s3-020

# Photoresponce of $Cu_2O$ loaded titania nanotube array in water splitting under visible light

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$TiO_2$ nanotube arrays (TNA) have broad potential applications such as photocatalysis, hydrogen generation and dye sensitized solar cells, due to their high surface area and 1D transport properties. However, titania's large band gap of 3.2 eV limits its absorption to the UV portion of the solar spectrum [1]. Here, we report the fabrication of highly smooth and ordered TNA by effective two-step anodization method. The synthesized TNA using this procedure showed a better surface smoothness and tube order as compared with the TNA prepared in one-step anodization process. In the next step, p-type cuprous oxide ($Cu_2O$) semiconductor was electrodeposited on the grown TNA. The effect of electrodeposition parameters on the photoelectrochemical (PEC) properties of $Cu_2O$/TNA system was studied systematically. The optimized values are -0.6 V, 500 mC, 0.3 M and 4.6 M for the applied deposition potential, deposition charges, $CuSO_4$ and lactic acid concentrations, respectively. The typical Cu(2p) XPS spectrum of the core level at 953.2 ($Cu(2p_{1/2})$) and 933.5 ($Cu(2p_{3/2})$) eV [2] for 500mC-$Cu_2O$/TNA demonstrates the existence of $Cu^+$, as shown in (Fig.1). PEC responses were measured by linear sweep voltammetry under 30 $mW/cm^2$ (Xe lamp) power density illumination in $Na_2SO_4$ electrolyte. Under visible light, the photocurrent density ($J_{ph}$) for water splitting reaction on the 500mC-$Cu_2O$/TNA system was obtained 0.3 $mA/cm^2$, which is about 30 times higher than of the pure TNA (Fig. 2). This is the highest value reported so far for this material under visible light.

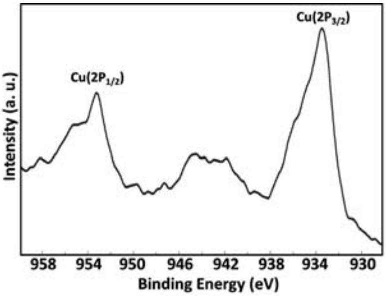

**Fig. 1.** XPS spectrum of the Cu (2p) for the 500mC-$Cu_2O$/TNA sample.

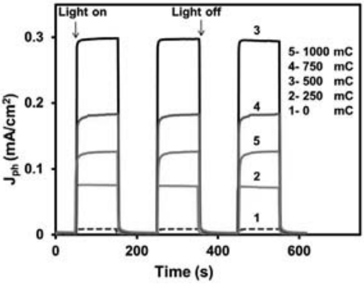

**Fig.2.** Photocurrent density of the $Cu_2O$/TNA samples at 0.5 V bias voltage.

s3-021

# Analysis of the synergistic effect of carbon black and iron phthalocyanine cathode modification in microbial fuel cells

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The oxygen reduction reaction (ORR) is a rate determining step at the cathode of microbial fuel cells. Studies have been performed to enhance this electron transfer process through the use of iron phthalocyanines on carbon based supports such as multiwalled carbon nanotubes (MWCNT)[1].

Here we examine the application of carbon black as a cost effective support for FePc at a glassy carbon electrode (GCE) and further examine the application thereof in a microbial fuel cell (MFC). FePc:carbon black modified GCE showed increased electrocatalytic characteristics for ORR relative to FePc modified GCE, with results comparable to that obtained in previous studies with MWCNT. Cathode modifications utilizing FePc:carbon black composites showed similar comparable enhancement in power densities at an *Enterobacter cloacae* MFC. Power density outputs were observed in the order agitated (anode+cathode modified) > quiescent (anode +cathode modified) > cathode modified > bare carbon paper MFC. Studies presented examine the use of beer brewery wastewaters as a feedstock for this MFC setup.

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s3-022

# Use of microbial fuel cells in the beneficiation of treated algal biomass for bioelectricity production

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The use of algae as feedstock in microbial fuel cells (MFCs) has been limited, despite being both abundant and relatively easy to mass culture. Spray-dried pure algae strains (nutraceutical grade) were compared to dessicated consortia of algae samples from a local wastewater treatment facility as feedstocks for MFCs utilising *Enterobacter cloacae* as the anodic biocatalyst. For both pure and consortia algal feedstocks, the effect of different algal pretreatment methods for enhancing nutrient bioavailability, and hence power density, were examined using a two-chambered H-type MFC setup. These studies showed that through careful pre-treatment, naturally derived algal consortia could yield over 30% greater power densities compared to select pure strains purchased. Furthermore, optimal power densities achieved were approximately 67% of that obtained utilising costly commercial nutrient media sources for *E. cloacae*.

In addition, the long-term performance of algal strains as a feedstock for MFC configurations was examined. Here anodes and cathodes, modified with multi-walled carbon nanotubes (MWCNT) and (MWCNT)/iron (II) phthalocyanine hybrid configurations, respectively, were examined and found to provide synergistic increases in the power density of MFCs, compared to their unmodified counterparts [1].

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s3-023

# Electrochemical Capacitors Based on Ultra-large Graphene Oxide and Graphene Sheets Integrated with Metallotetrapyrazinoporphyrazine

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Supercapacitors, known as electrochemical capacitors are excellent electrical energy storage devices; because of their attractive characteristics: including high energy and power density, durable longer cycle life as compared to secondary batteries [1]. Since their use for the storage of electrical charge in 1957, more research has focused on the improvement of their properties for applications in renewable energy power sources, such as fuel cells, dye solar cells and batteries [2].

The use of metallotetrapyrazinoporphyrazines (MTPyZ) as electrode materials for supercapacitors is less reported in literature to date. In addition, graphene oxide is rarely considered a suitable supercapacitor material. In this work however, MTPyZ (where M = Ni, Co) were integrated with ultra-large graphene oxide (ULGO) or graphene (ULG) and studied for supercapacitor applications. The electro-capacitive properties (i.e., specific capacitance, energy, power and cyclability) of the MTPyZ-ULGO and MTPyZ/ULG nanocomposites were investigated through cyclic and galvanostatic charge-discharge voltammetries, plus electrochemical impedance spectroscopy. ULGO was synthesized using the modified Hummer's method, and characterized using UV-Vis, with the SEM, and Raman spectroscopy presented in Figure 1 below.

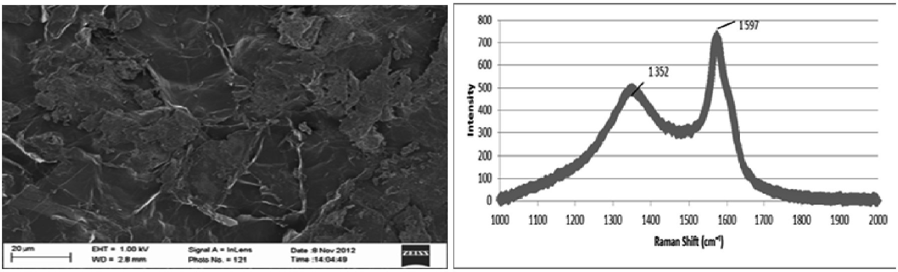

Fig 1: HRSEM and Raman of ULGO used in this work.

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s3-024

# Synthesis of nanostructured $Li_4Ti_5O_{12}$ materials using $TiO_2$ nanoparticles

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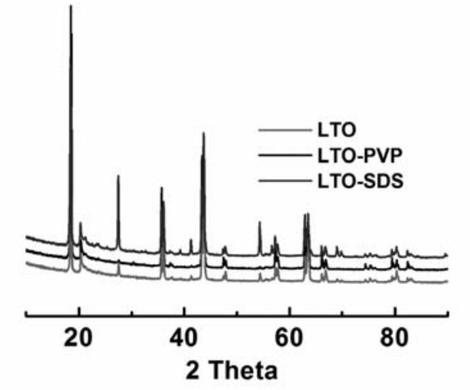
The spinel $Li_4Ti_5O_{12}$ materials is recognized to be a promising anode material for lithium ion battery, as they offer excellent reversibility, structural stability and have lithium ion mobility in the charge-discharge process as well as a higher lithium intercalation-deintercalation potential. Beyond advantages of $Li_4Ti_5O_{12}$ over commercial graphite anode, its low electronic conductivity is the most important technical barriers to commercialization, which seriously limits its high rate capability. Recently, nanostructured $Li_4Ti_5O_{12}$ has attracted a lot of attention because its large surface area which increases the electrolyte/electrode contact area, and leads to a decrease of the current density per unit surface area and an increase in the charge/discharge rate. Furthermore, the nanostructure provides a shorter path for lithium ion and electron transport and results in improved kinetic performance. In this work, our aim is to synthesize nanostructured $Li_4Ti_5O_{12}$ using $TiO_2$ nanoparticles as precursor and to maintain nanostructure of $TiO_2$ by using stabiliser during the thermal treatment. On the other hand, perhaps carbon source will be introduced into the process of synthesis through modifying method. The XRD patterns in below Figure display that the $Li_4Ti_5O_{12}$ structure was synthesized using different stabilizers.



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s3-025

# Development of High Performance $LiNi_{0.5}Mn_{1.5}O_4$ Spinel

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The need for high performance lithium ion batteries has increased over the years due to fast growing technologies of electronic portable devices. The recent research on the electric grid energy storage, plug-in hybrid and electric vehicles has increased research in improved battery technologies [1]. However, developing suitable cathode materials for lithium ion batteries is still a challenge [2].

In cathode materials for lithium ion batteries, fluorine doping is often added to replace oxygen and enhance the electrochemical properties of these materials [3]. It is assumed that $O^{2-}$ and $F^{-}$ ions are located at the 32e sites [3]. Literature reports indicate that doping method is important as different defects sites are introduced [4].

In this study, fluorinedoped $LiNi_{0.5}Mn_{1.5}O_4$ spinel are synthesized by a novel method. The obtained powders are characterized by PXRD, SEM, TEM, XPS, and AFM. The electrochemical properties (such as capacity, capacity retention, rate capability) of the materials are investigated and will be discussed.

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s3-026

# Dye-sensitized solar cells using natural dyes extracted from *Jathropha curcas* and *Citrus aurantium* Leaves

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This work examined the possibility of replacing the conventional ruthenium dye sensitizers in Gratzel/Dye-sensitized solar cells (DSSCs) with green/natural dyes extracted from jathropha curcas and citrus aurantium leaves. $TiO_2$ films were prepared with P-25 Degussa $TiO_2$ powder on FTO glass using three different methods: sol-gel process, chemical bath deposition and the slot coating. The chemical, structural, morphology and optical properties of the $TiO_2$ were determined using Energy Dispersive X-ray Spectroscopy, X-ray diffraction, UV-Visible-Infrared Spectroscopy and Scanning Electron Microscopy. Gratzel cells were assembled using both the natural and synthetic ruthenium and their properties compared. Results obtained show that the scanning electron micrograph of CBD showed that the coating is porous, homogenous and closely packed with no gaps between the coatings and that of sol–gel deposited $TiO_2$ showed soft and small agglomerates with irregular structure while the image of the slot coated $TiO_2$ shows a smooth coating with a nano-flower-like structure. The slot coated $TiO_2$ with jathropha leaf dye extract showed the highest overall efficiency of 1.26% with open circuit voltage of 350mv, short circuit current of 65.5 μA and a fill factor of 0.55.

Keywords: Jathropha curcas, Citrus aurantium, $TiO_2$, solar cell efficiency, nano-flower-like structure

s3-027

# New ceramic separators for Li-ion batteries

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Lithium-ion batteries are a fast-growing technology being widely used in portable electronic devices. Due to their relatively high specific energy and specific power they are becoming more and more attractive also for use in electric vehicles and hybrid electric vehicles.[1]. One of the most important issues regarding the use of batteries is safety, especially in vehicles. Separators are playing a decisive role regarding the safety of a battery. They are separating the electrodes from each other electronically and should be able to shut down at higher temperatures in order to avoid a thermal runaway of the battery. The basic properties of a separator include electrolyte absorption and retention, low ionic resistance (sufficient ionic conductivity), chemical stability to electrolyte and electrodes and stability during the electrochemical reactions occurring during the charge and discharge processes. Furthermore, a separator should be as thin and thus light as possible in order not to decrease the specific energy of the battery. Finally, from the economical point of view a separator is supposed to be low-cost.

In this study we present new ceramic separators provided by Sihl GmbH. We report about the characterization of these separators in terms of electrical resistance (MacMullin number)[1], air permeability (Gurley number)[2][3], porosity and pore size distribution (SEM, porometry) and thermal properties (DSC, TGA). Moreover, our study covers the electrochemical stability by conducting cyclovoltammetry in half cell setups by using cathode materials such as $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as working electrodes and 1M $LiPF_6$ in EC/DEC(3/7 wt) as electrolyte. Again, in similar cell configurations the C-rate tests were carried out from C/5 to 5C. For those separators proven to be electrochemically stable the cycling performance was also investigated in full cell setups at C/5 for 70 cycles using LCO and graphite electrodes. Finally, the achieved results were compared to results obtained with a tri-layer polyolefin separator.

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s3-028

# Reduction Mechanisms of Hierarchical Mesoporous Thin Films Anode (NiO-GDC) Fabricated by Sol-Gel Process – Application to Micro-SOFC

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Derived ceria-based materials electrodes nanoarchitectures were synthesized through the sol-gel approach and a one-step thermal treatment. The 3-D network is constituted of non-agglomerates nanoparticles (2 to 4 nm at 600°C) of NiO and Gd-doped ceria in anode. In this arrangement, particles in the nanoscale are kept because of the presence of secondary phases, both NiO and pores. The effect of the microstructure on their electrical conductivities in the range of 400-600°C is low, due to their stability. As the particle size is controlled, these mesostructured films can be used as model to study the impact of the size of the particle on the transport of both ions and electrons. After reduction, the Ni/GDC cermet microstructures evolved with time for temperature higher than 400°C.

The goal of the present work was to study the reduction mechanisms of the NiO-GDC initial composite into the Ni-GDC cermet anode. Impedance spectroscopy was performed as a function of the Ni/GDC ratio, the temperature and time in a single reducing atmosphere set-up. It has been demonstrated that a minimum of 4 single steps composed the resulting reduction of the anode materials, and the corresponding kinetics parameters were determined from this original study dealing with NiO-GDC thin layers (200 nm) as a promising anode for micro-Solid Oxide Fuel Cell.

s3-029

# Soft Carbon as anode material for Lithium-Ion Capacitor

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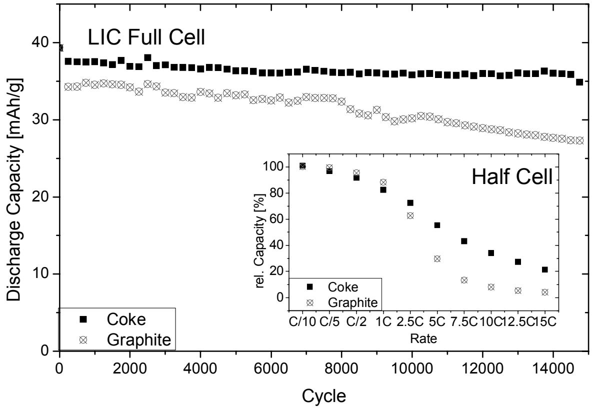
Lithium-Ion capacitors (LICs) are devices containing both a Lithium-Ion battery (LIB) and a Supercapacitor (SC) electrode. Thanks to this combination, LICs can display energy and power values in between those of LIBs and SCs, as well as a high cycling stability [1]. Considering the variety of active material used in LIBs and SCs many combinations are possible for the realization of LICs.

Graphite is currently the most used anodic material in LIBs. Although it displays a high theoretical capacity and good cycling stability, the capacity retention using high charging currents is rather low [2].

Taking this point into account, the use of a material which is able to guarantee the same cell voltage of graphite, but has an improved behavior at high current density could be beneficial for the realization of a high performance LIC. Among the materials available as replacement of graphite, amorphous carbon appears one of the most interesting. As a matter of fact, amorphous carbons guarantee the same operative voltage of graphite and though they have a higher initial irreversible capacity loss with respect to graphite, they have the advantage to outperform graphite at higher rates.



In the present work, we considered the use of a soft carbon, petroleum coke (PeC), as anode in a LIC containing an activated carbon as cathode.

When a correct pre-lithiation process is applied, LICs based on PeC outperforms a LIC using graphite as anodic material in terms of capacity and cycling stability (see figure). Over 50,000 cycles were reached with currents between 0.7 and 9.9 A/g (based on both electrode masses). Also in terms of energy and power density our devices show in the same current range superior properties compared to LIBs and SCs.

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s3-030

# Synthesis of $Li_2MnSiO_4$/C Nanocomposites for Lithium Battery Cathode Employing Sucrose as Carbon Source

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$Li_2MnSiO_4$/C nanocomposites were successfully synthesized by a novel synthesis route, i.e., a combination of spray pyrolysis and ball milling followed by annealing, employing sucrose as carbon sources. X-ray diffraction analysis indicated that the $Li_2MnSiO_4$/C nanocomposites were indexed to orthorhombic structure in $Pmn2_1$ space group. Field-emission scanning electron microscopy and transmission electron microscopy verified that the $Li_2MnSiO_4$/C nanocomposites were agglomerates of the primary particles that were less than 100 nm and carbon was distributed on the surface of the agglomerates (Fig .1a). The $Li_2MnSiO_4$/C nanocomposites were used as cathode active materials for rechargeable lithium batteries, and electrochemical measurements were carried out for Li|1 M $LiPF_6$ in EC: DMC = 1:1| $Li_2MnSiO_4$/C cells at 60 °C. $Li_2MnSiO_4$/C nanocomposite cell delivered a first-discharge capacity of 225 mAh $g^{-1}$ at 0.05 C (Fig. 1b).

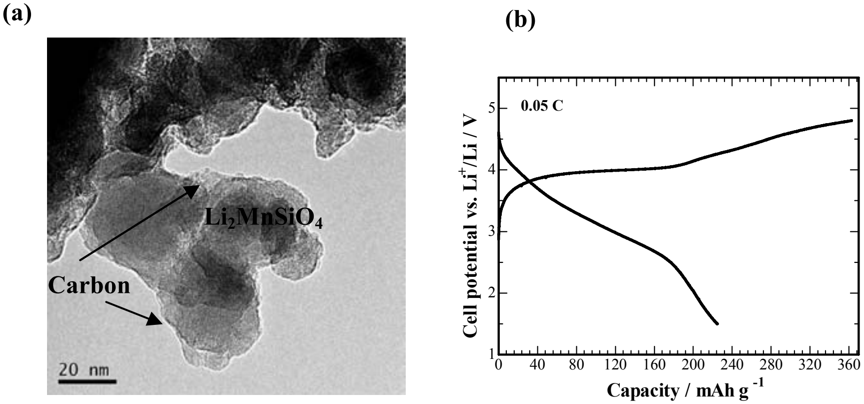

Figure 1 (a) TEM images of $Li_2MnSiO_4$/C nanocomposites. (b) First charge-discharge curves of $Li_2MnSiO_4$/C nanocomposite cell at 0.05 C and 60 °C.

s3-031

# Reaction Selectivity of Methanol and Oxygen at Pt/C Electrocatalysts Studied by Porous Microelectrode

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A direct methanol fuel cell is an electrochemical device that converts chemical energy to electric energy by feeding methanol and oxygen. The fuel cell shows a low performance in the presence of methanol and oxygen because of the methanol crossover and oxygen cross leak. In order to solve the problem, the methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) selectivity of seven types of Pt/C electrocatalysts were investigated in the coexistence of methanol and oxygen. Three Pt/C electrocatalysts exhibited MOR selectivity and the other three exhibited ORR selectivity.

The seven types of Pt/C (a~g) electrocatalysts were provided by Tanaka Kikinzoku Kogyo K. K. A porous microelectrode was used as working electrode after packing the Pt/C powder electrocatalysts. Pt coil and $Ag/Ag_2SO_4$ were used as counter and reference electrodes, respectively. Electrochemical measurements were performed using a classical tree-electrode cell equipped with these electrodes in Ar- and $O_2$-saturated 0.5 mol $dm^{-3}$ $H_2SO_4$ and 1 mol $dm^{-3}$ $CH_3OH$ + 0.5 mol $dm^{-3}$ $H_2SO_4$ solution. All the electrode potentials in this work are referenced to the reversible hydrogen electrode (RHE) potential.

The obtained voltammograms at Pt/C (d~f) showed a MOR selectivity in $O_2$-saturated 1 mol $dm^{-3}$ $CH_3OH$ + 0.5 mol $dm^{-3}$ $H_2SO_4$ solution. On the other hands, the voltammograms of Pt/C (a~c) showed an ORR selectivity in the same solution. Pt/C (d~f) had a typical Pt background cyclic voltammogram shape which exhibit H-adsorption and desorption peaks. These catalysts possess not ORR activity but MOR activity. As a characterization, XPS measurement was carried out to evaluate the Pt biding energy. In Fig. 1, we found the relationship between the current density and the biding energy shift of Pt. Regarding MOR currents, these currents decrease with increasing the Pt biding energy. And ORR currents also decrease with increasing the Pt energy.

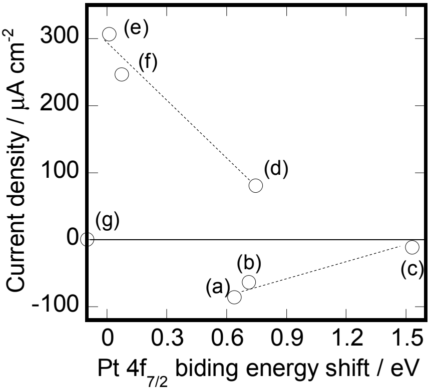

Figure 1 Relationship between the observed current density in $O_2$-saturated 1 mol $dm^{-3}$ $CH_3OH$ + 0.5 mol $dm^{-3}$ $H_2SO_4$ solution at 0.65 V vs. RHE and biding energy shift of seven Pt/C electrocatalysts.

s3-032

# Cobalt Hydroxide Nanowires Electrodeposited in Anodized Aluminum Oxide Templates for Supercapacitor Applications in Energy Storage Nanosystems

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Electrochemical supercapacitors based on pseudocapacitance are referred to as the ones possessing higher specific capacitance values comparing to double layer supercapacitors. Among them, metal oxides exhibit the highest specific capacitance with superior value of 2100 $Fg^{-1}$ shown by Lokhande et al. for cobalt oxides [1,2]. On demands of nano-structured electrochemical energy storage devices for autonomous micro- and nanosystems, cobalt hydroxide/oxide nanowires can be possible candidates for supercapacitors applications. Template electrodeposition, e. g., utilizing ordered anodized aluminum oxide (AAO) is of a better choice as a cost-effective way of manufacturing one dimentional (high aspect ratio) nanowires. Though, the system can be realized in near-neutral electrolytes only. Recently, we showed that the capacitance performance of cobalt hydroxide/oxide in near-neutral electrolytes is competitive with the one in conventional alkaline solutions comparing stored amount of charge, energy density, cyclic stability and showing broader potential window. Neutral solutions will not disturb 1D geometry of AAO templates with electrodeposited $Co(OH)_2$ nanowires.

In the current work, we electrodeposited cobalt hydroxide in AAO templates. By means of cyclic voltammetry, galvanostatic charging/discharging experiments capacitive properties of an array of cobalt hydroxide nanowires were investigated. Integral capacitance of 91.7±5.1 $Fg^{-1}$ was achieved for arrays of cobalt hydroxide/oxide nanowires in AAO template in neutral electrolytes for a discharging process. We measured a specific charge of 235.7±13.1 $Cg^{-1}$ distributed over a range of 2.57 V. It is comparable to 260±2 $Cg^{-1}$ for potential range -0.1 ÷ 1.3 V vs. $Ag/AgCl_{sat.}$ for bulk porous $Co(OH)_2$ deposited on flat Au surface. A high specific energy value of 302.8±7 $Jg^{-1}$ (84.1±4.7 $Whkg^{-1}$) was observed for cobalt hydroxide/oxide nanowires in AAO template. Cycling over 1000 cycles shows only 6.5 % loss in capacitance calculated from discharge semicycle (in the region from 25th to 1000th cycle).

1 D cobalt oxide/hydroxide nanowires deposited in AAO template are interesting for further studies and applications.

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s3-033

# Development of a High Pressure Solid Polymer Electrolyte (SPE) Electrolyser for the Production of Hydrogen

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As the world's fossil fuel reserves are fast becoming depleted, it is vital that alternative and cleaner fuels are found. Renewable energy sources offer a sustainable solution to the energy requirements, but due to their intermittency, most applications of renewable energy require energy storage. Traditional energy storage devices like lead-acid batteries have several disadvantages. Alternatively, hydrogen can be used as an energy carrier. An SPE electrolyser generates high purity hydrogen and oxygen, which can be stored and supplied to a fuel cell when needed to generate electrical power.

In order to store hydrogen efficiently in a container with a relatively low volume, it is necessary to compress the hydrogen. For small systems, the capital cost of adding a compressor to the system is high and it would therefore be advantageous if the hydrogen could be generated directly at high pressure. The primary aim of this project is to develop a practical, efficient, cost-effective SPE electrolyser system that produces and stores hydrogen directly under high-pressure (100bar) at a current density of $1A/cm^2$ at 1.7V.

Tests completed on a 100cm2 experimental cell have shown that these conditions can be met successfully at atmospheric conditions. However, problems arose during the pressurization of the cell, with a sudden drop in current density noticed.

New designs of the cell have been incorporated to counter the drop in current with increasing pressure. These include:

- Increased hydrogen endplate thickness
- Thinner pusher plate
- Springs and screw adjustable pusher plate

Factors affecting the final design of the electrolyser cell and the completed system are discussed in the paper as well as the effect of the operating conditions on the performance of the cell.

s3-034

# Electrochemical Characteristics of Titanium-Manganese-Ruthenium Oxide Composite Electrodes for Electrochemical Capacitors

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The demand for energy has been a primary focus in the scientific community. There have been greater interests in developing and refining more efficient energy storage devices to meet the ever-increasing demand for high power density devices. Since electrochemical capacitors (also known as supercapacitors) are characterized by fast discharge rates and low maintenance, the demand for them is predicted to be most extensive in frequency regulation applications [1]. Therefore immense attention has been geared towards finding inexpensive and effective electrode materials with improved performances.

This study explores the electrochemical behaviour of the synergistic incorporation of manganese and ruthenium oxide for improving the electrochemical capacitive properties of titanium oxide electrodes. Titanium oxide powder was mixed with manganese oxide and ruthenium oxide powders using a turbula mixer at varying compositions. Consolidation of the admixed powders was done using spark plasma sintering (SPS) at 1200°C, with a holding time of 5min, at a heating rate of 50°C/min and a pressure of 25MPa. SEM and EDX analysis of the polished sections were used to reveal morphologies of the consolidated composites. XRD analysis was carried out to identify different phases formed during sintering. Electrochemical characteristics of the composites (i.e., specific capacitance, energy density, power density, and cyclability) were examined by galvanostatic charge-discharge voltammetry, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods.

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s3-035

# Unique performance of SnO/Sn/ $Cu_6Sn_5$ three–layer anode for Li ion battery

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The evaluation and comparison of morphology and microstructure of Sn based anode materials are important for understanding the performances and behaviors of the anodes for Li-ion batteries. In present work, dense Sn film was pulse electrodeposited on Cu substrate and used as the control experiment. The $SnO/Sn/Cu_6Sn_5$ three-layer film was prepared by heating the electrodeposited Sn film at 200°C in atmosphere for 48 h. The microstructure and morphology of Sn film and the three-layer film were characterized by X-ray diffraction and SEM. These two films were then assembled in Li ion coin cells as anodes respectively and the electrochemical performances of these cells were studied by charge and discharge, cyclic voltammetry and the Ac impedance. Compared with the Sn-anode, $SnO/Sn/Cu_6Sn_5$ three-layer anode shows much smaller SEI film resistance and charge transfer resistance. The capacities of SnO, Sn and $Cu_6Sn_5$ phases were analyzed from the charge and discharge curve and $Cu_6Sn_5$ shows the highest capacity and capacity retention among the three phases in this three layer anode.

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s3-036

# Promotion of Pd/C catalyst for ethanol electro-oxidation by $TiO_2$ nanopartilces in alkaline media

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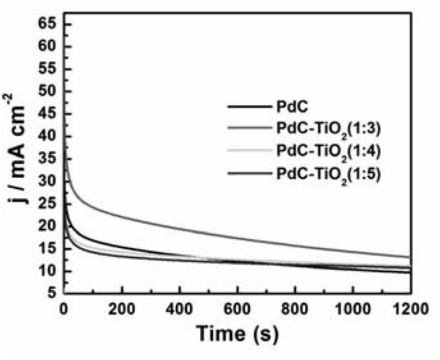
Although cost is clearly the most important barrier to widespread fuel cells implementation, perhaps the most important technical barriers currently being addressed relate to the electrodes. One of the challenges is to improve the durability and stability of catalysts electrodes. Carbon supported platinum or platinum alloy is commonly used as anode and cathode electrocatalyst in low temperature fuel cells fuelled with hydrogen or low molecular weight alcohols. Electrochemical oxidation of carbon support from carbon to carbon dioxide result in micro-structural degradation and surface chemical changes, which cause a loss of catalyst activity. The stability of carbon support affects the loss of platinum surface area following both platinum particle sintering and platinum release from the carbon support that is probably because the presence of surface oxides may weaken the platinum–support interaction, leading to a lower resistance to surface migration of Pt particles. These effects even a rapid degradation of the Pt catalyst and thus shorten the lifetime of the fuel cells. Therefore, some metal oxides such as $SnO_2$, $TiO_2$ and $CeO_2$ etc have been tried to boost durability and stability of Pt catalysts. In this work, we try to promote electrochemical activity and stability of Pd/C catalyst for ethanol oxidation by $TiO_2$ nanoparticles in alkaline media. Chronoamperograms for Pd/C-$TiO_2$ with different ratios were displayed in below figure. Pd/C with $TiO_2$ catalysts shows higher stability than that of Pd/C catalyst.



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# Index