

NEWSLETTER
Electrochem 2012:
Electrochemical Horizons
Special Issue
September 2-4, 2012
Trinity College Dublin, Ireland



Serving Electrochemical Science, Technology and Engineering
within the catchment of
The Royal Society of Chemistry
and
The Society of Chemical Industry

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Chemical Sciences



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Editorial

A big **THANK YOU** to Jay Wadhawan for keeping the Electrochemistry Newsletter alive and well over many years and indeed for starting the current pdf version. Jay, I will do my best to maintain standards, but it will be quite difficult to follow in your footsteps!

This is the second special edition of *The Electrochemistry Newsletter* featuring the programme and abstracts for the **Electrochem'2012** meeting, which was held at Trinity College Dublin September 2-4, 2012. The meeting was organised by Professor Mike Lyons and Jacqui Colgate (Society of Chemical Industry, UK) and has been a big success. **Many thanks also to the local organising committee with Professor Edmond Magner (University of Limerick), Professor Robert Forster (Dublin City University), and Professor Robert Dryfe (University of Manchester).** This newsletter special edition is meant to **celebrate** the success, and to provide visible documentation of the meeting. **With a wide range of national and international contributions this meeting has been exceptional in terms of quality and breadth of topics.** Particular highlights included plenaries by Professor Wolfgang Schuhmann (Bochum), Professor Zhong-Qun Tian (Xiamen), Dr Donal Leech (Galway), Professor Fraser Armstrong (Oxford), and Professor Richard Compton (Oxford).



The Faraday medal of the RSC Electrochemistry group was awarded to **Professor Zhong-Qun Tian** for outstanding contributions to the field of electrochemistry and internationally recognised contribution to the characterisation of electrode surfaces.



The Barker medal of the RSC Electrochemistry group was awarded to **Professor Fraser Armstrong** as outstanding UK electrochemist who contributed to the field of bioelectrochemistry with important experimental or theoretical achievements that are internationally recognised.

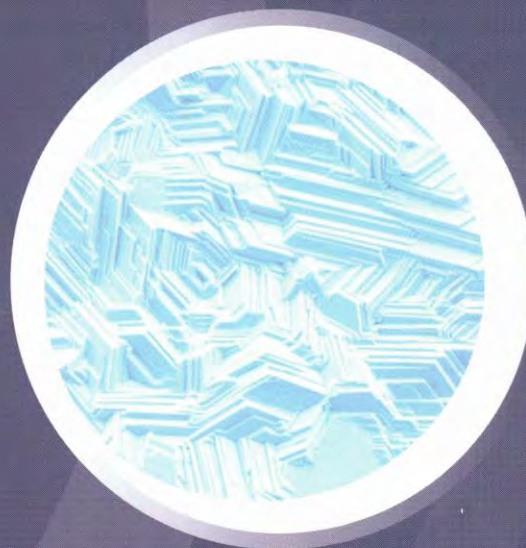
Symposia at this meeting included the “L.D. Burke Energy symposium”, the “Electrochemical Techniques and Sensors symposium”, the “Nanotechnology symposium”, the “Bioelectrochemistry symposium”, and the “Fundamental symposium”. All of this as well as poster sessions and contributions from exhibitors happened in the settings of the Hamilton building and the cricket pavillion of Trinity College Dublin.

Frank Marken
Editor-in-Chief

Electrochem 2012: Electrochemical Horizons

Sunday 2 - Tuesday 4 September 2012
Trinity College Dublin, Ireland

- Sponsor and Exhibition Details
- Programme
- Speaker Abstracts
- Poster Abstracts
- Delegate List



Organised by SCI's Electrochemical Technology Group, RSC's
Electrochemistry Interest Group & RSC's Electroanalytical Group

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Electrochem 2012

Welcome

Céad míle fáilte romhat. Welcome to Trinity College Dublin, Ireland and the 17th annual International Electrochemistry Conference, Electrochem 2012. Electrochem is hosted by SCI's Electrochemical Technology group and the Electrochemistry Interest and Electroanalytical Groups of the RSC. The Local Organising Committee are honoured to be hosting this great annual event in Dublin again.

We look forward to an exciting scientific programme with over 60 lectures and 80 posters on the conference themes of **LD Burke Energy, Electrochemical Techniques and Sensors, Nanoelectrochemistry, Bio-electrochemistry and Fundamental Electrochemistry.**

We meet up initially on Sunday 2 September at 18.00 in the Pavillion Bar for a mixer after registration. This is the College sports bar and is located immediately opposite the old chemistry building in the East end of College, and fronts onto the cricket pitch. Buffet food and refreshments will be served.

On Monday 3 September, the plenary talks will be a presentation by Prof Wolfgang Schuhmann on Localised investigation of modified electrodes using high-resolution scanning electrochemical microscopy, Prof Zhong-Qun Tian, recipient of the Faraday medal 2012 award lecture (RSC Electrochemistry group award) with his talk on Toward nanoelectrochemistry: gold nanoparticles with ultrathin shells for characterising electrochemical interfaces and electrocatalysis and Dr Dónal Leech will present on Bioelectrocatalysis using enzyme or microbe films on electrodes.

Tuesday 4 September will start with Prof Fraser Armstrong, recipient of the Barker award 2012 lecture (RSC Electrochemistry group award) presentation on What electrochemistry teaches us about enzymes and Prof Richard Compton will present his talk on, Simulation of voltammetry; some recent progress. There will also be keynote lectures for all themes.

All lectures, posters, catering and the exhibition will take place in the spacious Hamilton Building lecture theatres and foyer.

The organisers are grateful to our partners: SCI, RSC and sponsors: Science Foundation Ireland, International Society of Electrochemistry and The Electrochemical Society. To our exhibitors: Alvatek Ltd, Metrohm, Labquip, Gamry Instruments and EC Labs. Also to our supporters IJ Cambria, American Elements and the Journal of Electroanalytical Chemistry.

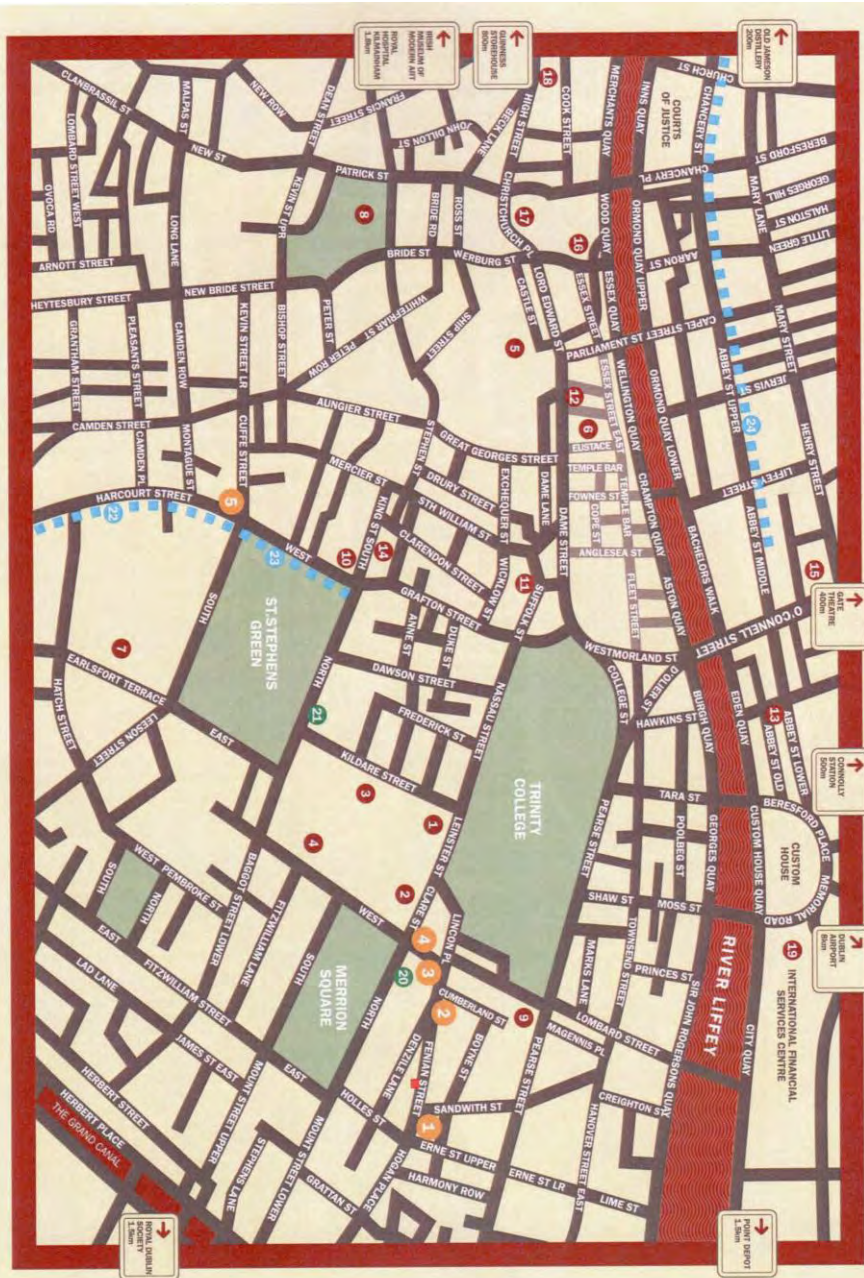
If you need any assistance, please do not hesitate to contact the registration desk.

Thank you for attending Electrochem 2012 and we hope you enjoy the conference, and indeed Dublin city.

Slán agus beannacht

Professor Mike Lyons
Trinity College Dublin, Ireland

Jacqui Colgate
Society of Chemical Industry, UK



DUBLIN CITY MAP

- 1 O'CALLAGHAN COURT
 - 2 THE ALEXANDER HOTEL
 - 3 THE DAVENPORT HOTEL
 - 4 THE MONT CLARE HOTEL
 - 5 STEPHEN'S GREEN HOTEL
 - 6 NATIONAL LIBRARY
 - 7 NATIONAL GALLERY
 - 8 NATIONAL MUSEUM
 - 9 GOVERNMENT BUILDINGS
 - 10 DUBLIN CASTLE
 - 11 TEMPLE BAR
 - 12 NATIONAL CONCERT HALL
 - 13 ST. PATRICK'S CATHEDRAL
 - 14 PEARSE STREET DART STATION
 - 15 STEPHEN'S GREEN SHOPPING CENTRE
 - 16 DUBLIN TOURISM - SUFFOLK STREET
 - 17 OLYMPIA THEATRE
 - 18 ABBEY THEATRE
 - 19 GAILEY THEATRE
 - 20 G.P.O.
 - 21 VIKING CENTRE
 - 22 CHRISTCHURCH CATHEDRAL
 - 23 DUBLINIA
 - 24 INTERNATIONAL FINANCIAL SERVICE CENTRE
 - 25 AIRCOACH
 - 26 AIRCOACH
 - 27 LUAS STOP
 - 28 LUAS STOP
 - 29 LUAS STOP
 - 30 LUAS STOP
- Car Park - Merion Square Hotels



ELECTROCHEM 2012: Sponsors

The organisers would like to thank the following companies for supporting Electrochem 2012:



Science Foundation Ireland (SFI) invests in academic researchers and research teams who are most likely to generate new knowledge, leading edge technologies and competitive enterprises in the fields of science and engineering underpinning three broad areas:

Biotechnology

Information and communications technology

Sustainable energy and energy-efficient technology.

SFI also advances co-operative efforts among education, government, and industry that support its fields of emphasis and promotes Ireland's ensuing achievements around the world.



The aim of the International Society of Electrochemistry is to serve the worldwide electrochemical community and that of related disciplines through the advancement of electrochemical science and technology, the dissemination of scientific and technological knowledge, and promotion of international cooperation.



ECS - Leading the world in electrochemistry and solid-state science and technology for 110 years.

The Electrochemical Society was founded in 1902 as an international nonprofit, educational organisation concerned with a broad range of phenomena relating to electrochemical and solid-state science and technology, today it has more than 9,000 members worldwide. ECS publishes Journal of The Electrochemical Society, the oldest peer-reviewed journal in electrochemistry, as well as other journals and books. ECS meetings are a forum for the latest scientific and technical developments in the field through a variety of formats, such as technical symposia, oral presentations, poster sessions, panel discussions, tutorial sessions, and special summits and workshops. www.electrochem.org

ELECTROCHEM 2012: Exhibitors

Stand 1



We are independent UK distributors of high performance research tools for Electrochemistry. We offer a wide range of potentiostats, impedance analyzers and fuel cell research equipment as well as complementary accessories such as cells and electrodes. Our customers conduct research into many applications including Coatings, Corrosion, Sensors, Battery, Fuel Cell and Supercapacitor technologies.

Our philosophy is simply to offer high performance, competitive products backed up by first class Customer Service and Support. We are very proud and pleased to support Electrochem2012. Please call round to the Alvatek stand to discuss any applications, see what's new or just say "Hello".

Steve Fryatt
Director
Mobile: 07768 396813



Stand 2



Dedicated to research, Metrohm Autolab supply a wide range of potentiostats/galvanostats, from entry level to high end instruments, to the electrochemical research community. Key features across the range include modular design, high performance, high voltage applications, multi-channel, compact design, there are unique possibilities allowing versatile custom built instrument for research.

Metrohm UK Ltd has been the official distributor of Metrohm Autolab products and support to the UK and Ireland since February 2011. Originally known as Eco Chemie, founded in 1986, Metrohm Autolab has been a member of the Metrohm Group since 1st October, 2009.

Known for innovation, the Autolab was the first commercial digital potentiostat/galvanostat that was completely computer controlled. Our later software package NOVA has again set a high standard for powerful electrochemical research.

Metrohm Autolab customers receive excellent sales and service support from a dedicated team of Electrochemists based at Metrohm's prestigious laboratories at Daresbury, Chemist.

ELECTROCHEM 2012: Exhibitors

Stand 3



Labquip are the Irish distributor for Solartron Analytical and Princeton Applied Research.

Solartron Analytical designs and manufactures instrumentation and software for the characterization of materials and cells using precision electrical measurement techniques, including electrochemical impedance spectroscopy (EIS).

Princeton Applied Research is a leading manufacturer and global distributor of instrumentation and software for research electrochemistry in corrosion, battery/fuel cell development and sensor research.



Stand 4



Gamry Instruments designs and manufactures a variety of electrochemical instrumentation and accessories that are designed to fit your needs and budget. We are, first and foremost, electrochemists and materials scientists who love creating quality instrumentation, and enjoy seeing it used creatively.

Stand 5



EC-Lab supplies electrochemical test systems and accessories, providing sales, service and support to both academia and industry. We offer the BioLogic range of high performance single and multi-channel potentiostats/galvanostats/FRAs for research laboratories, as well as high current systems and dedicated instruments for battery and fuel cell testing.

ELECTROCHEM 2012: Supporters



PROGRAMME AT A GLANCE

Lecture Venues

Sunday 2 September: Registration in Hamilton building foyer
Mixer in Pavilion bar (located opposite Old chemistry building)

Monday 3 September: Hamilton building
Plenary lectures located in McNeill lecture theatre
LD Burke energy symposium located in McNeill lecture theatre
Techniques/sensors symposium located in Maxwell lecture theatre
Nanoelectrochemistry symposium located in Joly lecture theatre
Refreshments, lunch, posters and exhibition located in Hamilton and Foyer

Tuesday 4 September: Hamilton building
Plenary lectures located in Joly lecture theatre
LD Burke energy symposium located in Joly lecture theatre
Bioelectrochemistry symposium located in Joly lecture theatre
Fundamental symposium located in Maxwell lecture theatre
Refreshments, lunch, posters and exhibition in Hamilton and Foyer

Sunday 2 September

16:00	Registration (open until 18:00)
17:30	Mixer in Pavilion bar (located opposite Old chemistry building)

Monday 3 September

08:00	Registration and refreshments		
09:00	Plenary: Prof Wolfgang Schuhmann, Ruhr-Universität Bochum (<i>McNeill lecture theatre</i>)		
Symposia	LD Burke Energy	Techniques/Sensors	Nanoelectrochemistry
Room	<i>McNeill lecture theatre</i>	<i>Maxwell lecture theatre</i>	<i>Joly lecture theatre</i>
09:50	Mike Lyons	Ronan Baron	Thomas Smith
10:10	Wen-feng Lin	Aoife Morrin	Jagdeep Sagu
10:30	Refreshments, posters and exhibition		
11:00	Kevin Ryan (Keynote)	Pedro Estrela (Keynote)	Michael Coey (Keynote)
11:30	Andrew Wain	Chee-Seng Toh	Karen Dawson
11:50	Robert Lynch	Eileen Yu	Neville Freeman
12:10	Micheál Scanlon	Prosper Kanyong	Amélie Wahl
12:30	Asura Jablonskyte		Stephen Lyth
12:50	Lunch		
13:30	Plenary: Prof Zhong-Qun Tian, Xiamen University (<i>McNeill lecture theatre</i>) Recipient of the Faraday medal 2012 award lecture (RSC Electrochemistry group award)		
14:20	Lorraine Nagle (Keynote)	Grégoire Herzog (Keynote)	Frank Marken (Keynote)
14:50	David Officer	Majid Ghahraman Afshar	Akihiro Uehara
15:10	Colm O'Dwyer	Damion Corrigan	Fengjie Xia
15:30	Joseph Giorgio	James Iacobini	Laura Cabo-Fernández
15:50	Refreshments, posters and exhibition		
16:15	Plenary: Dr Dónal Leech, NUI Galway (<i>McNeill lecture theatre</i>)		
17:10	Don McElroy (Keynote)		Uwe Schröder (Keynote)
17:40	Posters and exhibition in the Hamilton building and foyer		
18:40	Drinks reception and conference dinner at the Davenport hotel (see map)		

PROGRAMME AT A GLANCE... CONTINUED

Tuesday 4 September

09:00	Plenary: Prof Fraser Armstrong, University of Oxford (<i>Joly lecture theatre</i>) Recipient of the Barker award 2012 lecture (RSC Electrochemistry group award)	
Symposia	LD Burke Energy... continued	Fundamental
Room	<i>Joly lecture theatre</i>	<i>Maxwell lecture theatre</i>
09:50	Michael Brandon	Richard Doyle
10:10	Nick Van Dijk	Damaris Fernandez
10:30	Refreshments, posters and exhibition	
Symposia	Bioelectrochemistry	Fundamental
Room	<i>Joly lecture theatre</i>	<i>Maxwell lecture theatre</i>
11:00	Alan Bond (Keynote)	Stephen Fletcher (Keynote)
11:30	Christopher Blanford	Daren Caruana
11:50	Ross Milton	David Cook
12:10	Ula Salaj-Kosla	Kathryn Toghill
12:30	Lunch	
13:30	Plenary: Prof Richard Compton, University of Oxford (<i>Joly lecture theatre</i>)	
14:20	Ben Horrocks (Keynote)	Robert Dryfe (Keynote)
14:50	Kulveer Singh	Ying Wang
15:10	Partha Jana	Angel Torriero
15:30	Robert Johnson	Chris Bell
15:50	Refreshments, posters and exhibition	
16:15	Danny O'Hare (Keynote)	Laureline Mahe
16:45	Carol Crean	16:35 Chris Batchelor-McAuley
17:05	Edward Milner	
17:25	Closing remarks	
17:30	Close	

Symposia Key

LD Burke Energy

Electrochemical Techniques and Sensors

Nanotechnology

Bioelectrochemistry

Fundamental

Symposia Conveners

Mike Lyons and Noel Buckley

Peter Fielden, John Hart and Ritu Katuky

Robert Forster and Alan O'Riordan

Edmond Magner

Frank Marken, Andrew Doherty and Jay Wadhawan

Programme: Sunday 2 September

- 16:00 Registration (open till 18:00)
 17:30 Mixer in Pavilion bar (located opposite Old chemistry building)

Programme: Monday 3 September

- 08:00 Registration and refreshments
Plenary lectures to take place in McNeill lecture theatre
- 09:00 **Plenary: Localized investigation of modified electrodes using high-resolution scanning electrochemical microscopy**
 Prof Wolfgang Schuhmann, Ruhr-Universität Bochum, Germany
- 10:30 Refreshments, posters and exhibition
- 12:50 Lunch
- 13:30 **Plenary: Toward nanoelectrochemistry: gold nanoparticles with ultrathin shells for characterizing electrochemical interfaces and electrocatalysis**
 Prof Zhong-Qun Tian, Xiamen University, China
 Recipient of the Faraday medal 2012 award lecture (RSC Electrochemistry group award)
- 15:50 Refreshments, Posters and Exhibition
- 16:15 **Plenary: Bioelectrocatalysis using enzyme or microbe films on electrodes**
 Dr Dónal Leech, NUI Galway, Ireland
- 17:40 Posters and exhibition in Hamilton and Foyer
- 18:40 Drinks reception and conference dinner at the Davenport hotel (see map)

LD Burke Energy symposium (McNeill lecture theatre)

- 09:50 **Electrochemical water splitting at electrodeposited and hydrous nickel oxide films in base**
 Mike Lyons, Trinity College, Ireland
- 10:10 **New progress in direct alcohol fuel cells: from fundamental to applications**
 Wen-feng Lin, Queen's University Belfast, UK
- 11:00 **Keynote: Solution growth and assembly of nanorods and nanowires for advances in thin film PV and lithium ion batteries**
 Kevin Ryan, University of Limerick, Ireland
- 11:30 **Reactivity screening using scanning electrochemical microscopy: from photoactive dyes to nanoparticle electrocatalysis**
 Andrew Wain, National Physical Laboratory, UK
- 11:50 **Hydrogen evolution at the negative electrode in vanadium redox flow batteries**
 Robert Lynch, University of Limerick, Ireland
- 12:10 **Towards artificial photosynthesis at polarised liquid/liquid interfaces**
 Micheál Scanlon, Ecole Polytechnique Fédérale de Lausanne, Switzerland
- 12:30 **Transient metallo-hydrides and carbonyls related to biological hydrogen evolution: FTIR spectroelectrochemistry**
 Asura Jablonskyte, University of East Anglia, UK
- 14:20 **Keynote: Optimisation of nanostructured and nanoporous metal architectures for energy applications**
 Lorraine Nagle, Tyndall National Institute, Ireland
- 14:50 **Controlling the open circuit voltage in porphyrin-sensitised solar cell**
 David Officer, University of Wollongong, Australia
- 15:10 **Semiconductor nanowires for antireflection coatings, solar cell transparent contacts, junctionless thermoelectrics and li-ion batteries**
 Colm O'Dwyer, University College Cork, Tyndall National Institute and University of Limerick, Ireland
- 15:30 **Re-engineering the dye-sensitised solar cell**
 Joseph Giorgio, University of Wollongong, Australia
- 17:10 **Keynote: Solar energy conversion**
 Don McElroy, University College Dublin, Ireland

Electrochemical Techniques and Sensors symposium (Maxwell lecture theatre)

- 09:50 Amperometric gas sensors for monitoring air quality**
Ronan Baron, Alphasense Ltd, UK
- 10:10 Conducting polymers housed in microfluidic channels for electroanalytical applications**
Aoife Morrin, Dublin City University, Ireland
- 11:00 Keynote: Enhancing electrochemical DNA biosensing with active sensitisers**
Pedro Estrela, University of Bath, UK
- 11:30 Prussian blue nanotubes sensor powered by H₂O₂**
Chee-Seng Toh, Nanyang Technological University, Singapore
- 11:50 Layer-by-layer assembly of enzyme electrodes for non-esterified fatty acids biosensors**
Eileen Yu, University of Newcastle, UK
- 12:10 Development of a sandwich format, amperometric uric acid biosensor for urine analysis**
Prosper Kanyong, University of West England, UK
- 14:20 Modification of the interface between two immiscible electrolyte solutions with silica films**
Grégoire Herzog, CNRS – Université de Lorraine, France
- 14:50 Direct ion speciation analysis with ion-selective membranes operated in a tandem potentiometric time resolved chronopotentiometric sensing mode**
Majid Ghahraman Afshar, Imam Khomeini International University, Iran and University of Geneva, Switzerland
- 15:10 Impedimetric detection of MRSA from clinical isolates**
Damion Corrigan, University of Edinburgh, UK
- 15:30 The electrochemical and spectroscopic properties of boron doped diamond**
James Iacobini, University of Warwick, UK

Nanotechnology symposium (Joly lecture theatre)

- 09:50 Studies of photosensitised p-NiO electrodes for tandem solar cells**
Thomas Smith, Loughborough University, UK
- 10:10 Cobalt-based redox mediators for dye-sensitized solar cells**
Jagdeep Sagu, Loughborough University, UK
- 11:00 Keynote: Magnetically-structured electrodeposits**
Michael Coey, Trinity College Dublin, Ireland
- 11:30 Electroanalysis at gold nanowire electrodes**
Karen Dawson, Tyndall National Institute, Ireland
- 11:50 Comparison of performance of an array of nanoband electrodes with a macro electrode with similar overall area**
Neville Freeman, NanoFlex Ltd, UK
- 12:10 Concept of diffusional independence at gold nanowire electrodes in array: theory and experiments**
Amélie Wahl, Tyndall National Institute, Ireland
- 12:30 Electrochemical oxygen reduction on high surface area nano-porous nitrogen-doped graphene foams**
Stephen Lyth, Kyushu University, Japan
- 14:20 Keynote: electrochemical processes in mesoporous films of metal oxide nanoparticles**
Frank Marken, University of Bath, UK
- 14:50 Electrochemical understanding of gold deposition process at the water/1,2-dichloroethane interface**
Akihiro Uehara, University of Manchester, UK and Kyoto University, Japan
- 15:10 Hydrothermal core-shell nanocarbons**
Fengjie Xia, Wuhan University of Technology, China and University of Bath, UK
- 15:30 Electrochemical investigation of redox centres in gold nanoparticles and copper coordination compounds**
Laura Cabo-Fernández, University of Liverpool, UK
- 17:10 Keynote: Electromobility revisited: electrochemistry for biofuel generation?!**
Uwe Schröder, Technische Universität Braunschweig, Germany

Programme: Tuesday 4 September

Plenary lectures to take place in Joly lecture theatre

- 09:00 **Plenary: What electrochemistry teaches us about enzymes**
Prof Fraser Armstrong, University of Oxford, UK
Recipient of the Barker award 2012 lecture (RSC Electrochemistry group award)
- 10:30 Refreshments, posters and exhibition
- 12:30 Lunch
- 13:30 **Plenary: Simulation of voltammetry; some recent progress**
Prof Richard Compton, University of Oxford
- 15:50 Refreshments, posters and exhibition
- 17:25 Closing remarks
- 17:30 Close

LD Burke Energy symposium... continued (Joly lecture theatre)

- 09:50 **Enhancing the electrocatalytic activity of tetrahedral Pt nanocrystals by adatom decoration**
Michael Brandon, University of Limerick, Queen's University Belfast, UK
- 10:10 **Electrochemical impedance analysis of ITM power's proton exchange membrane electrolyzers**
Nick Van Dijk, ITM Power, UK

Bioelectrochemistry symposium (Joly lecture theatre)

- 11:00 **Keynote: Large amplitude fourier transformed AC voltammetry and new form of data analysis applied to the electrochemistry of cytochrome C peroxidase**
Alan Bond, Monash University, Australia
- 11:30 **New features in the mechanism of electrocatalytic dioxygen reduction by multicopper oxidases revealed by protein film electrochemistry and finite time-domain modelling**
Christopher Blanford, University of Manchester, UK
- 11:50 **Optimisation of a glucose oxidase / cellulose / carbon nanotube based bioelectrode**
Ross Milton, University of Surrey, UK
- 12:10 **Nanoporous gold electrodes as matrices for enzymes immobilization applied in biosensors and biofuel cells**
Urszula Salaj-Kosla, University of Limerick, Ireland
- 14:20 **Keynote: DNA-templated nanowires**
Ben Horrocks, Newcastle University, UK
- 14:50 **Inactivation processes of immobilised redox enzymes studied by an electrochemical quartz crystal microbalance**
Kulveer Singh, University of Manchester, UK
- 15:10 **Microbial fuel cell wastewater treatment using a low-cost membrane**
Partha Jana, National University of Ireland Galway, Ireland
- 15:30 **Denaturation of DNA at electrode surfaces: puzzles and applications**
Robert Johnson, University of Southampton, UK
- 16:15 **Keynote: Cells on chips: electroanalytical investigation of disease**
Danny O'Hare, Imperial College, UK
- 16:45 **Conducting polymer-metal nanoparticle composites from ionic liquids**
Carol Crean, University of Surrey, UK
- 17:05 **Aerobic biocathodes for microbial fuel cells**
Edward Milner, University of Newcastle, UK

Fundamental symposium (Maxwell lecture theatre)

- 09:50 **An electrochemical impedance study of the oxygen evolution reaction at hydrous iron oxide in base**
Richard Doyle, Trinity College Dublin, Ireland
- 10:10 **Magnetoelectrolytic production of hydrogen with controlled bubble size and departure direction**
Damaris Fernandez, Trinity College Dublin, Ireland
- 11:00 **Keynote: Beyond the butler-volmer equation. Curved tafel slopes from steady-state current-voltage curves**
Stephen Fletcher, Loughborough University, London
- 11:30 **Control of redox reactions at the solid/gas interface**
Daren Caruana, University College London, UK
- 11:50 **Electrodeposition of metals and semiconductors from supercritical fluids: towards metamaterials**
David Cook, University of Southampton, UK
- 12:10 **Voltammetry in supercritical CO₂ fluids**
Kathryn Toghiani, Ecole Polytechnique Fédérale de Lausanne, Switzerland
- 14:20 **Keynote: Graphene: electrochemistry in flatland**
Robert Dryfe, University of Manchester, UK
- 14:50 **Searching for authentic electrocatalytic nanoeffect: electro-oxidations of nitrite and L-ascorbic acid on Au-NPs modified electrode**
Ying Wang, University of Oxford, UK
- 15:10 **Electrochemistry of decamethylferrocene in ionic liquids. A critical evaluation and novel applications**
Angel Torriero, Deakin University, Australia
- 15:30 **Chronoamperometry at neighbouring inlaid microdisk electrodes**
Chris Bell, University of Oxford, UK
- 16:15 **Diagnosing sepsis: a graphene-based biosensor for procalcitonin**
Laureline Mahe, University of Exeter, UK
- 16:35 **A new method for studying poorly soluble species: the electrocatalysis of oxygen by quinizarin**
Chris Batchelor-McAuley, University of Oxford, UK

Plenary Speakers

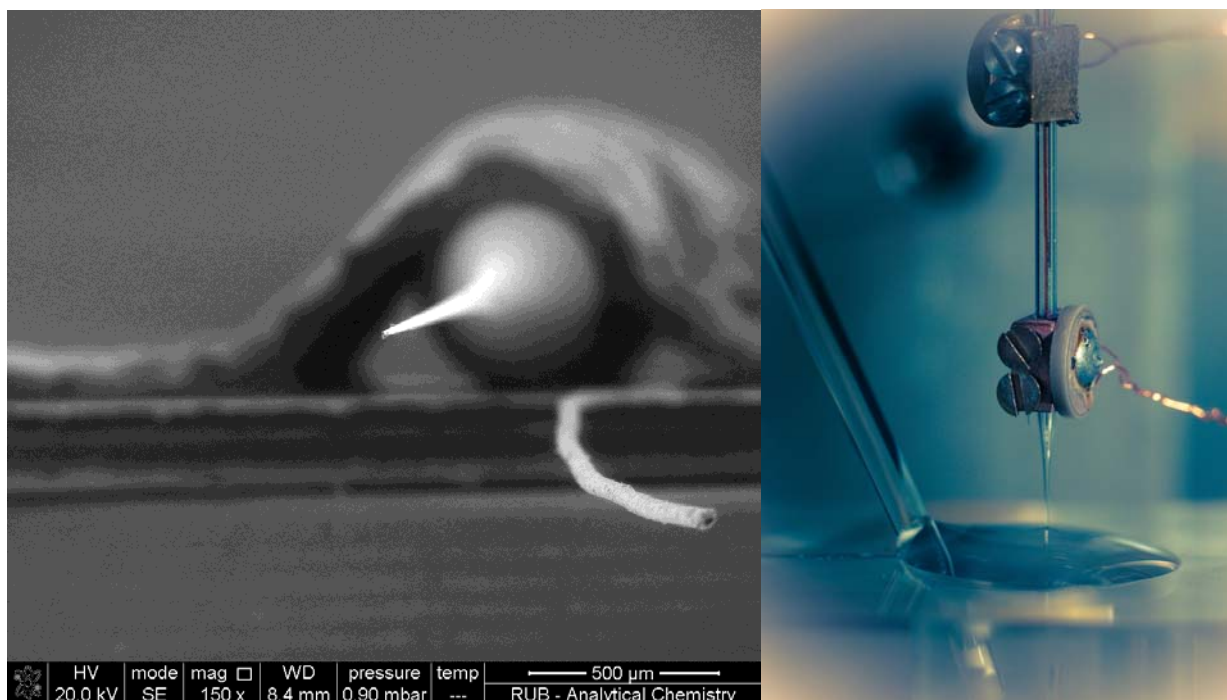
Localized investigation of modified electrodes using high-resolution scanning electrochemical microscopy

Wolfgang Schuhmann, Michaela Nebel, Aleksandar Zeradjanin,
Tharamani Chikka Nagaiah, Artjom Maljusch, Maike Pähler, Andrea Puschhof
Ruhr-Universität Bochum, Analytische Chemie - Elektroanalytik & Sensorik;
Universitätsstr. 150; D-44780 Bochum; Germany
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The development of chemical microscopy techniques with high resolution is of high importance for getting an in-depth insight into chemical reactions at surfaces including catalysis, electrocatalysis, photoelectrocatalysis, corrosion, design of bioelectrochemical interfaces such as biosensors and biofuel cells.

In this presentation after an introduction to scanning electrochemical microscopy (SECM) and possible applications a number of novel detection modes will be presented and their potential applications for the elucidation of reactions at modified surfaces will be discussed, including:

- gas evolution reactions at dimensionally stable anodes in chlorine production
- temperature dependent catalyst activity
- localised corrosion of AlMg alloys and corrosion protection by means of corrosion inhibitors
- non-noble metal catalysts in catalytic oxygen reduction
- localized visualization of bioelectrocatalytic activity



Toward nanoelectrochemistry: gold nanoparticles with ultrathin shells for characterizing electrochemical interfaces and electrocatalysis

Zhong-Qun Tian

State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

A distinction will be made between two similar terms: nanoscale electrochemistry and nanoelectrochemistry. The former focuses on size while the later focuses on specific properties. The later prompts more stimulating questions, such as how nanostructure geometry (e.g., size, shape, inter-structure spacing) in the solid and liquid states can determine specific electrochemical properties. It guides the tailoring of nanostructure composition to further expand the range of properties and usefulness of traditional materials in electrochemistry.

Two different approaches will be presented: coating gold nanoparticles with an ultrathin (1-4 nm) shell of an electrochemically-active material (e.g., Pd and Pt) or an inert material (e.g., SiO₂ or Al₂O₃) for enhancing catalytic activity or probing interfacial structure respectively.

We synthesized Au-core Pd-shell Pt-cluster trimetallic nanoparticles (Au@Pd@Pt NPs) for electrocatalysis. Their high catalytic activities depend on particle and cluster shape, and on shell thickness. We explored their electronic and morphological properties using CO as a probe molecule. A unique mushroom-like Pt cluster was created, and our new NPs are proposed to have a higher coordination number for specific reactions. The adsorption structures and energies of formic acid and its decomposition intermediates were investigated by density functional theory (DFT) simulations, and they were found to be responsible for the high experimentally-observed electrocatalytic activity.

Our second approach is to utilize a “borrowing surface plasmons” strategy and rationally design various nanostructures to break the long-standing (two decades old) limitation of materials generality. Very recently we have developed a new operation mode which we call “shell-isolated nanoparticle-enhanced Raman spectroscopy” or “SHINERS” [3]. We synthesized Au or Ag nanoparticles with ultrathin shells of inert SiO₂ or Al₂O₃. These nanoparticles can be spread over an electrode of virtually any material and any surface morphology to obtain high-quality, potential-dependent Raman spectra of adsorbates (e.g., CO, H, SCN⁻, H₂O, pyridine, adenine). We have already demonstrated that this method is applicable to Pt, Au and Rh single-crystal surfaces. Several examples will be given to illustrate that SHINERS expands the flexibility of spectro-electrochemistry and surface chemistry for a wide variety of applications [4,5].

Finally, an outlook on the future developments of nanoelectrochemistry will be given. Emphasis will be placed on emerging areas such as the progression from electro-catalysis and photo-electro-catalysis to electro-cassemblysis and photo-electro-cassemblysis, and in-situ measurement of the electronic jellium tail length for various electrodes using a molecular/atomic ruler approach.

[1] D. Y. Wu, J. F. Li, B. Ren, Z. Q. Tian, *Chem. Soc. Rev.*, 37 (2008) 1025.

[2] P. P. Fang, S. Duan, X. D. Lin, et al., *Chem. Sci.*, 2 (2011) 531.

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Bioelectrocatalysis using enzyme or microbe films on electrodes

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Bioelectrocatalytic processes can be harnessed to provide signals for devices such as biosensors or biological fuel cells. Selection of biocatalysts can range from individual enzymes to coupled enzyme cascades, to biological cells, and consortia of cells, depending on the application sought. Enabling electron transfer between these biocatalysts and an electrode surface is crucial for successful operation as electrochemical biosensing and biopower generation devices. However there are limitations that affect the rate of electron transfer between biocatalyst and electrode surface.

Here I report on research over the past few years on co-immobilization of enzymes with components, such as electron shuttling mediators, for improvement of bioelectrocatalytic signal generation. The approach is based on combination of a library of inorganic redox mediator complexes displaying a range of redox potentials and various functionalized ligands, with supports and surfaces and enzyme biocatalysts. The redox mediators can be incorporated into polymeric supports or tethered to different surfaces utilizing coupling or ligand-exchange chemistries. Covalent coupling of enzymes and mediators with structured and/or chemically functionalized electrode materials can improve enzymatic fuel cell stability and performance, as can design changes to the biocatalyst.

Preliminary results, based on an examination of the factors that affect electron transfer reactions of microbial biofilms induced to grow on electrodes, can provide insights into approaches to improve electron transfer within microbial biofilms, with a view to enhancing the performance of the microbial-based electrochemical systems.

What electrochemistry teaches us about enzymes

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Enzymes are widely accepted to be highly active, albeit non-robust catalysts; less well known is that many enzymes are also highly efficient electrocatalysts when attached directly to an electrode. The efficiency is displayed through their ability to catalyse reversible reactions of importance for energy technology . i.e. H^+/H_2 , CO_2/CO and $\text{O}_2/\text{H}_2\text{O}$ interconversions, using only a small overpotential. Such efficiency arises from several factors – low reorganisation energies of electron-transfer centres, synchronous proton-electron transfers, stabilization of reactive intermediates, and matching the potentials of the enzyme redox centres to the reaction being catalyzed. The structural foundations for these factors are much better defined than for most simple catalysts because enzymes are macromolecules for which detailed 3D information is available, usually allowing us to define the position of every non-hydrogen atom far out from the active site. The high electrocatalytic activity of enzymes yields large currents, enabling us to probe their properties by exploiting a range of electrochemical techniques. We are thus able to make new discoveries, such as novel aspects of biological H_2 production by hydrogenases and the mechanisms by which these enzymes deal with or are inactivated by O_2 . We are also finding convincing demonstrations of the ability of enzymes to perform rapid and efficient solar-fuel production when attached to semiconducting nanoparticles. It is important to identify fast and efficient catalysts that enable electronically energised materials to make fuels from raw materials, and enzymes such as hydrogenases and carbon monoxide dehydrogenases, with billions of years to evolve (where energy efficiency is an important driver) show us how this can be done.

Simulation of voltammetry; some recent progress

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Progress will be reported in three areas of the simulation of voltammetry.

First theories of electrode kinetics will be examined, interplaying simulation with experiment at all stages, and the Butler-Volmer theory compared with Marcus-Hush theory with the conclusion that the usual form of the latter based on *symmetric* Marcus-Hush theory gives significantly inferior fits to full voltammetric waveshapes for a diversity of redox systems in both aqueous and non-aqueous media where both reactant and product are free to diffuse in solution. A new Marcus-Hush type approach based on *asymmetric* intersecting parabola is developed and shown to be closely related to the classical Butler-Volmer formalism. Voltammetry for both solution phase and surface bound species is shown to be substantially better described by the new approach. The use of cyclic square wave voltammetry is shown to be extremely sensitive for revealing differences between various theories of electron transfer and to have high precision for the determination of the associated rate constant. The extension of the theory to variable temperature systems will be illustrated.

Second the simulation of voltammetry in the near absence of supporting electrolyte will be discussed and shown to lead to new chemical insights, unobtainable with conventional solution phase voltammetry in the presence of excess inert electrolyte.

Finally the modelling of ultra-low concentration cyclic voltammetry is considered and the transition between statistical (Fickian) and stochastic behaviour is explored in the context of solution phase voltammetry.

L.D. Burke Energy Symposium

Electrochemical water splitting at electrodeposited and hydrous nickel oxide films in base

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In recent years there has been a revival of interest in the optimization of oxygen evolution reaction (OER) anode materials. In practice, the large anodic overpotential of the OER is the principal factor in limiting the efficiency of alkaline water electrolysis [1], which is seen as an environmentally friendly route for the production of hydrogen gas. Currently, the optimal OER anode materials are RuO_2 and IrO_2 , since these oxides exhibit the lowest overpotentials for the OER at practical current densities [2]. However, the high cost of these materials and their poor long term stability in alkaline solution renders their widespread commercial utilisation both uneconomical and impractical [3]. In light of these limitations, the oxides of the first row transition metals offer a compromise solution due to their relatively low cost and their long term corrosion resistance in alkaline solution [3-6].

In this work, a range of nickel oxide films have been prepared via potential multicycling and electrodeposition techniques. The redox switching behaviour of these films are compared paying particular attention to pH dependence and the kinetics are examined using potential sweep voltammetry and potential step chronoamperometry. A full kinetic analysis for the OER at oxidized Ni electrodes has been developed with a specific focus on the enumeration of Tafel slopes and the reaction order with respect to OH^- ion activity as a function of layer thickness and preparation method. Tafel slopes range from 55 mV dec^{-1} to 80 mV dec^{-1} at low overpotentials rising to approximately 120 mV dec^{-1} at high overpotentials. A reaction order close to unity was observed irrespective of the reaction conditions and oxide preparation method. We suggest that a modified Kobussen mechanism involving a Ni(III)/Ni(IV) oxo intermediate may be considered a feasible pathway for the OER at oxidised Ni electrodes [7].

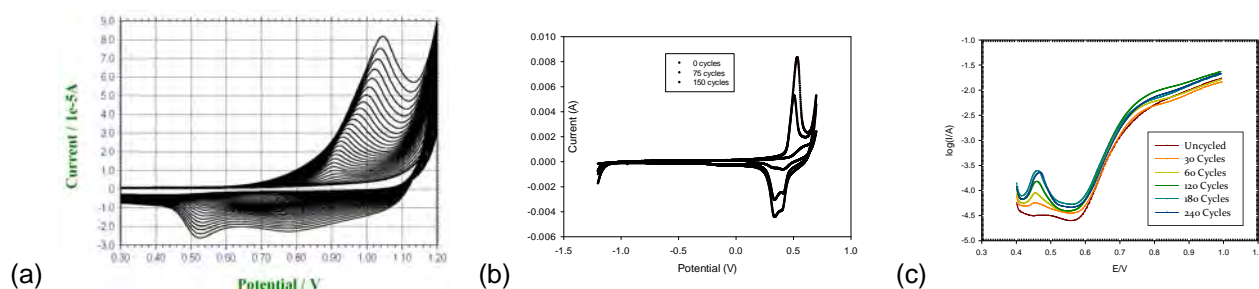


Figure 1: Cyclic voltammograms recorded (a) during electrodeposition of nickel hydroxide and (b) for hydrous nickel oxides prepared via potential multicycling. (c) Tafel plots recorded for various multicycled hydrous oxide layers.

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New progress in direct alcohol fuel cells: from fundamental to applications

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

First part of this talk is on fundamental electrocatalysis studies. The surface structure and reactivity of a series of well-defined model catalysts and the nanostructured and supported practical fuel cell catalysts towards the adsorption and electro-oxidation of a range of small organic fuel molecules in various electrolyte solutions have been studied by combined *in-situ* electrochemical FTIR spectroscopy, *ex-situ* electron diffraction and Auger electron spectroscopy, and Density Functional Theory calculations. New insights into the surface structures and electrocatalysis have been obtained at atomic and molecular level. The electrodeposition of Ru on Pt(111) and tetrahedral (THH) Pt nanocrystals forms a monatomic layer at low coverage, while at higher coverage higher layers are populated before the first layer is completed. Because of electronic effects and structural properties, the electrocatalytic activity of Ru-modified Pt(111) and THH Pt surfaces toward CO adsorbate (CO_{ads} , a surface poisoning specie) and methanol oxidation is substantially higher than that of the pure metals and even better than that of PtRu alloys. Both linear and bridged binding CO adsorbates were observed on Pt domains, whilst only CO_{L} was observed on Ru domains. On the other hand, both linear and threefold-hollow binding CO adsorbates were observed on the Ru(0001) electrode at lower potentials where an (2x2)-O/OH layer was present. It has been found that O-species are inactive, OH species with low coverages are inactive, but they become active when local coverages increase, towards CO_{ads} oxidation. For ethanol oxidation, it has been found that PtRu is not an efficient catalyst, but PtSn exhibits much higher activity, however, the selectivity towards total oxidation to CO_2 is not high. Origin of low CO_2 production has been revealed by detailed mechanism studied. New strategies to tackle both activity and selectivity have been proposed and demonstrated, and will be reported.

Second part of this talk is on fit-for-purpose fuel cell system development, novel electrode structure, MEA assembly, single cell and stack design and fabrication will be reported.

Keynote

Solution growth and assembly of nanorods and nanowires for advances in thin film PV and lithium ion batteries

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Semiconductor crystals with sizes in the order of tens of nanometers can be synthesised and processed from solution creating a new paradigm in materials design where wet chemistry can produce inorganic structures with unique size and shape tuneable properties. Here we report recent advances from our research on the solution synthesis of a range of semiconductors: II-VI, IV, I-VI, I-III-VI₂, I₂-II-IV-VI₄ in nanorod and nanowire form. We can subsequently assemble these nanostructures from solution over device scale areas with precise control. Recent highlights from our work on the application of these materials in solar cells and batteries will be discussed. In particular, the first formation of copper zinc tin tetrasulphide (CZTS) nanorods will be outlined. This semiconductor is highly sought for thin-film PV due to the material abundance of all the constituent elements combined with high efficiencies. For battery applications, the solution synthesis of tin-seeded silicon nanowires will be discussed in addition to their investigation as a hybrid composite lithium battery anode, where both the semiconductor and the seed cycle lithium.

Reactivity screening using scanning electrochemical microscopy: from photoactive dyes to nanoparticle electrocatalysis

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Scanning electrochemical microscopy (SECM) is a powerful and versatile technique that allows the interrogation of surface reactivity on the local scale using a microelectrode as an electrochemical probe. Recent work has demonstrated the application of SECM as a screening tool for electrocatalyst and photocatalyst arrays deposited on conducting surfaces, typically utilising the substrate as a current collection electrode. Doing so offers a unique method to optimise the reactive performance of such catalytic materials in addition to mapping surface reactivity variations with micron scale resolution.

In this work we explore the use of tip-collection modes of SECM as an alternative approach to materials reactivity screening. We demonstrate this with respect to two applications. First we evaluate the photoelectrochemical activity of dye-sensitized TiO_2 surfaces, a growing requirement for the commercialisation of dye-sensitized solar cell devices. We exploit a simple 2-electrode substrate generation/tip collection approach which enables mapping of the photoactivity of immobilized dyes under illumination and demonstrate this by comparing the relative performance of commercial dyes. We then move our attention to the electrocatalytic properties of immobilized gold nanoparticles, focusing on the oxygen reduction reaction and the electrocatalytic oxidation of hydrogen peroxide, in which important size effects are investigated.

Hydrogen evolution at the negative electrode in vanadium redox flow batteries

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Flow batteries are an attractive technology for a variety of energy storage applications.¹ Vanadium flow batteries² offer the advantage that, because the species on both sides of the membrane are just different forms of vanadium in H₂SO₄, cross-contamination problems are effectively eliminated.³ The anolyte and catholyte in a vanadium flow cell may be prepared⁴⁻⁶ from VOSO₄ by, respectively, a two-electron reduction leading to V²⁺ and a one-electron oxidation leading to VO²⁺.

However both the reduction of VO²⁺ to V³⁺ ($E^0 = 0.360$ V vs SHE) and the reduction of V³⁺ to V²⁺ ($E^0 = -0.255$ V vs SHE) are slow and the potential of the latter is below the theoretical potential for hydrogen evolution in the electrolyte. Because of the high overpotential, the reduction of VO²⁺ to V³⁺ on carbon can also occur below the reversible potential for hydrogen formation. In this paper we examine the formation of hydrogen as a by-product at the negative electrode of a vanadium flow battery during the anolyte preparation phase. Experiments were carried out at 25°C in a flow cell constructed of perspex. The electrodes consisted of carbon felt, 5 mm in thickness, separated by a 180- μ m Nafion® 117 membrane supplied by DuPont. The electrodes were 35 mm \times 15 mm in area and were contacted by means of carbon-filled polymer contacts supplied by Bac2 Ltd. When the cell components were clamped together, the felt electrodes were compressed to a thickness of 3 mm. The starting electrolyte consisted of 1.5 mol dm⁻³ VOSO₄ in 3 mol dm⁻³ H₂SO₄ in both the anolyte and catholyte chambers and this was circulated by means of a dual peristaltic pump, typically at a flow rate of 0.15 cm³ s⁻¹. Potentials were measured relative to a saturated mercury/mercurous-sulphate reference electrode (Hg/Hg₂SO₄). The evolved hydrogen gas was measured volumetrically. During reduction of VO²⁺ to V³⁺ substantial hydrogen evolution was observed. In constant current experiments, the rate of hydrogen evolution decreased roughly linearly from a high of 3.0×10^{-3} cm³ s⁻¹ cm⁻² at STP (equivalent to 26.4 mA cm⁻²) to 0.8×10^{-3} cm³ s⁻¹ cm⁻² (8.6 mA cm⁻²) at 38,800 s and then dropped rapidly when all the VO²⁺ was reduced. This suggests that the presence of VO²⁺ enhances the rate of hydrogen evolution. The effect of adding VO²⁺ ions to 3 mol dm⁻³ H₂SO₄ in which the carbon electrode is held at a constant potential of -1.050 V vs Hg/Hg₂SO₄ was investigated. Initially, there was no directly observable evolution of hydrogen gas. However when VOSO₄ was added, substantial evolution of hydrogen gas began. The effect of VO²⁺ and other vanadium species, on charging of anolyte, will be described and possible mechanisms discussed.

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Towards artificial photosynthesis at polarised liquid/liquid interfaces

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Developing technology to realistically satisfy global energy demand in an environmentally friendly manner at low-cost, in comparison to the current ubiquitous release of energy from fossil fuels, is a pressing grand challenge facing the scientific community this century. The oxidation of water represents the only viable source of electrons to create clean fuels on a grand scale, for example *via* the hydrogen evolution reaction (HER) whereby protons are reduced to release molecular hydrogen. The concept of artificial photosynthesis at a polarised liquid membrane is presented.¹ This involves two catalytic systems, one at each interface for the hydrogen and oxygen evolution reaction, respectively.

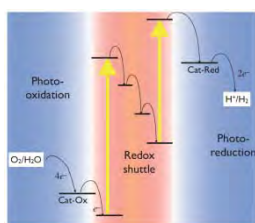


Figure 1: Z-scheme in artificial photosynthesis using catalysts at two soft interfaces. This strategy is based on photoelectrochemistry at polarised liquid/liquid interfaces.¹

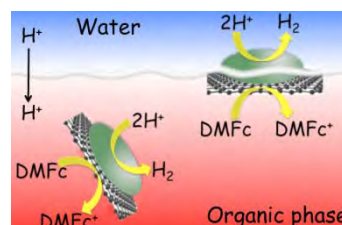


Figure 2: Schematic of the hydrogen evolution reaction by DMFc in the presence of catalyst present at the liquid/liquid interface and in the bulk organic phase.^{2(a)}

The HER at the liquid/liquid interface has been extensively probed by our group.² Protons can be reduced at these defect free soft electrified interfaces to produce molecular hydrogen if an organic reducing agent such as cobaltocene or decamethylferrocene (DMFc) is present in the organic phase. We have catalyzed this process by the *in situ* reduction of metallic salts, forming adsorbed nanoparticles of Pt or Pd, or by suspending MoS₂ particles at the liquid/liquid interface.² Recently, we presented highly active carbon supported MoS₂ catalysts capable of proton reduction across nano-Schottky barriers in a biphasic system.^{2(a)} The more challenging oxygen evolution reaction (OER) at the liquid/liquid interface is currently under investigation and our latest findings will be presented.

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Transient metallo-hydrides and carbonyls related to biological hydrogen evolution: FTIR spectroelectrochemistry

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One of the most attractive means of future energy storage and generation is hydrogen. A lot of research has gone into finding routes that will make the use of H_2 in the future more viable. Taking inspiration from nature seems to be a good starting point. Understanding the chemistry that takes place at the active site of [FeFe]-hydrogenase is both of high interest and potential technological impact in the context of hydrogen generation and utilization [1].

Mixed valence Fe(I)-Fe(II) hydrides have been postulated as intermediates in the catalytic cycle of dihydrogen evolution of the enzymatic system. Using advanced FTIR spectroelectrochemical cell, DFT calculations and EPR spectroscopy we have characterised the first discrete mixed-valence $[2Fe_2S] \mu$ -hydride species [2]. This is a valence-delocalised system and isotopic-labeling studies have established that substantial radical character resides on the strongly coupled bridging hydride. We also show a reduction of first $[2Fe_3S]$ bridging hydride species and examine the common pathway that these systems might share in the route of catalytic hydrogen generation by natural and unnatural systems.

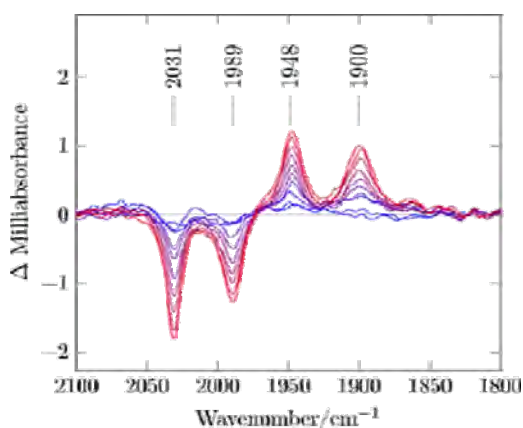


Figure 1. Difference spectrum for the reduction of $[HFe_2(pdt)(CO)_4(PMe_3)_2][PF_6]$ in the time range 0.25 s (blue) to 1.79 s (red) relative to scan at 0.08 s

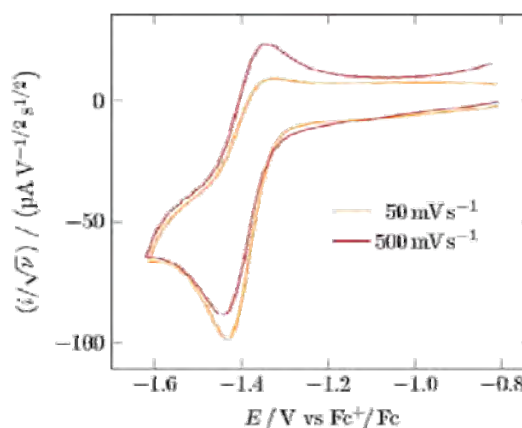


Figure 2. Normalized cyclic voltammograms of $[HFe_2(pdt)(CO)_4(PMe_3)_2][PF_6]$ recorded at vitreous carbon working electrode in MeCN at 25 °C

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Keynote

Optimisation of nanostructured and nanoporous metal architectures for energy applications

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In this talk I will give an overview of several research themes pursued in the Electrochemical Materials and Energy group in Tyndall that exploit nanotemplating and dealloying in the creation of functional nanoscale and nanoporous catalyst architectures. Nanotemplated materials have significant potential for applications in energy conversion and storage devices due to their unique physical properties. Nanostructured materials provide enhanced electrode surface area with short path lengths for electronic and ionic transport and thus the possibility of higher reaction rates.

Silicon-integrated anodic aluminium oxide templates with sub-100 nm dimensions that provide an inexpensive route for generating functional 1-D nanostructures will be presented. We report on the controlled growth of metal and alloy electrodeposited templated nanostructures for micro energy applications. Platinum deposited in nanowire arrays exhibited ca. 100 fold increase in activity towards methanol oxidation for use in micro direct methanol fuel cells (DMFCs) over bulk Pt. Templated CuSn alloy anodes that possess high capacity retention with cycling for lithium microbattery integration are also presented. We report on a facile templated electrodeposition approach to fabrication of nanotubular catalysts (Pt and PtCo) for micro DMFCs. The hollow nanotubular morphology introduces an advantage over nanowires in reducing Pt mass loading while increasing surface area. We demonstrate control of nanotube wall thickness in the 10-35 nm range. The mass activity for methanol oxidation at the Pt nanotubular catalyst of 523 mA mg⁻¹ represents >7 fold increase over that of commercial ETEK catalyst (20 wt. % Pt on high surface area carbon).

The introduction of dealloying to the toolbox of nanoscale processing methods for the creation of ultra-thin high surface area nanoporous metal catalysts with similar surface area and loadings merits attention. Nanoporous catalysts can outperform carbon-supported nanoparticle based systems by eliminating the (i) need for the carbon support (ii) degradation issues associated with carbon corrosion and (iii) reduction of active surface area due to nanoparticle sintering. In an open nanoporous sponge-like metal network, all of the surface area is inherently electrically accessible and mass transport of the reactant to the active sites and release of gaseous by-products is enhanced. We have investigated the oxidation of borohydride and ammonia borane at nanoporous gold (NPG) as an anode catalyst in a direct borohydride fuel cell (DBFC) and in a direct ammonia borane fuel cell. The overpotential for oxidation of these 'zero-carbon' fuels was 0.28 and 0.21 V lower than at bulk planar gold, while the oxidation current efficiency increased by a factor of 5 and 25, at borohydride and ammonia borane, respectively. Microfabricated DBFCs with electrodeposited nanoporous MnO₂ cathode catalyst and low loading Au anode catalyst (10 µg cm⁻²) delivering 2 to 10 mW cm⁻² power output in passive air-breathing cells without a polymer membrane at room temperature will be presented.

Controlling the open circuit voltage in porphyrin-sensitised solar cell

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In 2007, we reported that several porphyrin dyes gave dye sensitised solar cell (DSSC) power conversion efficiencies up to 7.1%, which was unprecedented for porphyrin sensitizers at that time.⁽ⁱ⁾ However, these porphyrin dyes consistently showed a lower open circuit voltage (V_{oc}) than the commonly used ruthenium dyes. We subsequently examined this limitation using porphyrin dye GD2 and postulated that this generally 100-200 mV lower voltage might be related to a negative shift of the conduction band potential of the TiO_2 following dye sensitisation, or to a reduced electron density due to a reduced electron lifetime.⁽ⁱⁱ⁾ By measuring the electron lifetimes and conduction band level of the TiO_2 , it could be shown that the lower V_{oc} of GD2-sensitized solar cells is not due to a shift of the conduction band potential but due to a 200 times shorter electron lifetime of electrons in porphyrin DSSCs at matching electron densities compared to N719, a ruthenium based standard dye. It was assumed that the major reason for this shorter electron lifetime is the enhanced recombination of the electrons in the TiO_2 with the I_3^- species in the redox mediator. This enhancement was proposed to originate from the different shape and symmetry of the porphyrins and how they were arranged on the nanoparticulate TiO_2 surface compared to N719. Zn-porphyrins have a planar structure and bind at angles of 40-60° to the semiconductor surface. The I_3^- species in the electrolyte is attracted by the positively charged Zn ion at the porphyrin centre, which enhances the recombination rate through the proximity of I_3^- to the TiO_2 surface. In contrast, N719 has a more spherical structure and binds to the surface such that the approach of I_3^- to the semiconductor surface is shielded by the negatively charged NCS ligands, which repel these ions. It is anticipated that, by eliminating these recombination pathways and subsequently increasing the electron density, a V_{oc} similar to N719-sensitized devices could be obtained for porphyrin-DSSCs, affording higher porphyrin-sensitised solar cell efficiencies.

Two approaches to controlling recombination, and hence V_{oc} , have been undertaken; the introduction of non-light absorbing surface additives onto the photoanode, following sensitisation by the porphyrin dye, in order to block the approach of I_3^- to the TiO_2 surface, and the use of sterically hindered porphyrin dyes with structural features designed to inhibit porphyrin redox mediator interactions. Measurement of the standard photovoltaic characterization parameters of the solar cells revealed that the transparent additives have a detrimental effect on V_{oc} and other photovoltaic characteristics in contrast to the use of sterically hindered dyes, which exhibit increases in V_{oc} in comparison to other reference dyes. The results of these studies along with investigations of photophysical parameters such as the electron lifetime will be discussed.

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Semiconductor nanowires for antireflection coatings, solar cell transparent contacts, junctionless thermoelectrics and li-ion batteries

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A nanostructured three-dimensional electrode using transparent conducting oxide (TCO) is an effective approach for increasing the efficiency of optoelectronic devices used in daily life. We summarise MBE grown tin doped indium oxide (ITO) with high conductivity and high work function for application as solar cell back contacts with excellent antireflection and plasmon polariton-assisted transmissivity. The growth of highly porous, large area ITO nanowire layers with superior optical and electrical properties is correlated to the graded porosity nanostructured layers.

For energy storage considerations such as Li-ion batteries, ITO has a theoretical reversible charge capacity of 883 mAh g⁻¹, making it ideal transparent and conductive Li-ion battery anode. We present detailed structural and electrochemical investigations of unprecedented defect-free indium-tin oxide and tin oxide nanostructures grown by molecular beam epitaxy completely without any heterogeneous seed or growth-facilitating phase. By controlling the growth conditions, a variety of high quality nanostructures are possible and their electrochemical response is correlated with specific structural changes during insertion, alloying and removal of lithium. We detail the correlation between electrochemical lithium insertion and removal processes during charging and discharging for these transparent battery anodes.

By using silicon, comparable optical, electrical and charge storage paradigms can also be examined and developed. We show here, that by controlling the topology and surface crystallinity of metal-assisted chemically etched Si nanowire layers and electrochemically formed 3D heterophotonic and phononic crystal membranes, thermoelectric materials are realised by exploiting the variable thermal conductivity of silicon due to thermalized phonon processes, determined using *in-situ* temperature-dependent Raman scattering spectroscopy. The result is the first range of processable on-chip thermoelectric silicon-based materials from quantum-confined nanostructure and topology variation, without necessitating a p-n junction.

Finally, as Si is receiving significant renewed interest for Li-ion batteries and emerging alternatives, we show recent work on the electrochemical response of Si and electrolessly etched Si nanowire layers to lithium insertion and removal. Silicon has the highest theoretical specific charge capacity which has been realised with nanostructured silicon with limited cycle life. The specific details on nanostructured versus bulk Si to high rate charging will also be summarised. Overall, both Si and ITO exhibit a range of potentially exploitable properties for energy storage and generation.

Re-engineering the dye-sensitised solar cell

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Transparent conductive oxides (TCO) in dye-sensitised solar cells (DSSCs) place considerable limits on the size of a cell module, leading to a number of module development challenges. These challenges can be overcome if the TCOs are replaced with metal electrodes. Metal cathodes have been investigated in traditional 'sandwich' style DSSCs. Metal anodes can be utilised in back-illuminated DSSCs. However the back-illuminated design is plagued by the lack of transparency of both the cathode and electrolyte. Nonetheless, if metal electrodes are utilised for both the cathode and anode considerable advantages to devices can be obtained, and many obstacles in regards to cell design can be overcome.

With both the cathode and anode being metallic, a back-contact cell design is essential to facilitate light transmission to the photo-sensitised dyed titanium dioxide. In this type of cell the cathode is located behind the anode. Advantages of this design include utilising a highly transparent front cover to improve light transmission to the photo-active material as well as lower cell resistance giving increased device current due to the improved electrical conductivity of metallic electrodes.

With the removal of expensive and size limiting TCO, devices can be glass free and flexible. Consequently, light weight and flexible back-contact DSSC modules can potentially be fabricated utilising a roll-to-roll process. This innovative solar cell variant has great commercial potential since the design can be easily fabricated and integrated into a wide variety of surfaces and substrates such as tiled roofs, building facades, walls and so on. In this talk, we will discuss our investigations into new approaches for metal electrodes in DSSCs and differing fabrication techniques for back-contact DSSCs.

Keynote

Solar energy conversion

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The Strategic Research Cluster consists of 19 academic research groups housed at University College Dublin, Dublin City University and the University of Limerick. The aims of the Cluster are to develop 3rd generation photovoltaic (PV) and photoelectrochemical (PEC) cells for solar fuel production and H₂ storage and release. This presentation will focus on recent research achievements of the cluster in these areas.

Enhancing the electrocatalytic activity of tetrahedral Pt nanocrystals by adatom decoration

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The preparation of tetrahedral Pt nanocrystals (THH Pt NCs), reported in 2007, marked the first successful synthesis of Pt nanoparticles bound by well-defined high index facets.[1] Development of such materials offers the prospect of convergence between model electrocatalyst research and practical catalyst development. In agreement with theoretical predictions, the {730} surfaces of the THH Pt NCs are particularly active for the electro-oxidation of small organic molecules, owing to their high density of atomic step and kink sites. Unfortunately high intrinsic activity is often accompanied by a propensity towards self-poisoning and in situ FTIR measurements have confirmed the presence of strongly bound poisoning CO on the THH surfaces at very low potentials, owing to the dissociative adsorption of fuels such as formic acid or methanol.

Here we describe the decoration of THH Pt NC surfaces by foreign metal adatoms, with the aim of conferring poisoning tolerance upon the catalyst. Ru has been chosen in the case of the methanol oxidation reaction, while Au has been applied for formic acid electro-oxidation. Catalytic performance has been characterised by cyclic voltammetry, chronoamperometry and in situ FTIR spectroscopy. Ru decoration lowers the onset potential for methanol oxidation by over 100 mV and indeed Ru modified THH Pt NCs display much superior catalytic currents and CO₂ yields in the low potential range relative to a commercial PtRu alloy catalyst.[2] In the case of formic acid oxidation chronoamperometric current densities at low potentials are enhanced by over an order of magnitude in the presence of Au adatoms.

In-situ FTIR data and anodic CO stripping experiments suggest that the origins of the adatom induced promotional effects are different for either system. The Ru adatoms enhance methanol oxidation through a bi-functional mechanism whereas a third-body effect underlies the beneficial effect of Au adatoms on formic acid electro-oxidation. These results represent a step forward in the transfer of knowledge from single crystal electrode studies to the practical realm and as such are significant in the development of anodic catalysts for direct alcohol fuel cells.

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Electrochemical impedance analysis of ITM power's proton exchange membrane electrolyzers

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ITM Power

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Water electrolysis is becoming increasingly important because of the need for clean hydrogen as an energy carrier medium. Combining proton exchange membrane (PEM) electrolyzers with renewable energy sources produces zero carbon hydrogen that is extremely pure. To cope with the increasing demand for clean hydrogen ITM Power has developed extremely efficient PEM electrolyzers at a number of scales from small applications to megawatt refuellers. These electrolyzers are based upon ITM's patented membrane technology.

Whilst a number of electrochemical methods are utilised to characterise both electrode materials and electrochemical systems, the use of electrochemical impedance spectroscopy (EIS) is becoming increasingly common. EIS is a powerful technique for the characterisation of electrode materials, and can be used for in-situ non-destructive diagnosis of electrochemical systems; however, unfortunately EIS is often poorly understood.

This paper presents the use of EIS to both characterise and develop ITM's PEM electrolyser and will discuss what AC techniques can and cannot tell you about electrochemical systems.

Electrochemical Techniques/Sensors

Amperometric gas sensors for monitoring air quality

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Olalekan A. M. Popoola,^b Roderic L. Jones^b*

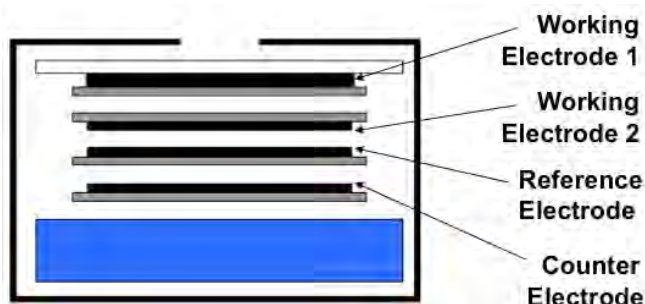
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Electrochemical sensors have been present in the gas sensing industry for more than 40 years and they are classically used to measure concentrations of toxic gases in the 10-10000 ppm range [1-3]. There is today a growing interest in measuring lower concentration ranges for monitoring air quality (ppb levels). The use of electrochemical sensors for monitoring air quality would provide a low cost alternative to the existing methods. However, the measurement of low concentration represents a challenging task. We propose first to review the operating principles of amperometric gas sensors, second to discuss how we adapted the current sensor design for low concentration measurements and third to illustrate applications by presenting some data obtained during a deployment of these sensors.

Standard amperometric sensors are 3-electrodes cells based on the fuel cell technology. Gases are detected on a solid sensing electrode at the interface between the gas phase and the internal liquid electrolyte phase [1-3].

Recently, a new range of amperometric sensors has been developed for measuring low concentration of NO₂, NO, CO, O₃, H₂S and SO₂. These sensors include two working electrodes: one is used as the sensing electrode while the other one is used to determine and subtract the background signal. Linearity, noise and cross-sensitivity issues are addressed. The influence of environmental parameters, such as temperature variations, needs to be accounted for. And particularly important is the methodology used to correct for the background current.



These sensors were deployed in the urban area of Cambridge and high frequency measurements were made. Collected data demonstrate the possibility of measuring environmental NO₂, NO and CO.

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Conducting polymers housed in microfluidic channels for electroanalytical applications

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Microfluidics, the ability to manipulate fluids that are geometrically constrained to sub-millimetre spaces has revolutionized lab-on-a-chip technology. Microfluidics enables such analytical and bioanalytical tasks as sample preparation and extraction, molecular separations and waste processing to be carried out on nanolitre and picolitre volumes by confining the liquids to micro-channels. One challenge facing this area is the introduction and integration of easily-controllable and miniaturised sensing and separation methods. The use of electrochemistry offers immense benefit because of the ease with which electrodes can be implemented in microfluidic chips without any loss of analytical sensitivity and the positive benefits of the use of electrodes in fluidic structures. We are interested in exploring electroanalytical tasks that could be achieved by the integration of conducting polymers into microfluidic channels.

The fabrication of microfluidic chips housing electrochemical cells is described. For example, one configuration comprises a sputtered three-electrode cell with gold serving as the electrode material. Conducting polymers such as polyaniline (PANI) can then be chemically or electrochemically grown in the microfluidic channel to have dimensions of the channel (e.g. 150 μm x 50 μm). Both bulk and inverse opal PANI structures are demonstrated to run the length of the microfluidic channel. The inverse opal structure is achieved by depositing an ordered polystyrene bead colloidal crystal prior to polymerisation. Electrochemical polymerisation of monomer (e.g., aniline) then takes place through this template, which is subsequently removed to leave a three-dimensional highly ordered, reproducible honeycomb structure of conducting polymer.

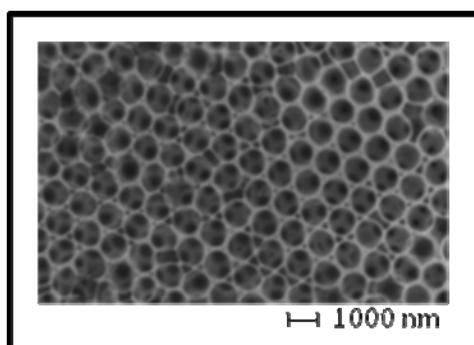


Figure 1: Polypyrrole microstructure fabricated via templating with polystyrene beads (1 micron).

It is envisaged that these conducting polymer-modified microfluidic chips could serve as flow-through stationary phases for lab-on-a-chip (LOC) chromatographic applications, drug delivery or flow-through electrochemical (bio-)sensors.

Keynote

Enhancing electrochemical 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, e.g., genetic disorders and infections by pathogens. Electrochemical genosensors are of particular interest because they are miniaturised more readily than optical sensors, typically require small sample volumes, little sample pre-treatment, and are suitable for use with portable instrumentation by minimally trained clinical personnel.

We here present 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, either DNA or PNA (peptide nucleic acid) 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, establishing a detectable electronic contact, thus acting as “sensitisers” for the electrochemical detection.

Electrochemical impedance spectroscopy and cyclic voltammetry measurements were carried out using two types of sensitisers: a Co aqphen complex binding to dsDNA through intercalation and a cationic quaterthiophene binding through the minor groove.

The intercalation of a cobalt(II) complex containing mixed-ligands of 12,17-dihydronaphtho-2,3-hdipyrido-3,2-a:2',3'-c-phenazine-12,17-dione (aqphen) and glycolic acid (GA), [Co(GA)₂(aqphen)] with DNA was investigated by electronic absorption spectroscopy. The corresponding phen complex, with an oxidation potential of 0.12 V vs Ag/AgCl, had previously shown weak intercalation [2]. Increasing the conjugation with an anthraquinone increased significantly the binding affinity of the complex.

The use of an optoelectronically active cationic quaterthiophene as a sensitizer was also explored. This water-soluble quaterthiophene interacts with dsDNA with an affinity of 10^5 M^{-1} and has an oxidation potential of 1.0 V vs Ag/AgCl.

Both sensitizers show promising enhancement of electrochemical DNA detection and highlight structural features favouring selectivity in sensing, paving the way towards a new generation of point-of-care electrochemical biosensors for genotyping.

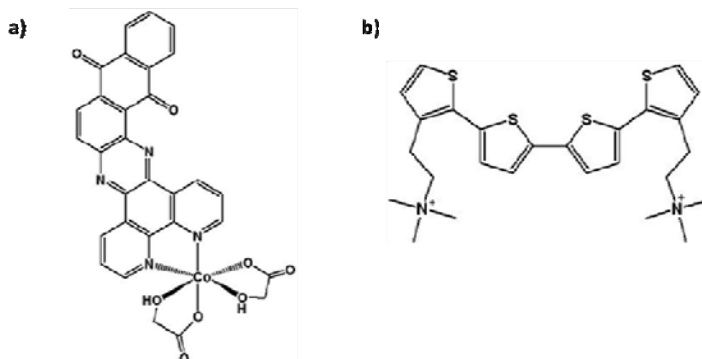


Figure 1 - Sensitisers developed: a) Co aqphen complex; b) cationic quaterthiophene.

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Prussian blue nanotubes sensor powered by H₂O₂

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We describe a Prussian blue nanotubes sensor using a two-compartment cell which derives the current signal from the chemical energy of the hydrogen peroxide analyte, without input of electrical potentials. The Prussian blue reduces hydrogen peroxide and is itself reduced by electron flow from the counter reaction at the auxiliary electrode. The concentrations of the Prussian blue (PB) and Everitt's salt (ES) forms of the Prussian blue are maintained at steady-state values, by the hydrogen peroxide reduction and the galvanic cell reaction. This strategy gives low detection limit of 0.1 μM H₂O₂ with linear range up to 80 μM and is further demonstrated in a model glucose biosensor. The sensor is applied to a unique virus sensor powered by hydrogen peroxide based on the formation of antibody-virus complexes within the sensor's membrane nanochannels. This strategy exploits the change in membrane resistance of the chemically powered sensor, comprising a Prussian blue nanotubes (PB-*nt*) membrane cathode and a platinum mesh anode. The method reports response time of ~ 5 min toward unlabelled virus target, at low concentration values of 3 to 45 plaque forming unit per mL (pfu mL⁻¹) and can clearly differentiate dengue virus serotype 2 from serotype 3. When filled with Nafion[®] perfluorinated resin, the PB-*nt* membrane demonstrates potential utilization as a standalone probe without input of electrical power, offers the promise of a sustainable, low cost and rapid H₂O₂-powered virus detection tool.

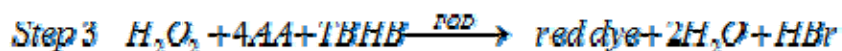
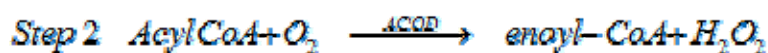
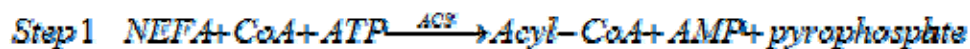
Layer-by-layer assembly of enzyme electrodes for non-esterified fatty acids biosensors

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Diabetes is increasingly understood as disordered energy metabolism involving both sugar and fat utilisation. Patients with Type 2 diabetes often show a higher level of non-esterified fatty acids (NEFA). NEFA, like glucose can reflect acute change of the energy status from an individual, thus its concentration in blood can be used as a biomarker for diabetes. The monitoring of changes of both sugar and NEFA during metabolic processes would provide a more accurate means of diagnosis and disease prevention. Moreover, it would offer more comprehensive information of the patient's metabolic profile and leads to better disease management.

Current commercial in-vitro enzymatic colourimetric assay available for quantitative determination of NEFA in serum samples involves few steps and has to be carried out in the lab. The assay from Roche consists:



Therefore, there is an urge to develop electrochemical biosensors for NEFA to allow simultaneous monitoring of glucose and NEFA, which can be the basis for a multiplex sensor platform for the future development of personalised intervention programmes for treatment and management of the disease.

In this study, an electrochemical biosensor for non-esterified fatty acids (NEFA) based on enzyme electrodes is demonstrated. Multilayer film of poly(dimethyldiallylammonium chloride) (PDA) wrapped multi-wall carbon nanotubes (MWCNTs) and acyl-CoA oxidase (ACOD) and acyl-CoA synthetase were assembled on a carbon screen-printed electrode by the Layer-by-Layer (LbL) technique. The versatility of the LbL technique enables simultaneous immobilization of two or more enzymes in different polymer layers on one electrode. The polymer-CNTs and enzyme modified electrode exhibited linear increase of oxidation current with elevating oleic acid and palmitic acid as a promising technique to develop novel NEFA biosensor.

Development of a sandwich format, amperometric uric acid biosensor for urine analysis

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The purpose of the present investigation was to develop a uric acid (UA) biosensor for biomedical diagnostic applications. A water-based carbon ink containing the electrocatalyst cobalt phthalocyanine (CoPC) was used to fabricate screen-printed electrodes (designated CoPC-SPCEs) which acted as the base transducer for biosensor construction [1].

Voltammetric studies were performed with these devices in the presence and absence of H₂O₂ and UA to characterise their redox behaviour under various solution conditions. The results indicated that a suitable oxidation peak could be obtained for H₂O₂ which was a pre-requisite for the operation of the proposed biosensor. A sandwich biosensor was fabricated by first depositing cellulose acetate (CA) onto the transducer, followed by uricase (UOX) and finally a polycarbonate (PC) membrane. The final biosensor designated as PC-UOX-CA-CoPC-SPCE, was used in conjunction with chronoamperometry in order to optimise the conditions for the analysis of urine. The proposed biosensor was applied to urine from a healthy subject and the resulting precision and recovery was 4.21 % and 97.3 % respectively. The linear working range of the biosensor was found to be 0.015 mM - 0.25 mM, the former represents the detection limit; the sensitivity was calculated to be 2.10 μ A/mM. This paper will describe the steps involved in the development of the proposed biosensor.

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Keynote

Modification of the interface between two immiscible electrolyte solutions with silica films

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Modification of an electrode surface has been motivated by the need to improve electroanalytical performances. Among different modification strategies, electrogeneration of a silica thin film on electrode surfaces has recently emerged as a promising method for the development of electroanalytical sensors [1]. Similarly to solid electrodes, the interface between two immiscible electrolyte solutions (ITIES) can be modified to provide improved sensitivity [2] and selectivity [3].

At the convergence of these two research fields, we have investigated the modification of the ITIES with silica films by two electrochemical means. Firstly, a silica film was formed by the electrochemically-controlled transfer of cetyltrimethyl ammonium from the organic phase to an aqueous phase containing hydrolised tetraethoxysilane. The presence of these two species in the aqueous phase leads to the formation of a silica film. Experimental conditions (pH, tetraethoxysilane and cetyltrimethyl ammonium concentrations) were investigated. The second method involved the electrodeposition of a silica thin film on top of a solid-state nanoporous membrane. The localisation of the thin film electrodeposition was controlled by scanning electrochemical microscopy [4]. The silica films were characterised by scanning electron microscopy and XPS analysis.

This research presented here will contribute to the development of a new class of electrochemical sensors based on ITIES modified with silica films.

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Direct ion speciation analysis with ion-selective membranes operated in a tandem potentiometric/time resolved chronopotentiometric sensing mode

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In this communication, we present a new methodology able to detect free and total ion concentration in the physiological range with highly selective membrane electrodes. A sensing element, based on polypropylene ion-selective membrane doped with high amount of ionophore, is, during a first period, interrogated by potentiometry (open circuital potential determination) and, subsequently, by a fast galvanostatic and potentiostatic pulse. Data gathered from both modes of operation with the same membrane electrode allows one to distinguish between uncomplexed and available ion concentrations in the sample.

When the membrane, which presents permselective features due to the incorporation of ion-exchanger sites, is measured in the potentiometric mode, the logarithm of the so-called free concentration of the analyte is obtained from the potential reading, in complete analogy to classical ion-selective electrodes. Afterwards, a cathodic constant current pulse is applied to the same membrane (150 A for 4s), achieving a selective local ion depletion near the membrane surface that is accomplished within a few seconds measurement time. The observed transition time is a direct measure of the total available ion concentration in the sample. After this perturbation step, a potentiostatic pulse (0-100 mV for 30 s) is required to regenerate the ion-selective membrane. Fig.1a shows the chronopotentiogram as a function of increasing calcium concentration. The observed inflexion point corresponds to the localized calcium depletion event. The square root of time of each inflexion point is an intrinsic value of each calcium concentration (Fig.1b), in accordance to the Cottrell equation. Numerical simulations of this experiment correlate very well with experimental findings.

Fast and simple calcium speciation of undiluted blood is still an issue in clinical analysis. The methodology proposed here allows one to determine total calcium levels of up to 3 mM, which is compatible with the blood calcium concentration range of 2.2-2.6 mM, where 50% is in the ionized form and the remaining 50% is in the form of various complexes. The direct detection of ionized and total calcium in undiluted blood samples will be demonstrated.

Fig 1: a) Chronopotentiograms for Ca-ion selective membrane, demonstrating the direct detection of total calcium. b) Transition peaks for each concentration (inset calibration curve: Square root of transition time vs calcium concentration)

Impedimetric detection of MRSA from clinical isolates

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The emergence of antibiotic resistant bacteria such as MRSA is a growing public health concern. To better guide clinical decision making it would be desirable to develop an electrochemical sensor capable of rapid MRSA detection. Using in PNA form a nucleic acid probe sequence developed from experiments on glass microarrays we were able to develop an impedimetric assay for MRSA using planar gold electrodes. PCR was carried out on bacterial samples and the antibiotic resistance conferring *mecA* gene amplified from MRSA cells. Testing was performed on patient samples from Edinburgh Royal infirmary. Following amplification, impedimetric detection of *mecA* target DNA was achieved by measuring hybridisation induced increases in the charge transfer resistance (R_{CT}). The assay's L.O.D was found to be 10 pM and the proximity of the probe sequence to the electrode surface was found to be a key parameter in improving assay sensitivity. The assay could be performed either in batch mode with elevated temperatures and stringency washing steps or on screen printed electrodes in an "online" fashion under ambient conditions where real time hybridisation induced changes in the charge transfer resistance were continuously measured. Assay specificity was also evaluated and it was found that cross reactivity with DNA from other bacterial species was not significant, even under ambient conditions. These findings pave the way for the possibility of rapid analysis of MRSA samples in clinical situations.

The electrochemical and spectroscopic properties of boron doped diamond

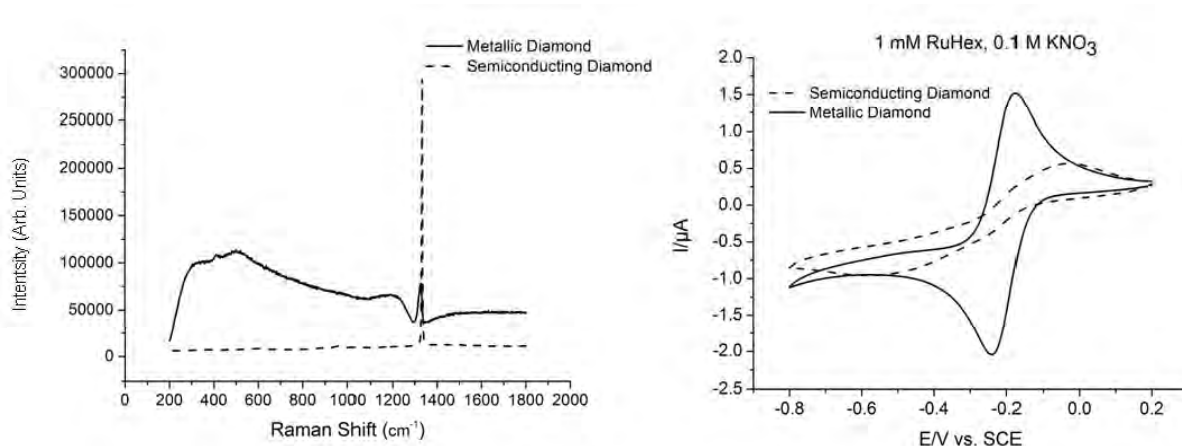
James Iacobini, Laura Hutton and Julie Macpherson

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Boron doped diamond (BDD) has emerged as an important material for electrochemists due to its truly unique properties such as low background currents, large potential window, high thermal and electrical conductivity and its resistance to chemical attack.¹ In order to be utilised as an analytical electrode material however, diamond must first be fully characterised in order to relate fundamental material properties and electrochemical behaviour.

In this work, Raman spectroscopy, resistivity and voltammetric measurements are used to show the impact of boron and sp^2 carbon concentration on the electrochemical response of BDD electrodes. Electrochemical behaviour for common redox species was studied using samples obtained from different sources and of various doping levels.

In order to exploit the high thermal conductivity of diamond, thermal modulation via light irradiation of BDD electrodes has also been investigated. An enhancement in current is observed at elevated temperature, where short pulse times have been used to avoid the effects of convection in solution.³



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Nanoelectrochemistry

Studies of photosensitised p-NiO electrodes for tandem solar cells

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Traditionally, photovoltaic cells are constructed based on a single light harvesting semiconductor. The maximum achievable light to electricity conversion efficiency ($\eta\%$) of such devices is given by the Shockley-Queisser limit and it is around 31% [1]. In order to move beyond the Shockley-Queisser limit while reducing the production cost to an affordable level, novel solar cell structures with new materials such as Tandem solar cells need to be explored. A typical Tandem cell is composed of two or more photoactive anodic and cathodic semiconductors.

NiO is a promising cathodic semiconductor material to construct mesoporous electrodes. In fact, it has been proven that NiO electrodes can be employed in dye-sensitised Tandem solar cells consisting of a dye-sensitised photoanode and a dye-sensitised photocathode [2]. The focus of this work is to construct porous NiO mesoporous photocathodes on transparent conducting glass substrates fabricated using several methods such as aerosol assisted chemical vapour deposition (AACVD), doctor blade. Such electrodes were then photosensitised using narrow bandgap semiconductors which are strong visible light absorbers (i.e. CuO and Cu₂O). These photosensitised NiO cathodes were characterised for their material, optical, electrical and photoelectrochemical (PEC) properties. PEC properties were recorded using standard 3-electrode photoelectrochemical (PEC) cell setup. As expected, the electrodes have shown the photocathodic behaviour but further improvements are needed.

It is anticipated that these photosensitised cathodes can be employed in Tandem solar cell configurations and construct efficient photovoltaic cells.

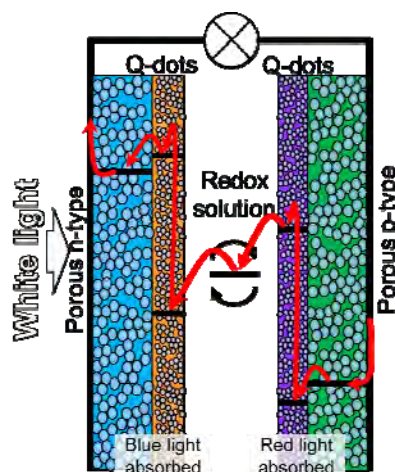


Figure 1. Schematic of Tandem solar cell

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Cobalt-based redox mediators for dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs), pioneered by Grätzel and co-workers [1], have received great interest as low-cost alternatives to silicon-based photovoltaic devices [2]. The best performing DSSCs make use of a nanocrystalline TiO_2 semiconductor electrode sensitized with ruthenium based dyes, together with an iodide/tri-iodide redox couple; these DSSCs have delivered efficiencies of around 11-12 % in the lab scale to date [3]. However, recently, it has been of great interest to find alternative redox mediators to the iodide/tri-iodide redox couple, as performance of DSSCs employing this redox couple have been limited by the position of its redox energy level with respect to quasi-Fermi level of TiO_2 . It is thought that using a redox mediator with a high redox potential would result in higher open circuit voltage (V_{oc}), and hence increase overall efficiency. Furthermore, the high visible light absorption of the tri-iodide and its volatility together with its high corrosiveness hinder attempts to develop DSSCs with long life times. [4].

Cobalt-based redox mediators offer many key advantages over the iodide/tri-iodide redox couple, such as their weak visible light absorption, their non-corrosive and non-volatile nature, and the relative ease of structure (and hence property) modification. In this study, a new cobalt complex $[\text{Co}(\text{bip})_2]^{2/3+}$ (bip = 2,6-bis(2-benzimidazolyl)pyridine) was synthesised for use as a redox mediator in DSSCs; its redox position was determined by conducting cyclic voltammetric studies and its performance in DSSC was evaluated by employing it as a redox mediator in the cell. The performance of $[\text{Co}(\text{bip})_2]^{2/3+}$ was compared with other cobalt bis-benzimidazolyl pyridine derivatives, $[\text{Co}(\text{dmbip})_2]^{2/3+}$ (dmbip = 2,6-bis(1'-methylbenzimidazolyl)pyridine) and $[\text{Co}(\text{dbbip})_2]^{2/3+}$ (dbbip = 2,6-bis(1'-butylbenzimidazolyl)pyridine). The new cobalt complex exhibited a higher redox potential than the other well studied derivatives, however, this did not translate in to a higher V_{oc} , although the DSSCs did show much higher current densities (J_{sc}).

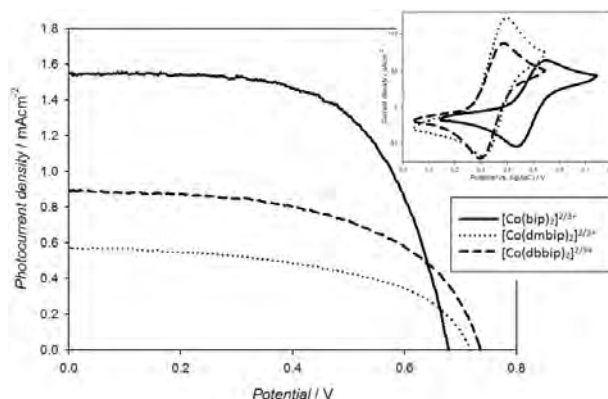


Figure 1. *Current-voltage* characteristics of DSSCs employing Co-based redox mediators. Inset: cyclic voltammograms of Co complexes.

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Keynote

Magnetically-structured electrodeposits

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An overview of the uses of magnetic fields for structuring electrodeposits will be given, illustrated with recent results on the patterning of cobalt, nickel, copper and zinc electrodeposits with linear or dot arrays [1] of permanent magnets. The magnetic properties of the metal ions in their oxidized and reduced states, together with variables including the array structure, ion concentration, bias magnetic field, ion concentration, cell orientation (gravity) and deposition time all influence the patterns of the electrodeposits, often in beautiful and unexpected ways. An understanding of the physical forces, and chemical and hydrodynamic factors involved is established by systematic modification of the variables.

The results for direct deposits from paramagnetic cations such as Cu^{2+} , when convection is minimized, are largely explained in terms of magnetic pressure, which governs the width of the *diffusion layer*, thereby modifying mass transport. The effects are absent at very short times, before the diffusion layer has had a chance to form, and at very long times, when the modulation is much less than the diffusion layer thickness. The patterning depends on the presence of *orthogonal* magnetic field gradient and concentration gradient in the electrolyte, and a critical feature is the magnetic susceptibility of the electroactive species relative to the nonelectroactive background.

An inverse effect arises when the electrolyte contains a high concentration of strongly paramagnetic, but nonelectroactive lanthanide ions. Which make electroactive Zn^{2+} or Cu^{2+} behave as if they were strongly diamagnetic, and they therefore deposit in inverse patterns, where deposition tends to be concentrated in regions where the magnetic field is lowest. There may be blocking of surface sites in the double layer by the lanthanide ions. Magnetic contrast is also operative at overpotentials where hydrogen is produced. Arrays of hydrogen bubbles can be structured with arrays of magnets.

Another effect of magnetic field is on the *double layer*. There Maxwell stress can deform ones of the electrolyte rich in magnetic ions, and the capacitance is changed. This, in turn, can significantly influence the reaction kinetics. The example of the influence of a magnetic field on the nucleation of zinc crystallites will be discussed.

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Electroanalysis at gold nanowire electrodes

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As critical dimensions of electrodes enter the nano regime, radial diffusion profiles to the electrode dominate resulting in enhanced analyte mass transport, leading to higher current densities, reduced double layer capacitance, increased S/N and steady-state voltammograms. A variety of different fabrication approaches of nanoelectrodes have been reported to date. However challenges arising from difficulty in fabrication pathways, lack of reproducibility and small electrochemical currents (<100 pA), are still prevalent. Recently 1-dimensional nanostructures based on bands and wires are being explored as nanoelectrodes to provide practical solutions. 1-dimensional nanoelectrodes, such as nanowires, benefit from nanoscale critical dimensions (width) ensuring enhanced mass transport, while the high aspect ratio permits higher measurable currents in the ≥ 1 nA regime and with uniform current densities.

In the work, we report the fabrication and in-depth electrochemical analysis of discrete gold nanowire electrodes for use in electrochemical applications. The single nanowire electrodes and nanowire electrode arrays were fabricated using a hybrid E-beam / photolithography approach, providing electrodes with well defined and reproducible dimensions. Finite element diffusion domain simulation studies were employed to explore mass transport to nanowire electrodes. Simulation results suggested that radial diffusion to nanowires should be present at fast scan rates. This behaviour was confirmed experimentally where CVs obtained in FcCOOH, were observed to be steady-state, with high currents (nA) and sigmoidal up to 1000 mV s⁻¹. The electrochemical responses of nanowires, in model redox mediators, were excellently described by Butler-Volmer kinetics. The nanowire electrodes are applied to reproducible determination of heterogeneous electron transfer-rate constants, k_0 , for three key model redox analytes, FcCOOH, Fe(II)(CN)₆⁴⁻, and Ru(NH₃)₆³⁺.

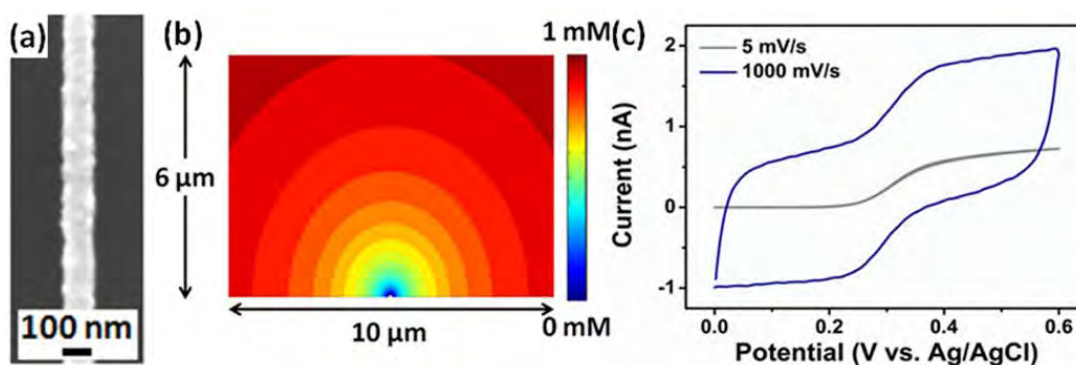


Fig 1: (a) High resolution SEM micrograph of gold nanowire electrode, (b) Concentration profile simulations of a plane perpendicular to a single nanowire electrode at 0.5 V @ 1000 mV s⁻¹. (c) Steady-state voltammograms measured in 1 mM FcCOOH at 5 mV s⁻¹ and 1000 mV s⁻¹.

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Comparison of performance of an array of nanoband electrodes with a marco electrode with similar overall area

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We compare the behaviour of an array of platinum nanoband electrodes with a single electrode having approximately the same active electrode area. The nanoband electrode array exhibited highly elevated current fluxes and faster heterogeneous electron transfer rates than observed at the single electrode analogue. The nanoband electrode array also exhibited low susceptibility to stirring and convection of the electrolyte and an absence of diffusion limitation even at elevated scan rates. When the nanoband array structure is polarised for extended periods of time (greater than a few seconds) diffusion field overlap between neighbouring elements was apparent. The low noise and significant currents passed by the nanoband arrays suggest that this approach may offer significant benefits in a number of areas of electroanalytical and fundamental electrochemical research.

Concept of diffusional independence at gold nanowire electrodes in array: theory and experiments

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There is a need to understand diffusion of molecules at nanowire electrodes in order to improve their efficiency as nanosensors. Radial diffusion of electroactive species at single gold nanowire electrodes results in enhanced analyte mass transport, leading to higher current densities, reduced double layer capacitance, increased S/N and steady-state response. Furthermore, these enhancements are expected to be of a greater extent at gold nanowire electrodes in array. As such, maximum efficiency may be obtained when the diffusion at each nanowire is independent from its neighbouring nanowire.

In this work, we employed finite element diffusion domain simulation studies to assess the minimum separation between neighboring electrodes allowing diffusion independence. Therefore, we simulated diffusional mass transport at three gold nanowire electrodes in array, separated by 5, 10, 15 and 20 μm . Simulation results suggested that radial diffusion to nanowires should be present at fast scan rates for a separation between 10 μm , where diffusional overlap of adjacent concentration profile is observed, and 15 μm , where the diffusion profiles of each nanowire is independent. In order to validate this, electrodes were then fabricated and corresponding experimental measurements were carried out. Experimental results appeared to be in excellent agreement with simulated results.

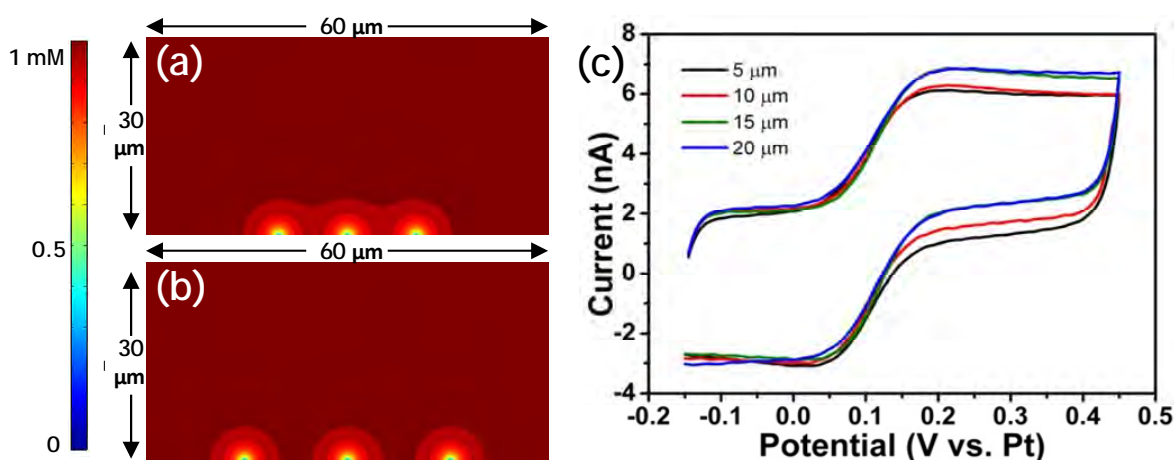


Fig 1: 2D simulations of FcCOOH concentration profiles at 5000 mV.s⁻¹ normal to three nanowire electrodes in array separated by (a) 10 μm and (b) 15 μm . (c) Corresponding experimental cyclic voltammogram.

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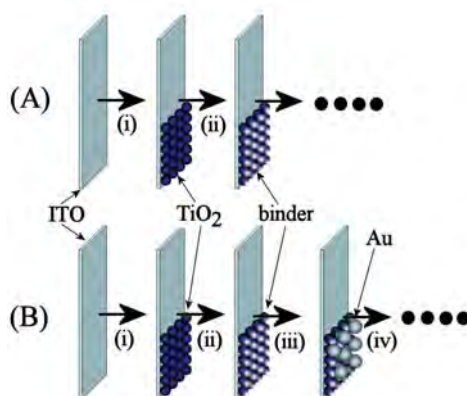
Keynote

Electrochemical processes in mesoporous films of metal oxide nanoparticles

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Very thin films of metal oxide nanoparticles are readily formed in a layer-by-layer approach for example with TiO_2 [1], SnO_2 [2], CeO_2 [3], or Fe_2O_3 [4]. The resulting films provide an extended triple phase boundary contact zone to the underlying electrode and the effective shielding from pore-electrolyte eliminates potential gradients. The resulting films can be studied by voltammetry and spectro-electrochemistry. Processes including photo-activation and electron hopping are discussed.



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Electrochemical understanding of gold deposition process at the water/1,2-dichloroethane interface

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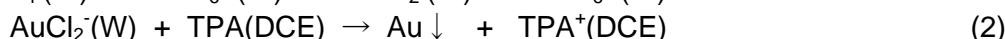
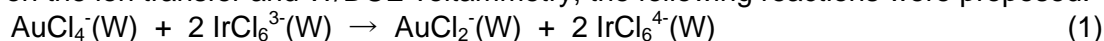
The formation of nanoparticles has been widely investigated due to their broad potential applications in many areas such as catalysis, electronics and coating applications. The deposition of various metals, e.g. Au, Pd, Pt, and Ag has been investigated at the liquid/liquid interface [1]. However, few studies of the spontaneous growth process have been carried out based on electrochemical considerations [2]. In this study, spontaneous process of gold deposition was investigated based on ion transfer voltammetry at the water/1,2-dichloroethane (W/DCE) interface and the corresponding redox voltammetry of the metal precursor (in W) and the reductant, triphenylamine (TPA) in DCE. The metal precursor can be present as either Au(III), or as Au(I), the latter being formed by reduction of the Au(III) with Iridium(III) hexachloride. Electron transfer between the Au salts and TPA is only spontaneous if the distribution potential of the W/DCE interface is controlled via partitioning of an appropriate hydrophilic ion, in this case Na⁺, i.e.:

(W) 5 ml	(DCE) 5 ml
0.5 mM HAuCl ₄	5 mM TPA
0 OR 5 mM	5 mM Na tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate
(NH ₄) ₃ IrCl ₆	(TFPB)
0.1 M NaCl	

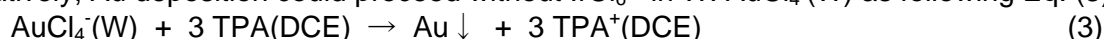
It was found that gold particles formed at the interface. The reduction process was analyzed using the Galvani potential difference, $\Delta^w_o\phi$, established between W and DCE from the standard transfer potential of the AuCl₄⁻, AuCl₂⁻, and Na⁺ ions and the reduction potentials of the AuCl₄⁻|AuCl₂⁻, IrCl₆⁴⁻|IrCl₆³⁻, and TPA|TPA⁺ couples dissolved in W and DCE. The electron transfer could also be observed voltammetrically by using the following system, where the metal deposition is driven externally (potentiostatically) rather than by the Nernst-Donnan equilibrium in the first cell:

(W)	(DCE)
0.5 mM HAuCl ₄	5 mM TPA
0 OR 5 mM	1 mM bis(triphenyl)phosphoranylidene ammonium TFPB
(NH ₄) ₃ IrCl ₆	(as a supporting electrolyte)
0.1 M NaCl	

Based on the ion transfer and W/DCE voltammetry, the following reactions were proposed.



Alternatively, Au deposition could proceed without IrCl₆³⁻ in W. AuCl₄⁻(W) as following Eq. (3).



We are currently investigating the influence of the applied potential on the deposition rate and morphology of the Au particles.

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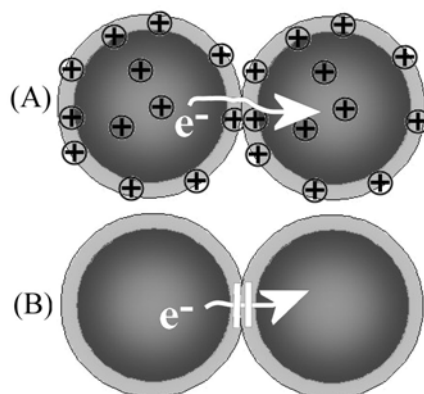
Hydrothermal core-shell nanocarbons

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Carbon nanoparticles (ca. 9-18 nm diameter) with phenylsulfonate surface functionality (Emperor 2000, Cabot Corp.) have been successfully employed in electroanalytical processes [1-4] and are here coated with chitosan-based hydrothermal carbon to give a novel highly pH-responsive core-shell nanocarbon material. With optimised core-shell ratio modified electrodes exhibit highly pH-sensitive resistance, capacitance, and Faradaic electron transfer. A shell “double layer exclusion” mechanism is proposed to explain the voltammetric features and the observed pH switching effects. Based on this mechanism, a broader range of future applications of responsive core-shell nanoparticles is proposed.



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Electrochemical investigation of redox centres in gold nanoparticles and copper coordination compounds

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Redox systems that could lead to Negative Differential Resistance behaviour based on conformational changes and Coulomb blockade effects have been investigated. The properties of copper coordination compounds with macrocycles and gold nanocluster with redox centres were studied with a view to build oscillators in the nanoscale with a possible application in associative memories.^[1]

Hexanethiolate gold nanoparticles with an average core diameter of 1.8 nm and a well-defined capacitance were synthesised by a two-phase method.^[2] These clusters were further functionalised with 6-(ferrocenyl)-1-hexanethiol by a place-exchange reaction.^[3, 4] The electrochemistry of hybrids containing an average of 10, 7 and 4 ferrocene units per cluster was studied and Quantized Double Layer (QDL) charging events of the core and of the redox Fc^+/Fc couple were investigated by Differential Pulse Voltammetry (DPV) and Cyclic Voltammetry (CV). A transition from multiple to single electron transfer was observed as the number of ferrocene sites per cluster was decreased. An electrostatic switching mechanism in the nanoscale also resulted from the oxidation of all the ferrocene centres that resulted in the quenching of electron transfer between the nanoparticle gold core and the electrode.

The electrochemical reduction of Cu(II) centres to Cu(I) leads to a conformational switch from a distorted octahedral to a tetrahedral geometry.^[5, 6] The properties of the Cu(II)/Cu(I) redox couple in coordination compounds with macrocyclic ligands depend on the ring cavity size and the nature of the donor set. In the present work, three tetraamine ligands with increasing size from 14- to 16-membered ring and two macrocycles with mixed donor atoms (N_2S_2) were investigated to study the influence of the cavity size on the electrochemical response and the effect of the donor atoms present. The stability of Cu(II) species decreased for larger macrocycles in which softer donor atoms (i.e., sulfur) and substitution in the amines groups of the ligand were introduced.

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Electromobility revisited: electrochemistry for biofuel generation?!

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Despite the strong political and scientific efforts to develop and to establish the fundamentals for electromobility (a domain for electrochemistry) combustion engines will still, and possibly for decades, be the dominating technology on our streets. Thus, to assure mobility under the considerations of sustainability the search for new and efficient routes to produce fuels from biomass, i.e. biofuels, has not lost significance. On the other hand, electricity based on wind power and photovoltaics reaches significant market shares. Here, the fluctuating nature of these renewable energies calls for new technologies to convert the so far mainly unused electricity during overproduction into a storable form. An example is the current strong effort to convert wind energy into gaseous fuels like hydrogen or methane via electrolysis

In this lecture the use of electrochemistry for the production of liquid biofuels is proposed and discussed by means of recent research examples. It is demonstrated that electrochemistry can provide an interesting – and sustainable – alternative to existing, petrochemical conversion routes.

Bioelectrochemistry

Keynote

Large amplitude fourier transformed AC voltammetry and new form of data analysis applied to the electrochemistry of cytochrome C peroxidase

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Almost all studies to date on cytochrome C peroxidase have used DC cyclic voltammetry to probe the electron transfer and coupled chemical reactions that may occur. However, because of their large size, a relatively small number of molecules are confined to the surface and hence the DC faradaic currents of interest tend to be masked by the background DC current. This poor signal to background current ratio creates great difficulty in providing detailed understanding of the mechanisms. In recent years, we have shown that when large amplitude AC techniques are subjected to Fourier Transform methods of analysis, then the DC and up to 8-harmonic components can be resolved. Of particular interest are the non-linear terms that give rise to second and higher harmonics when a sinusoidal waveform is used. In this lecture, studies with surface confined cytochrome C peroxidase will be considered. In particular, new data analysis strategies that can now be implemented very efficiently and effectively will be described. Contributions from surface heterogeneity and thermodynamic and kinetic dispersion arising from molecules not being exactly equivalent will also be considered. New studies with new forms of data analysis that have been undertaken very recently will also be described.

New features in the mechanism of electrocatalytic dioxygen reduction by multicopper oxidases revealed by protein film electrochemistry and finite time-domain modelling

Christopher F. Blanford

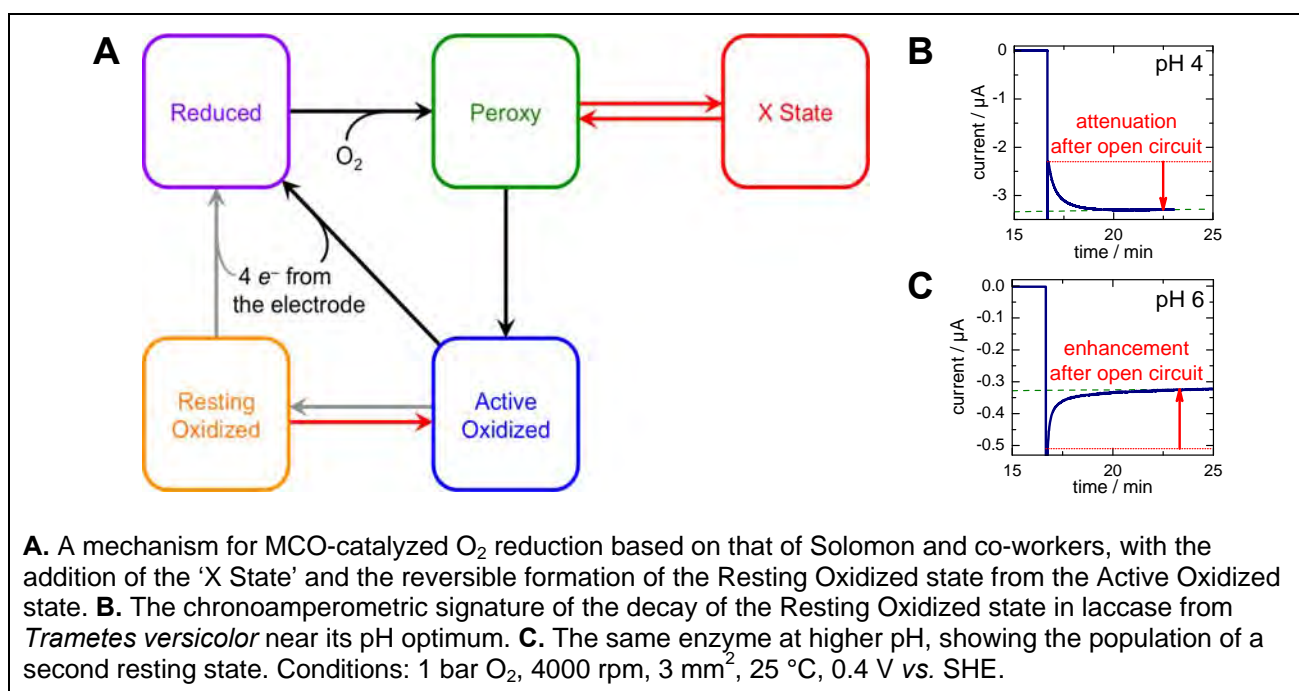
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The multicopper oxidases (MCOs) are a broad family of enzymes found in all kingdoms of life. The MCOs couple the catalytic reduction of O_2 to H_2O to the oxidation of a wide range of inorganic and organic substrates. In addition to industrial biotechnology applications ranging from medical diagnostics to food technology and dye decolorization, MCOs have been extensively investigated as real or inspirational catalysts for cathodes in low-temperature fuel cells.

A widely accepted mechanism for MCO-catalysed four-electron O_2 reduction has been assembled from extensive spectroscopic investigations and DFT/MM modeling. The scheme consists of four states which are distinguished by the oxidation state and coordination of the enzymes' copper ions. Three of these states comprise the main catalytic cycle; the fourth 'Resting Oxidized' state forms in the absence of reducing equivalents (**Panel A**).

I will present electrochemical and computational evidence of additional features in the mechanism. Using protein film electrochemistry, we found that the dormant 'Resting Oxidized' state must be in equilibrium with a catalytically active form (**Panel B**), in contrast to the prevailing model.¹ We also observed electrocatalytic behavior consistent with a second reversible resting state (**Panel C**) that lies outside the main catalytic cycle (the 'X State') in MCOs of fungal, plant and bacterial origin. The X State was most apparent when the enzymes were turning over O_2 at pH values several units above their respective optima. These findings were elucidated through computational finite time difference modeling and numerical analysis, which allowed this previously undescribed state to be positioned in the catalytic cycle as a dead-end state from the Peroxy-level catalytic intermediate.



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Optimisation of a glucose oxidase / cellulose / carbon nanotube based bioelectrode

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The potential application of glucose oxidase (GOd) as an enzymatic biological fuel cell (BFC) component has been extensively studied. Direct electron transfer (DET) between the enzyme and the electrode is of great strategic interest because the exclusion of toxic mediators would be beneficial for use of GOd-based devices *in vivo*. Traditionally, DET by GOd has been obtained by using advanced materials, such as: carbon nanotubes and graphene which transfer electrons from the flavin adenine dinucleotide (FAD) cofactor located within the enzyme structure.

This work reports the optimisation of an electrode architecture, formed from multi-walled carbon nanotubes (MWCNT) and ionic-liquid-reconstituted cellulose, which acts as a cheap yet robust platform for DET by GOd. Enhanced bio-electrocatalytic oxidation of glucose is observed, with a 20-fold increase in current density relative to the work of others.

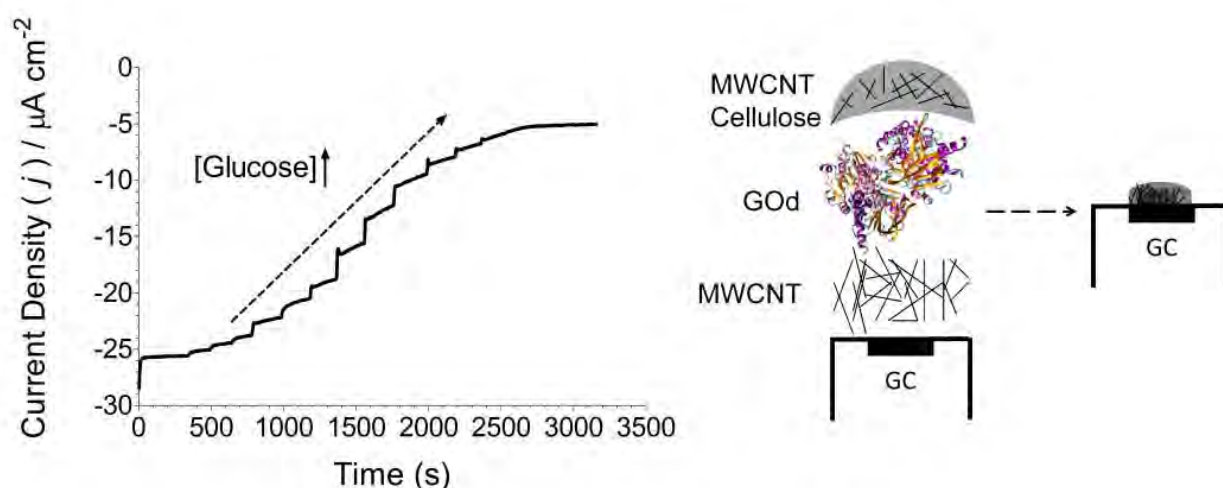


Fig. 1. (Left) Chronoamperometric response of the GOd bioelectrode to glucose on a rotating disk electrode. (Right) Scheme of the GOd bioelectrode configuration.

Nanoporous gold electrodes as matrices for enzymes immobilization applied in biosensors and biofuel cells

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The creation of an efficient biosensor and biofuel cell is dependent on a few essential factors: the choice of the conductive support material, the choice of the redox enzyme and the choice of the method capable of developing a stable connection and a fast electron transfer.

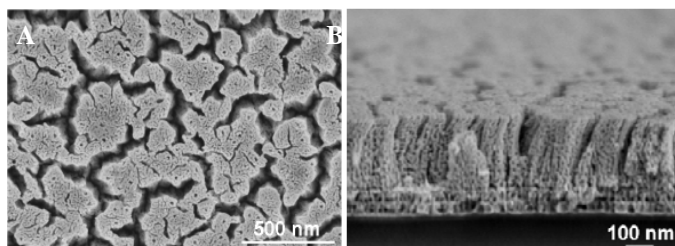


Fig. 1 Top-down (A) and cross-section (B) scanning electron microscopy image of a nanoporous gold electrode

Nanoporous gold electrodes (**Fig. 1**) with 28 times higher active surface area compared to the surface area of planar gold electrodes are used as a support material. Nanoporous gold is made by dealloying of Au-Ag alloy in a concentrated nitric acid. In the dealloying process the gold atoms assemble into a 3D-structure to form a material with tunable pore sizes ranging from few nanometres to several microns in diameter. The desired pore diameter is achieved by varying the temperature and the preparation time. The surfaces of the pores can be easily modified what allows to achieve even 11 times higher redox enzymes loading compared to the planar gold surface.

The previously optimized enzyme/mediator system as well as the newly developed method for direct immobilization is used to fabricate altered types of bio-cathodes and bio-anodes with redox enzymes: glucose oxidase (GOD), cellobiose dehydrogenase (CDH), laccase (Lc) and bilirubin oxidase (BOD). Obtained bio-electrodes are utilised in the development of biofuel cells based on both mediated and direct electron transfer.

Keynote

DNA-templated nanowires

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DNA is an excellent template on which to prepare a variety of conductive inorganic and organic materials because it is chemically robust, available in controlled lengths and has a persistence length of about 50 nm. Micrometre lengths of DNA are insulating for all practical purposes, but metals¹, binary semiconductors^{2,3} and conjugated polymers^{4,5} can all be synthesized on a DNA template in the form of wires of diameter 5-20 nm and lengths up to 100 μm . Typically a small excess of the metal ion is mixed with aqueous λ -DNA and reduced to the metal or precipitated with hydroxide or sulfide. Conjugated polymers are templated by oxidative polymerisation in the presence of DNA.

Despite the differences in the chemical processes to form these materials, the evolution of the morphology of the nanowires shares several common aspects. We will describe a simple thermodynamic model that rationalizes the AFM data and explains the observed variations in electrical properties compared to the bulk materials.

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Inactivation processes of immobilised redox enzymes studied by an electrochemical quartz crystal microbalance

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Blue multicopper oxidases (BMCOs) such as laccase and bilirubin oxidase (BOx) are efficient electrocatalysts for the technologically important four-electron reduction of dioxygen to water.¹ Immobilizing these enzymes on conductive electrode surfaces allows us not only to study their catalytic behaviour but also to harness their efficient catalysis in the cathodes of fuel cells.²⁻⁴ Adsorption to solid surfaces such as gold, however, is known to cause rearrangements to the enzyme structure,^{5,6} and may also place the enzyme in an orientation where electron transfer to the molecule is slow. Deciphering the mechanisms through which these and other redox-active enzymes undergo changes in shape, orientation and function is key to their effective use in technological applications.

A common approach for adsorbing enzymes on gold surfaces is to modify the surface with organic thiols such as 3-mercaptopropionic acid. This molecule, for example, provides a negatively charged hydrophilic surface, which can facilitate stable enzyme binding adsorption and still permit electron transfer between the electrode and the copper atoms within the enzyme.

Here we use an electrochemical quartz crystal microbalance (E-QCM) to monitor the adsorption of BOx from *Myrothecium verrucaria* on both bare and thiol-modified gold-coated sensors. Electrochemical measurements of the immobilized protein film give sensitive feedback on activity and orientation, while subtle changes in crystal frequency and the resonator's energy dissipation rate reveals coverage of the enzymes and its mechanical coupling to the electrode.⁶ We are working to understand both the fundamental processes of redox-enzyme inactivation on surfaces, and how to engineer these surfaces to provide robust, long-lasting, specific attachment.

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Microbial fuel cell wastewater treatment using a low-cost membrane

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One of the major limiting factors in practical implementation of microbial fuel cells (MFC) is the polymeric ion exchange membrane (IEM), which is expensive and can be short-lived. In this present study, we examine the performance of two MFCs employing Nafion-117 and an earthen plate as IEM. We also present results from wastewater treatment and simultaneous electricity production at sub-ambient temperatures (15°C) in an MFC.

Earthen plate membrane were operated in up-flow dual-chambered cylindrical MFC with acetate as an electron donor and a mixed culture from anaerobic sludge as inoculum, and the performance of MFCs were evaluated in the form of electricity generation and simultaneous acetate oxidation. It was observed that the earthen plate MFC generated ~40% less power than the Nafion-based MFC, showing promise as an alternate, low-cost, technology.

Continuous flow Nafion-based MFCs were also operated on synthetic dairy wastewater with 4g L of COD at sub-ambient temperatures (15°C) to evaluate the performance as a form of electricity generation and substrate degradation in moderate (Irish!) climates. The MFC design achieved 65% COD removal efficiency whilst producing volumetric power, normalized to the net liquid volume of the anode chamber, of 8.4 Wm⁻³.

Keywords: Proton exchange membrane, Microbial fuel cell, Earthen plate, Power density, Chemical oxygen demand.

Denaturation of DNA at electrode surfaces: puzzles and applications

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Double-stranded DNA (dsDNA) immobilised at an electrode surface can be unwound and denatured at negative potentials^{1, 2}. Despite over 30 years of studies, the mechanism for this denaturation process is still poorly understood. In this work, we outline recent investigations of dsDNA denaturation at nano-structured gold electrodes (Figure 1). Surface enhanced Raman spectroscopy (SERS) is utilised to monitor the denaturation of dsDNA *in situ* when the potential at the surface is swept negative. Changes and attenuation of the spectra of a reporter molecule, either synthetically attached to the DNA or bound within the dsDNA minor groove are utilised to follow the denaturation process.

In addition to highlighting recent insights into the denaturation mechanism, we demonstrate how electrochemically driven denaturation can be combined with SERS monitoring to discriminate between DNA sequences of varying composition³, and in particular, for applications in genetic diagnostics⁴ and forensics⁵. This approach offers several key advantages over existing solution and surface-based methods, including the potential for integration into low cost portable devices that could one day be used at the point of need, for example, in a Doctor's surgery or hospital.

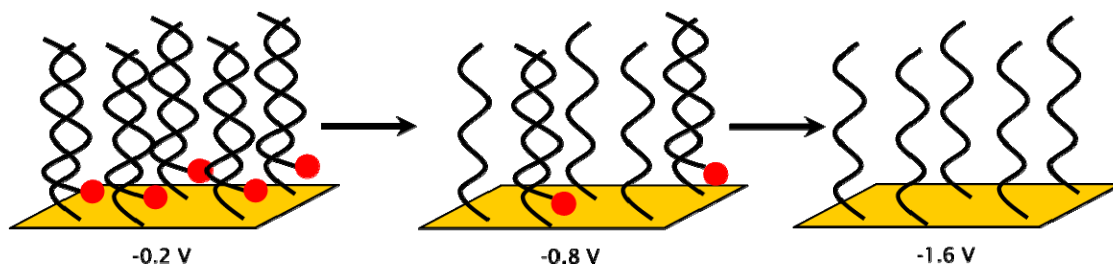


Figure 1. DNA duplexes are bound to a gold surface through sulfur linkages at one of the nucleotides. Application of a negative voltage at the surface results in DNA denaturation, and the nucleotides separate. The denaturation rate is monitored via a SERS active label attached to the non-surface bound nucleotide, the signal from which deteriorates during denaturation and diffusion of the labeled nucleotide away from the surface.

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Keynote

Cells on chips: electroanalytical investigation of disease

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Electrochemical sensors offer significant advantages for biomedicine including ease of miniaturization, low cost, multiple significant analytes, compatibility with CMOS processing techniques and excellent scalability. To extend this technology to cultured cells, we have produced microfabricated sensor arrays(i), (Fig 1) comprising six or eight working electrodes as platform technology. Choice of operating potential allow quantification of O₂, H₂O₂, and NO and, with further modification, glucose and lactate. Biocompatibility and adequate sensor function in cell culture medium was studied with various potentially biocompatible films. We have used cyclic voltammetry, steady state voltammetry and a.c. impedance spectroscopy to quantitatively characterise the effects of adsorption on the electrode reactions of interest(ii), (iii) and develop a standardise protocol for biodevice development. We have also examined the effects on cell growth and the effect of operating potential on cell viability of using trypan blue staining. Fibronectin was identified as the most satisfactory film from both the perspective of the cells and that of the sensors.

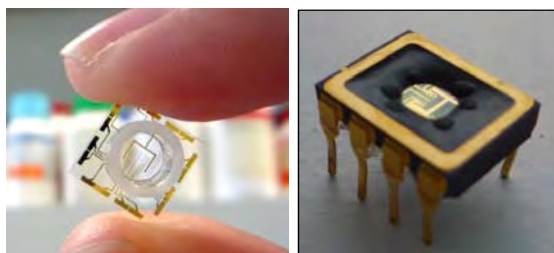


Figure 1: Microfabricated gold microsensor arrays

These devices have been used to study angiogenesis, the growth of new blood vessels, which is a key drug target in preventing cancer metastasis. We have recently shown(iv), that presentation of the ubiquitous angiogenic factor, angiogenin activates nitric oxide synthase (NOS) and that the release of NO and its oxidation products can be detected electrochemically within minutes. This work has been extended to intact tissue samples and different growth factors(v) and given comparable data. The convenience of the electrochemical method enables real time investigation of the effects of inhibition of known intracellular processes including PI-3 kinase and ERK to elucidate the pathways of NOS activation in a variety of cell types: porcine endothelial cells, HUVECs and endothelialised human stem cells(vi). We have most recently extended the application of these versatile devices to the study of infectious disease and the interaction of pathogenic antigens with immortalized macrophages. This has led to the discovery of some of the control pathways of iNOS activation in the early stages of anthrax infection and identified potential new drug targets(vii). Biocompatible microelectrode arrays enable real time *in situ* and continuous measurements from cells and tissue samples in culture. Fundamental understanding of the effects of the biological milieu on sensor performance has enabled long-term measurement of real biological significance.

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(vii)*Biosensors and Bioelectronics* (in press May 2012) DOI: 10.1016/j.bios.2012.05.012

Conducting polymer–metal nanoparticle composites from ionic liquids

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Conducting polymers have applications in areas such as batteries, anti-static materials, smart windows, biosensors, and even solar cells. There is an increased drive toward the fabrication of nanostructured conducting polymers, due to the fact that they possess many advantageous properties over their conventional, bulk counterparts. Combining nanostructured conducting polymers with gold nanoparticles provides an effective immobilisation platform for biomolecules in combination with an electrode material. Conducting polymer coatings and fibres are being researched as components of electronic textiles for uses in biomedical applications. The incorporation of silver nanoparticles into these materials may afford advanced textiles complete with anti-bacterial coating.

Ionic liquids are excellent media for the synthesis and utilisation of conducting polymers as they can exhibit excellent oxidative and reductive stability, allowing access to larger electrochemical potentials than previously achieved by molecular solvent/electrolyte systems. The synthesis of polypyrrole (Ppy) and polyethylene-dioxythiophene (PEDOT) with unusual fibrillar morphologies was achieved by chemical polymerization using ionic liquids.(i) Using ionic liquids with gold chloride or silver nitrate as the oxidant polymers (Ppy and PEDOT) containing incorporated gold or silver nanoparticles were formed in one simple step.(ii) Recent results suggest that the hydrophobicity / hydrophilicity of the ionic liquid can lead to preferential metal nanoparticle incorporation. Electrochemical release of silver ions from these polymers has been observed and they are currently undergoing testing for anti-bacterial applications. The simple and versatile methods described, produced conducting polymer nanofibrils and allowed for facile incorporation of metal nanoparticles into conducting polymers. The incorporated metal nanoparticles are clearly visible by TEM, and the composites have been further analyzed by CV, UV-Vis, Raman, XPS and scanning TEM coupled with EDS analysis. The significantly larger surface area and charge accessibility of nano-sized conducting polymers and metal nanoparticles have potential to yield materials with great academic and industrial interest.

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Aerobic biocathodes for microbial fuel cells

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Domestic wastewater treatment requires considerable energy. Wastewater treatment currently accounts for 1-1.5% of the total electricity used, whereas the wastewater itself contains biodegradable organic matter that can contain 9.3 times the amount of energy that is used to treat it.⁽¹⁾ Therefore increasingly, wastewaters are being seen as an energy resource as opposed to a waste. Microbial Fuel Cells (MFCs) that use bacteria to release the energy available in wastewater to produce power could offer a means of making this wastewater infrastructure self-sustainable.

In an MFC, organic matter is oxidised at the anode by bacteria which generate electrons, while the common cathode reactions are oxygen reduction catalysed by chemical catalysts, or reduction of an aqueous catholyte, such as ferricyanide at an abiotic cathode. Oxygen reduction catalysts such as Pt are expensive and show poor performance in neutral media and at low temperature, and catholytes such as ferricyanide are expensive, toxic and unsustainable, therefore suitable alternatives need to be found. One alternative is to use bacteria as cathode catalysts. Low cost and self-sustainable, biocathodes can be developed by incorporating aerobic or anaerobic bacteria.

Cathode biofilms were inoculated from activated sludge, and the effect of applied potential on biofilm growth on a carbon felt electrode in an aerated system examined. The cathode biofilm operated at a potential at +0.15V exhibited a peak cathodic current of 3 $\mu\text{A}/\text{cm}^2$. Passive air diffusion to the biocathode will also be examined using a gas diffusion electrode, and both passive and active aerated biocathode systems will be tested in a full MFC configuration.

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Fundamental Electrochemistry

An electrochemical impedance study of the oxygen evolution reaction at hydrous iron oxide in base

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Electrochemical impedance spectroscopy (EIS) is a potentially useful experimental tool in probing the kinetics of electrocatalytic reactions and in characterising the properties of the electrode/electrolyte interfaces at which such reactions occur. In the present work, we focus on the redox properties and electrocatalytic behavior with respect to anodic oxygen evolution of polymeric iron oxyhydroxide electrodes in aqueous alkaline solution. These films can be prepared simply *via* potential multi-cycling an iron electrode in alkaline solution to form a microdispersed hydrous oxide film. Redox switching of the hydrated layer involves a mixed ionic/electronic conduction mechanism and the physical transport processes within the material may be described in terms of a dual rail electrical transmission line model of the type proposed by Bisquert and coworkers [1] for electronically conducting polymers and transition metal oxide materials. It is found that a highly conducting oxide layer is formed, particularly under conditions of active oxygen evolution.

Building on the earlier findings of Lyons *et al.* [2] the oxygen evolution performance of a multi-cycled iron electrode is shown to be significantly enhanced relative to an uncycled electrode. Here, the kinetic behaviour with respect to active oxygen evolution of a series of hydrous oxide coated iron electrodes is examined using a combination of steady state polarization and EIS studies with excellent agreement being observed between these techniques. Particular attention is focused on the significance of the oxide layer thickness and the electrolyte concentration. Tafel slopes of approximately 60 mV dec^{-1} and 120 mV dec^{-1} were observed at low and high overpotentials respectively, with the former value reducing to 40 mV dec^{-1} for thick oxyhydroxide films. A reaction order of unity was obtained at both low and high overpotentials and the reaction order was found to be invariant with oxide layer thickness. Based on the available kinetic data, a modified Kobussen mechanism utilising the active surfaquo group concept is proposed [3]. Significantly, the proposed mechanism, involving an iron oxo intermediate species, dispenses with the need to admit the direct participation of lattice oxygen atoms in the OER, which should make it a more widely acceptable representation.

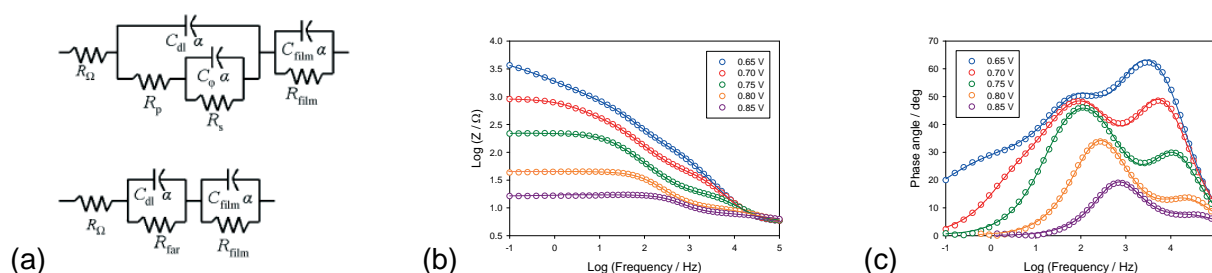


Figure 1: (a) Equivalent circuits used to interpret the OER impedance data. (b) Bode modulus and (c) Bode phase plots for impedance data recorded during active oxygen evolution at hydrous oxide modified iron electrode.

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Magnetoelectrolytic production of hydrogen with controlled bubble size and departure direction

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Growth of hydrogen bubbles from gas evolving microelectrodes under the influence of magnetic fields has been characterized via electrochemical noise and high speed photography. The effect of electrode position relative to both magnetic fields and gravity was considered, as well as the effect of field polarity. Uniform fields up to 5 T were applied either horizontally (B_H) or vertically (B_V) to electrode surfaces located vertically (S_V) or horizontally facing up (S_H), allowing free detachment of bubbles from the microelectrodes surface. Platinum and Copper were used as working electrodes. The system response is characterized by modulated oscillations of the overpotential, and is related to the growth and detachment cycle of single hydrogen bubbles, as shown in Figure 1. This occurs in a periodic regime, depending on the combination of forces acting upon the growing bubble. Magnetoconvection in combination with upthrust, determine growing time of bubbles and hence their size, as Figure 2 shows. They also determine the direction of departure from the electrode surface. In consequence, it is possible to reduce or increase the bubble size, and control the break-off direction by a proper combination of the convective forces – magnetically and gravitationally induced – acting on it.

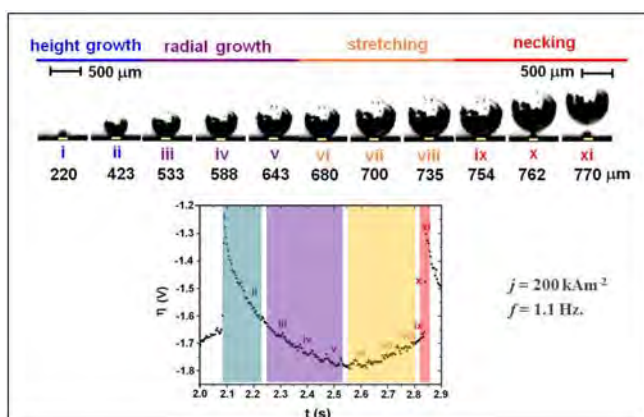


Figure 1: Voltage oscillations associated to growth and detachment cycle of hydrogen bubbles from a Pt microelectrode (125 μm in diameter) in a 1.2 M H_2SO_4 electrolyte

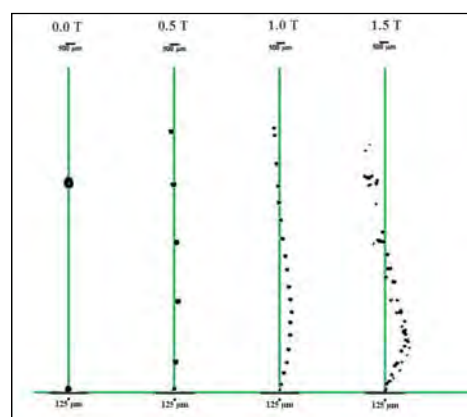


Figure 2: Changes of bubble size and departure direction obtained by applying horizontal magnetic fields to Pt microelectrode facing upwards, in the same conditions of figure

Acknowledgements: This work was supported by SFI through the MANSE project.

Keynote

Beyond the butler-volmer equation curved tafel slopes from steady-state current-voltage curves

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We report the discovery and analysis of curved Tafel slopes from the electrochemical reduction of hexamminecobalt(III) under steady-state conditions. In order to confirm the existence of the curvature, random assemblies of carbon microelectrodes (RAM™ electrodes) were employed to obtain experimental data over more than three orders of magnitude, without significant double layer charging currents and without ohmic distortion. Since the rate-determining step in the reduction reaction is electron transfer, and no ligand substitution reactions occur on the timescale of experiments, the curvature of the Tafel plot is attributed to the dependence of the symmetry factor on electrode potential.

Control of redox reactions at the solid/gas interface

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To date, redox reactions in the gas phase (electron attachment or detachment) are commonly studied using photoelectron spectroscopic, or related techniques, in conjunction with mass spectrometry for analysis of products and/or reactants.[1] There are few examples using plasmas as media where redox reactions are investigated. Vennekamp, Brettholle and Ogumi, described the use of non-thermal plasma for metal surface oxidation.[2-4] However, apart from experiments performed at especially designed interfaces[5], there are no examples of voltammetry in the gas phase at a true solid|gas interface. Our new approach can help apply the well-heeled cornerstones of electrochemistry developed almost exclusively in liquids, to the new context of gas plasma.[6] Successful electrochemical measurements at the solid/gas interface were demonstrated by doping the flame plasma with a metal oxide salt and recording distinct faradaic peaks at defined potentials in cyclic voltammograms. After careful experimentation and appropriate control experiments, we conclude that the features observed are specific reduction processes at the solid/gas interface. The most significant innovation that made these measurements possible was the formation of a reference electrode. Extensive assessment of several materials showed that titanium wire oxidized on the surface to produce a self-limiting layer of TiO₂, which is stable and forms a nonpolarisable electrode surface, and maintains a stable potential in the hydrogen flame that we use.[7] Undoubtedly, and perhaps expectedly, there are significant departures from the analogous process in condensed phases. We shall discuss the physical origin of these electrochemical signals measured in flame plasma and provide a framework of interpretation upon which a full mechanistic understanding can be based. The scope of technological impact is extensive. For example, quantitative gas phase voltammetry may be developed, complementing analytical techniques such as atomic absorption, inductively coupled plasma and fluorescence spectroscopies. In addition, it is possible that substantial impact on other less well established fields where solid/gas surface redox reactions may also be anticipated, such as electrostatic charging, catalysis and astrochemistry.[8]

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Electrodeposition of metals and semiconductors from supercritical fluids: towards metamaterials

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The literature on electrochemistry in supercritical fluids is fairly limited and is often concerned with the study of corrosion (relevant in nuclear reactor cooling) or development of analytical techniques for supercritical chromatography. However there have also been some studies of electrolyte solubility, conductivity and other fundamental properties like double layer capacitance¹ and viscosity² that suggest that supercritical fluids may also provide a viable medium for electroplating.

There has been some success in electrodepositing silver from near critical ammonia and copper from near critical water. While supercritical ammonia and water have relatively high dielectric constants (facilitating electrochemistry) they are not ideal solvents as they are highly corrosive and difficult to work with. More recently Miyata and Sone *et al.* electroplated nickel from an aqueous emulsion in supercritical CO₂³ and polypyrrole has been deposited from supercritical CO₂ using acetonitrile as a co-solvent to increase the dielectric constant⁴.

In 2009 we published the first examples of metal deposition from homogeneous, single phase supercritical solvents⁵. By judicious choice of electrolytes, metal precursors, plating conditions and (where appropriate) co-solvents we have been able to electrodeposit copper⁶, silver, iron, cobalt, platinum and germanium⁷ from supercritical fluids. Furthermore we are also able to exploit the absence of surface tension to facilitate electroplating of silver and copper into high aspect ratio nanopores; producing wires of approximately 3 nm diameter.

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Voltammetry in supercritical CO₂ fluids

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Over the past 25 years a number of publications have emerged, exploring electrochemistry in supercritical CO₂¹⁻⁴ (scCO₂), with and without polar co-solvents. However, the publications are few, and extensive studies of the system with regards to the interplay of co-solvent, the enhancement of mass transport and the influence on diffusion coefficients and reaction kinetics have not been reported. In particular, investigations on the macro scale are highly scarce, owing to the low dielectric constant for scCO₂ and poor solvation of ionic species as electrolytes, thus resulting in high resistivity and ohmic drop in voltammetry.

Recently the synthesis of a highly lipophilic ionic liquid electrolyte, that is soluble in scCO₂ and organic co-solvent, has permitted macroscale voltammetric studies to be performed in the supercritical fluid with little ohmic distortion. Herein we present voltammetric investigations of well-known metallocene redox couples in the supercritical medium, discussing the apparent steady-state voltammetry observed at moderate scan rates.

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Keynote

Graphene: electrochemistry in flatland

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The explosion of interest in graphene has led to a substantial number of reports on the electrochemical behaviour of this material, with specific applications in energy storage [1] and electroanalysis [2] in mind. However, the “fundamental” aspects of graphene electrochemistry - which also feed into the wider debate about the electrochemical properties of graphite and carbon nanotubes – have been neglected in comparison, with only a few notable exceptions [3-6].

Our most recent work in this area will be presented, covering our approaches to electrochemistry of individual graphene flakes [7] via masking and droplet-based approaches. Very recent work on the non-oxidative electrochemical production of graphene will also be presented.

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Searching for authentic electrocatalytic nanoeffect: electro-oxidations of nitrite and L-ascorbic acid on Au-NPs modified electrode

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The investigation of electrocatalytic nanoeffects is tackled via joint electrochemical measurements and computational simulations. Thus, the response of an electrode modified with nanoparticles is simulated assuming that the particles are of the same size and evenly dispersed on the substrate surface and that they “retain” the electrode kinetics extracted for the bulk material. This enables to predict the response expected in absence of nanoelectrocatalysis. Separately electrochemical experiments are performed with nanoparticle-modified electrodes, the characteristics of the modification being examined by electrochemical and imaging techniques. Finally, the comparison of simulated and experimental voltammograms allows for the detection of differences between the kinetics at the bulk material and at the nanoparticles and, therefore, for revealing nanoeffects.

This approach is applied to the experimental assessment of electrocatalytic effects by gold nanoparticles (Au-NPs) in the electro-oxidation of nitrite and L-ascorbate. Glassy carbon electrode is modified with Au-NPs of 20-90 nm diameters via seed-mediated growth method. Divergence between the kinetics of these processes on gold macro electrodes and gold nanoparticles is examined. Whereas claimed electrocatalysis is discounted for the electro-oxidation of nitrite, electrocatalytic nanoeffects are verified in the case of L-ascorbate. This is probably due to that the electron transfer process follows an adsorptive mechanism.

Electrochemistry of decamethylferrocene in ionic liquids a critical evaluation and novel applications

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Ionic liquids, ILs, represent a fascinating, and yet to be fully understood, medium for a variety of chemicals, physical and biological processes. Electrochemical processes form an important subset of these processes that are particularly of interest, since ILs tend to be good electrochemical solvents and exhibit interesting conductive properties, which make them useful as the electrolyte in energy production and storage devices, electrodeposition, and electroanalytical studies, both in academia and for industrial applications.^[1] However, very little information and understanding are available regarding frequently used internal reference scales. This is because ILs are relatively new materials and the role of different ILs, which may impact differently on the potential scale, is poorly understood.^[2]

The electrochemistry of decamethylferrocene, DmFc, has been studied in organic solvent systems and proven to be a superior redox standard to ferrocene, as the methyl substitution on the cyclopentadienyl ring prevents both specific and nonspecific interaction between DmFc and external molecules by hindering the access of solvent and supporting electrolyte molecules both to the metal centre and to the ring. However, this ferrocene derivative has been scarcely studied in ILs.^[3]

In this presentation, the effect of IL structure, water concentration, and nature of the atmosphere on the electrochemical behaviour of decamethylferrocene is presented. A number of recent examples from our lab base around the extent of similarities with conventional electrochemical solvents will be presented, and some surprising differences noted.

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Chronoamperometry at neighbouring inlaid microdisk electrodes

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Inlaid microdisk electrodes are frequently used as electrochemical sensors. They have many advantages, since they are easily fabricated and are less susceptible to the effects of ohmic drop and double-layer capacitance. Dual microdisk electrodes can be used in generator-collector mode, whereby a species is generated at one electrode and then detected at the other. Arrays of microdisk electrodes are used to increase the total signal generated, whilst still maintaining the advantages of low ohmic drop and double-layer capacitance. In both cases, it is important to understand theoretically the impact of the neighbouring electrodes on the current response through each electrode. Here we derive an approximate analytical solution for the long-time-dependent chronoamperometric current response through a pair of neighbouring electrodes. The solution is valid whenever the distance between the centres of the disks is large compared to the radii of the disks. It allows for disks of unequal radii, different potentials at each disk, and quasi-reversible reactions, as well as unequal diffusion coefficients for the oxidant and the reductant. If the disks are set up in generator-collector mode, then we show that the solution provides simple expressions for the long-time transient current at the generator and the collector, from which collection efficiencies can be estimated.

Diagnosing sepsis: a graphene-based biosensor for procalcitonin

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Accurately diagnosing paediatric sepsis, a common complication of burns, is currently very difficult and relies primarily on clinical judgment. Children with sepsis have a clinical presentation almost identical to children with Systemic Inflammatory Response Syndrome (SIRS), but treatment of SIRS and sepsis is very different. Currently, clinicians suspecting sepsis will prescribe antibiotics, thereby contributing to the antibiotic resistance and “over treatment” of the child, which can slow healing. Early diagnosis of sepsis is crucial for the patient’s outcome and failure to do so is likely to lead to rapid (hours) deterioration of a child’s condition resulting in increased morbidity and mortality.

Our key challenge is to eliminate the subjectivity from diagnosis, by developing a point-of-care, electrochemical test using multiple biomarkers for sepsis in blood, namely: C-reactive protein, procalcitonin, tumour necrosis factor α , and the interleukins IL6 and IL10. Although certain semi-quantitative tests are available commercially (notably for procalcitonin), we aim to use electrochemistry (in possible future combination with spectroscopic techniques) to produce a quantitative sensor technology, capable of rapid (sub-1 hour) results.

In this work, we report an early-stage, proof-of concept biosensor for procalcitonin. This has been achieved by creating an enzyme-linked immunosorbant assay (ELISA) sandwich, tethered to a glass-backed CVD graphene electrode, using horseradish peroxidase as the enzyme and *o*-phenylenediamine (OPD) as the co-substrate for the enzyme-catalysed oxidation of H_2O_2 . The oxidised OPD, and hence the procalcitonin in the ELISA, is detected via its reduction at graphene using square-wave voltammetry. Also presented are preliminary results for the electrodeposition of gold nanoparticles on the graphene and their surface-plasmon-resonance and surface-enhanced-Raman responses, in anticipation of future combined electrochemical/spectroscopic sensing formats.

A new method for studying poorly soluble species: the electrocatalysis of oxygen by quinizarin

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The redox chemistry of quinones are implicated in a large number of academic studies. Their roles vary from industrial applications, with the production of hydrogen peroxide, through to involvement in a number of biologically relevant pathways including the electron-transport chain. Of the biological examples the anthracycline antibiotics, a family of highly effective chemotherapeutic drugs, represent an interesting case wherein the redox-active group is found to be a quinizarin moiety. It is known that this quinizarin structure may readily undergo redox cycling within the cellular environment, resulting in the production of highly deleterious reactive-oxygen species (ROS). It is this ROS formation that has been implicated as one of the primary causes of the chemotherapeutic drug's high cardiotoxicity.[1] However, direct study of this oxygen reduction electrochemical pathway has, in part, been hindered due to the difficulty of delineating the *mediated* response from that of the underlying electrode. Moreover, the low solubility of the quinizarin species represents a secondary challenge for its investigation and use as a model species for the larger anthracycline family.

In protic media the reduction of the quinone moiety is a two-electron, two-proton process. The formal potentials for these two electron transfers are found to be environment sensitive. The preliminary section of this presentation aims to provide a more fundamental framework for understanding this multi-electron transfer system and importantly highlights how the thermodynamics of the system may be 'tuned' through altering the identity of the supporting electrolyte.[2,3]

Catalytic mechanisms (EC') have historically been employed to lower the over-potential associated with an electron transfer of interest. Conversely, this present work utilises the EC' mechanism so as to provide a method for the detection and study of the mediating species. Success of this approach is predicated upon the direct-redox process occurring at the electrode substrate to be minimal. Experimentally this is achieved through the use of a boron-doped diamond electrode.[4] This methodology not only allows the mediated electron transfer process to be unambiguously studied, providing previously unavailable information regarding the reactivity of the semiquinone intermediate but, also, through redox-amplification the investigation of the poorly soluble quinizarin species is enabled down to nano-molar concentrations.

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Poster Abstracts

Thin film semiconductor photo-anodes for solar hydrogen production

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At the turn of the century, the global average energy consumption rate was 13 TW; this has been predicted to rise to 27 TW by 2050.¹ This increase, in connection with the demand for a decrease in reliance on fossil fuels has lead to an interest in the development of clean, renewable fuels. One energy vector that continues to receive substantial attention of hydrogen. Solar hydrogen production through the photolysis of water at semiconductor electrodes offers a route to a renewable source of hydrogen. Much has been made of the use of TiO₂ as a photocatalyst, however, with a band gap of ca. 3.2 eV, it can only convert roughly 4 % of the solar spectrum into electron-hole pairs. Thus there is a drive to develop photocatalysts that are responsive to visible light.²

Herein, the use of visible-light activated photoanodes will be discussed. For example, the development thin film photoanodes consisting of iron vanadate (FeVO₄). Iron vanadate thin film electrodes were prepared following a sol-gel synthesis and spin coating. The resultant photoanodes were responsive to visible light, with an indirect band gap of 2.05 eV. Film thickness varied from 200-1000 nm and was almost linearly dependent on the number of layers deposited. Measured photocurrent densities under simulated sunlight were dependent on the film thickness, annealing temperature and the precursors used. An annealing temperature of 600 °C was required to produce films that were well crystallized, below this temperature, Raman microscopy and XRD revealed films lacked crystallinity; this had a deleterious effect on the photocurrent density.

Whereas there remains work to improve the synthesis of FeVO₄ electrodes to increase film stability and measured photocurrent densities, Fe₂O₃ and WO₃ electrodes have received considerable attention and afford photocurrents of over 2 mA cm⁻².³ A question remains as to how to improve charge carrier lifetime. Here the use of transient absorption spectroscopy to determine charge carrier dynamics will be discussed.^{4, 5}

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Promotion of titanium oxide nanotubes capacitance by hydrogen insertion

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We present a new and simple way to control the capacitive properties of TiO_2 material. It is possible to control of capacitance of TiO_2 by hydrogen insertion in TiO_2 structure. A self-structured and highly ordered array of titanium oxide nanotubes were fabricated with different dimensions by anodization of titanium foil in aqueous fluoride solutions. The results obtained for nanotubes oxide were compared with compact oxide prepared by anodization in sulfuric acid as bulk structure. Cyclic voltammetry measurements in the electric double layer region show dependence of the capacitance on surface area. Titanium oxide nanotubes (TNT), offer electrical capacitance of 89.2 and 42.8 $\mu\text{F}/\text{cm}^2$ for crystalline or amorphous TNT respectively, larger than that for compact oxides, 10.1 and 5.5 $\mu\text{F}/\text{cm}^2$ respectively. Electrical capacitance was increased as the length of nanotubes was increased due to the increase of surface charge with increased surface area for the electrodes. A large increase in capacitance was observed after immersion of annealed TNT, and it was estimated to be 1108.1 $\mu\text{F}/\text{cm}^2$ while the capacitance of other three kinds were within 50-100 $\mu\text{F}/\text{cm}^2$. Likewise, the charge density was increased after immersion, as a result of hydrogen insertion, from 7e-2, 3.2e-2, 7.-3 and 4e-3 mC/cm^2 to 0.886, 0.064, 0.060 and 0.046 mC/cm^2 respectively for TNT (crystalline and amorphous) and compact oxide (crystalline or amorphous), which are causing an increase in the capacitance of the oxides. Activation of electrode after immersion, led to the contribution of Faradic capacitance (pseudocapacitance) in the electrical capacitance. Electrochemical impedance spectroscopy for oxides were carried at OCP indicated favorable charge transfer at surface during immersion. The enhancement of TiO_2 capacitance at all states is attributed to more charge carriers produced on its surface by adsorption of hydrogen. Hydrogen reduces Ti^{4+} to Ti^{+3} and the concentration of charge carries increase at surface. The immersion in acidic medium has the same effect of negative potential on the electrode which would lead to an evident increase in the capacitance and the conductivity that can improve pseudocapacitor, hybrid pseudocapacitor and other storage charge devices.

Copolymerization and characterization of polypyrrole-poly(3,4-ethylenedioxythiophene) copolymer in an air stable ionic liquid

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Polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) have desirable properties as electrochromic materials. PPy is characterized by high specific capacitance and good mechanical properties^[1] while PEDOT has high electrical conductivity, good mechanical properties^[2] and high porosity^[3]. This work describes the electrochemical copolymerization of pyrrole (Py) with 3,4-ethylenedioxythiophene (EDOT) in the air stable ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF₄). Copolymerization was performed in a small volume (20 μ l) electrochemical cell which permits the use of ionic liquids in a very economical manner. PPy-PEDOT/ BMIM BF₄ copolymers were formed on optical transparent electrodes (indium tin-oxide, ITO) and characterized electrochemically and by SEM. The films displayed an olive green in the reduced form and a grey blue in the oxidized form when spectroelectrochemical and electrochromic properties were investigated in detail.

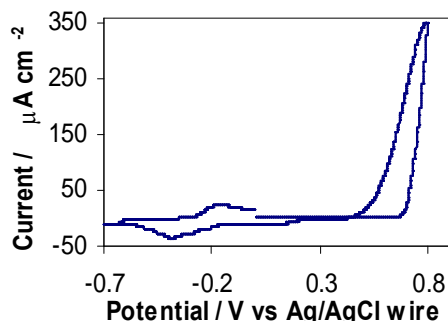


Fig.1. Cyclic voltammogram for copolymerization of Py with EDOT (Py:EDOT, 2:1 monomer ratio) in BMIM BF₄. Scan rate: 50 mV s⁻¹.

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Hydrogen oxidation reaction at the Ni/YSZ anode of solid oxide fuel cells from first principles

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In spite of decades of experimental investigations and kinetic modelling of electrode reactions [1], the detailed mechanism of hydrogen oxidation at the anode of solid-oxide fuel cells (SOFC) is still a matter of debate [1].

Based on ab-initio simulations, we here propose a mechanism for the hydrogen oxidation reaction [$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$] occurring at three phase boundary of the typical SOFC anode made of a nickel/yttria-stabilized-zirconia cermet.

The elementary steps of possible oxidation pathways, namely O_2^- , H^+ or OH^- surface spillover and of the different processes leading to water desorption from the Ni/YSZ cermet are studied by means of molecular dynamics and free energy methods, as implemented in the CP2K suite of programs [2].

We find that the favoured oxidation pathway corresponds to the spillover of two consecutive hydrogen atoms from Ni to YSZ.

Water formation take place at the YSZ surface and is mediated by the diffusion of a hydroxyl group on a Zr site, close to the Ni/YSZ interface. The overall rate limiting step for the oxidative reaction is represented by charge transfer reaction associated with hydrogen spillover from the metal to the YSZ surface [3].

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Electrochemical green ozone and hydrogen technologies – a cost-effective and sustainable solution for water treatment and clean energy conversion

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Ozone has been finding increasing use as a greener alternative in a wide variety of industrial applications as it is a powerful oxidant and produces only oxygen as a by-product. As ozone is highly reactive it cannot be stored and therefore must be generated in-situ. Electrochemical ozone production (EOP) has several advantages over currently used technologies such as Cold Corona Discharge and UV-radiation, including simple system design which is easily scalable, low voltage operation, the potential for high efficiency and no requirement for oxygen gas at the input. Recently, several papers have reported EOP using Ni/Sb-SnO₂/Ti anodes with high current efficiency but their service life has been shown to be only ca. tens of hours at the optimum cell voltage. Additional doping metals have been investigated for their effect on the catalytic activity and lifetime of these novel anodes.

The anodes were prepared using 2.5 cm² Ti mesh substrates (Dexmet, USA), a Sn:Sb:Ni:x precursor solution where x = additional doping elements with optimum molar ratios. Doping with Au led to significant increases in the lifetime of anodes under accelerated lifetime testing conditions, see figure 1. Doping with Niobium led to increased activity toward EOP of the anodes under normal conditions, see figure 2.

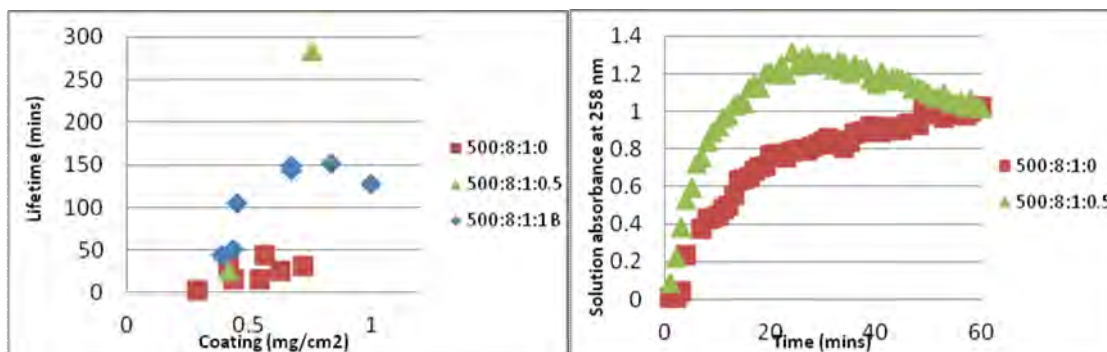


Figure 1(LHS): Coating mass - Lifetime for Gold doped anodes.

Figure 2 (RHS): Ozone solution UV absorbance at 258 nm from Niobium doped anodes.

Hydrogen is produced as a by-product at cathode side in the EOP, which is a clean fuel and can be used to offset the energy cost of the EOP.

Transient metallo-hydrides and carbonyls related to biological hydrogen evolution: FTIR spectroelectrochemistry

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One of the most attractive means of future energy storage and generation is hydrogen. A lot of research has gone into finding routes that will make the use of H_2 in the future more viable. Taking inspiration from nature seems to be a good starting point. Understanding the chemistry that takes place at the active site of [FeFe]-hydrogenase is both of high interest and potential technological impact in the context of hydrogen generation and utilization [1].

Mixed valence Fe(I)-Fe(II) hydrides have been postulated as intermediates in the catalytic cycle of dihydrogen evolution of the enzymatic system. Using advanced FTIR spectroelectrochemical cell, DFT calculations and EPR spectroscopy we have characterised the first discrete mixed-valence $[2Fe_2S] \mu$ -hydride species [2]. This is a valence-delocalised system and isotopic-labeling studies have established that substantial radical character resides on the strongly coupled bridging hydride. We also show a reduction of first $[2Fe_3S]$ bridging hydride species and examine the common pathway that these systems might share in the route of catalytic hydrogen generation by natural and unnatural systems.

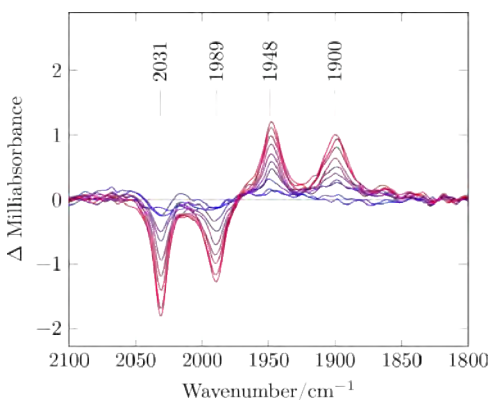


Figure 1. Difference spectrum for the reduction of $[HFe_2(pdt)(CO)_4(PMe_3)_2][PF_6]$ in the time range 0.25 s (blue) to 1.79 s (red) relative to scan at 0.08 s

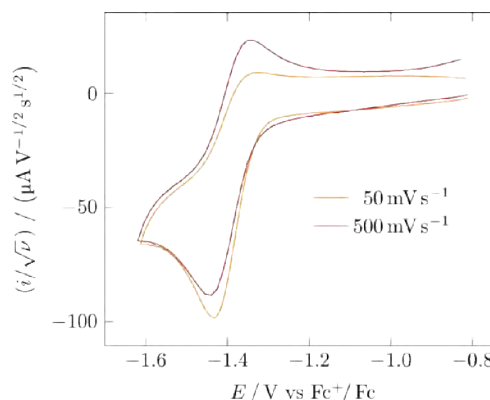


Figure 2. Normalized cyclic voltammograms of $[HFe_2(pdt)(CO)_4(PMe_3)_2][PF_6]$ recorded at vitreous carbon working electrode in MeCN at 25 °C

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Group IV semiconductor nanowires as high capacity anode materials for next generation lithium ion batteries

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Si and Ge nanowires have attracted attention recently as high capacity, next generation anode materials for lithium ion batteries due to their very high theoretical capacities (4200 mAh/g and 1600 mAh/g respectively) and the fact that the nanowire morphology can lead to better performance over bulk or thin film electrodes. Nanowire electrodes outperform their bulk counterparts as the small nanowire diameter can accommodate the large volume changes associated with lithium insertion and extraction without pulverisation of the material which can occur in bulk electrodes.¹ Also the nanowire morphology results in shorter Li ion diffusion distances and offers good electrical contact with the current collector and good electrical conductivity along the length of each individual nanowire.² The most common approach used for synthesising Si or Ge nanowires is via a gold seeded mechanism however this approach has its drawbacks as gold is expensive and its contribution to the capacity of the electrode is negligible.¹⁻⁴ Thus the identification of materials which can catalyse the growth of Ge and Si nanowires and also add significantly to the capacity of the anode by alloying and dealloying with Li is desirable.

Herein we report the synthesis of Si nanowires using indium as a catalyst and the synthesis of Ge nanowires using tin as a catalyst. Tin and Indium have relatively high theoretical capacities (1900 mAh/g and 1400 mAh/g respectively) and good cycling stability and so can contribute significantly to the overall capacity and performance of the anode. The nanowires are grown directly from stainless steel which provides good electrical contact between the current collector and the active material and eliminates the need for conducting additives and binders which lower the overall specific capacity of the battery.

Structural characterisation of the as synthesised materials was carried out using scanning electron microscopy (SEM), transmission electron microscopy and X-ray diffraction (XRD). Electrochemical characterisation of the electrodes was also performed by galvanostatic charging and discharging, cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

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Polysulfone-polyvinyl alcohol hydrogellic organic donor systems in hybrid photovoltaic cells

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The main component of a photovoltaic device is the semi-conductor material which determines how much energy is taken up by the photovoltaic device. The most widely used semi-conductor is the crystalline silicon (90 %). This is due to its reportedly high stability and high efficiency (24%) in converting the light energy into electrical energy. However, the main challenge in the development of the solar cells is the high cost of ultrapure silicon. This has led to the exploration of organic molecules as substitutes for silicon in solar cells. The focus of this research is the production and characterisation of composite polymeric materials and nanoalloys for application in the construction of hybrid solar cells. This work reports detailed electrochemical-spectroscopic analysis of the performance of the hydrogel-nanoalloy photovoltaic cells. The studies are based on a polysulfone-polyvinyl alcohol hydrogel which acts as the donor component of the hybrid solar cell. The inorganic components are ZnGa and ZnW nanoalloys which act as the acceptor. UV, visible and photoluminescence studies have shown that the energy levels of the hydrogel in comparison with the donor compound allow for the efficient transfer of the electrons from the hydrogel to the nanoparticles. D.C. voltammetry was employed to obtain current-voltage plots, fill-factors, efficiencies and effective cell resistances. The hybrid system was also probed using impedimetric measurements which assists in the determination of the resistance and capacitance of the bilayer heterojunction. The results shown in this work indicate the importance of electrochemical-analytical techniques in the quantitative analysis of the photovoltaic cell.

Chronoamperometric responses of graphenated platinum group metals nanoalloy supercapacitors

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Electrochemical capacitors (ECs) provide a mode of electrical charge and energy storage, complementary to that by batteries. Electrochemical capacitors are a special kind of capacitors based on charging and discharging the interfaces of high specific-area material such as porous carbon material or porous oxides of some metals. They can store electric charge and corresponding energy at high densities in a highly reversible way, as does a regular capacitor, and hence can be operated at specific power densities (watts/kg) substantially higher than can most batteries. They (ECs) have promising applications as backup or auxiliary power sources in electric vehicles and other electronic devices for the purpose of power enhancement. In this study, we combine the exceptional properties of graphene nanosheets with that of some of the Platinum Group Metals (Pt, Pd and Rh) to provide uncompromised electrochemical properties of the composite for application in electrochemical supercapacitors. Platinum group metals (PGM) are of our main interest due to their attractive electronic and physical properties alongside carbon based materials such as graphene nanosheets (GN). GN sheets have been considered as one of the most promising flexible electrode materials because of their low cost, high specific surface area, ultra-low resistivity for electron transport and extraordinary pliable properties. The composite of graphene/PGM was constructed by electrodeposition of the nano-alloys of PGM onto a graphene modified glassy carbon electrode in order to examine the electrochemical properties of the composite. Galvanostatic charge-discharge cycles of the composite demonstrated an improved capacitance of the modification. An increasing trend of specific capacitance of the constructed composite was established with significant improvement from graphene/nanoparticles < graphene/binary nano-alloys < graphene/ternary nano-alloys of the platinum groups elements.

Keywords: Supercapacitors, Galvanostatic charge/discharge, Graphene nanosheets, PGM binary and ternary nano-alloys

On demand electrochemical production of hydrogen for mobile applications: development of alkaline electrolyser

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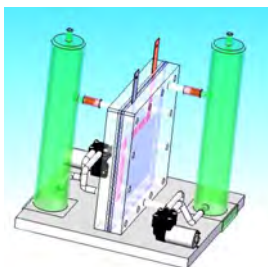
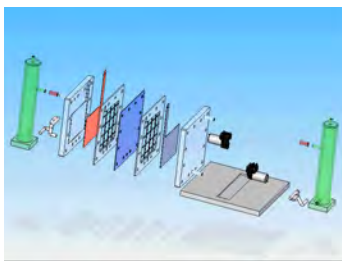
Global warming and the energy crisis are two of the greatest challenges on which mankind is currently focused. This has forced governments and other organisations to think how to protect the environment and how to reduce fuel costs. A variety of new and exciting technologies is being investigated to address the energy problem.

Alternative energy sources such as solar power, fuel cells, wind power and tidal waves are active areas of commercial and scientific pursuit [1-3].

Current research is moving towards the hydrogen economy and hydrogen based energy systems. Hydrogen can be produced in many ways, most commonly by steam reforming of hydrocarbon (70% to 85% thermal efficiency) but the downside is that it releases carbon dioxide (CO_2) [1], compared with commercial PEM electrolyzers where performance has been reported to be 56 - 73% [1] at normal temperature pressure (NTP) with zero carbon emission. Electrochemical production of hydrogen has several advantages: (i). It gives pure hydrogen. (ii). Allows portability (eg. Solar energy can be used to power the electrochemical cell). (iii). It can be produced on demand.

The paper presents our recent work on the fabrication of low cost continuous flow alkaline (KOH, up to 30%) electrolyzers using low cost electrodes (stainless steel 316) and membranes based on ultrahigh molecular weight polyethylene (UHMW PE) and production of hydrogen.

A high coulombic efficiency of up to 90% has been achieved. Typical cell voltage is 2.5 ± 0.5 V at a current densities ranging from 30 to 120 mAcm^{-2} .



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Investigation of hydrogen evolution on stainless steel electrodes coated with nickel and zinc oxide nanoparticles for on-demand applications

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Hydrogen is regarded as an ideal energy carrier [1-3]. Low cost production of hydrogen is essential for commercialisation of hydrogen fuel cells. One of the most promising methods of producing hydrogen is electrolysis of water using a variety of energy sources such as solar, geothermal, hydroelectric and nuclear energy. Alkaline water electrolysis represents one of the best choices for hydrogen production since it has been well established over a century. In order to make the water electrolysis more efficient and economical, the reduction of cell voltage is key. Various catalysts, such as Raney nickel and nickel . molybdenum alloys, misch metal ($\text{Ni}_{3.6} \text{Co}_{0.75} \text{Mn}_{0.4} \text{Al}_{0.27}$) and Ti_2Ni , have been extensively studied as possible cathode materials [1] to reduce the cell voltage and to improve the efficiency.

The paper presents our investigation into the efficiency of hydrogen evolution reaction at stainless steel electrodes (316) and compares the performance on nickel coated (electroplated Ni) and ZnO spin-coated (sol-gel method) stainless steel electrodes in an alkaline electrolyser (KOH, 5-30%) using cyclic voltammetry and the measurement of gas evolved on 1 cm^2 electrodes (mini-cell) and 48 cm^2 electrodes (maxi-cell).



Mini-Cell Electrode area: 1 cm^2



Electrode Area: 48 cm^2

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Robust electrocatalysts for proton exchange membrane water electrolysis

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The widespread adoption of proton exchange membrane (PEM) water electrolysis technology requires electrocatalysts that are stable when subjected to operational electrolysis conditions. Such conditions may include running at high current densities to increase the rate of hydrogen production and variable current inputs that might be expected if the electrolyser is connected to a renewable energy source. The energy losses associated with the anodic oxygen evolution reaction are considerably greater than those associated with the cathodic hydrogen evolution reaction. Optimisation of oxygen evolution catalysts is therefore preferable to improve the energy efficiency of the electrolyser cell. The aim of this project is to investigate and develop oxygen evolution electrocatalysts for PEM water electrolysis that are tolerant of real-world cell operating conditions. A series of pure and mixed IrO₂-RuO₂ electrocatalysts have been prepared at a range of heat treatment temperatures. Catalyst electrodes were prepared as thin film rotating disk electrodes and the activity and durability examined by polarization and cyclic voltammetry measurements. Additional analysis has been performed by XRD, EDX and TEM. The influence of the preparation details on the activity and durability of the catalysts will be reported.

Nanotemplated electrochemical energy materials

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The integration of electronic and energy devices for advanced micro and nanosystems technology requires the development and optimisation of energy sources with increased performance per unit substrate area. Nanostructured materials have significant potential for applications in energy conversion and storage devices due to their unique physical properties. They provide additional electrode surface area, short path lengths for electronic and ionic transport and thus the possibility of higher reaction rates. Control of the active materials at the nanoscale is required to minimise the catalyst dimension and cost for fuel cell materials or active battery materials particularly where solid-state ionic diffusion is a limiting factor in the electrode reactions.

Anodic aluminium oxide processing on Si is a means to optimise the materials nanotemplating and integration of passive devices with Si technology. This is seen as a method to extend electronics roadmaps and has been termed *More than Moore* in which not only are the feature dimensions scaled as is typical with successive electronics generations but added functionality is incorporated through the convergence of Analog . RF - sensors . actuators . biochips - energy harvesters, etc. for adding functionality to ICs integrated on CMOS platforms. A significant issue in the integration of passive devices on Si is the footprint and its minimisation is essential. Maintaining the functionality of the energy source while minimising footprint may be achieved by structuring of the energy source components and maximising the characteristics of the materials to eliminate unnecessary materials such as binders or support materials.

Optimising active materials not only requires assessment of the electrochemical properties for the given application but also the electrical and mechanical characteristics during reaction. Coating of active materials to form core-shell structures has been found to be a useful technique to improve electrical characteristics. An alternative method is the use of high conductivity support materials that are electrochemically deposited and the formation of active materials as a shell. Electrochemical methods to achieve controlled nanotemplated materials for microenergy systems integration with electronic devices have been demonstrated [1-4] and research continues to achieve optimised metal and alloy active materials in templates for energy applications.

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Ionic liquid electrolytes for fuel cells

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Protic ionic liquids (PILs) are liquids that are formed by neutralisation of a Brønsted acid by a Brønsted base. Some of the most attractive features of PILs are their very high thermal stability and proton conductivities, which means that they are very promising electrolytes for medium temperature fuel cells (fuel cells that operate above 100 °C). Indeed, it has recently been shown that extremely large open circuit voltages (OCVs) can be achieved in fuel cell systems using PIL electrolytes (values that exceed that achievable in conventional hydrated fuel cells).^[1] These large OCVs have been attributed to the high operating temperatures and the lack of H₂O in the system, which is known to inhibit O₂ reduction in aqueous systems.

In this contribution, we describe the first fundamental insights into fuel cell catalysis in PILs. Using electrochemical analysis and X-ray photoelectron spectroscopy, we show that oxidation of trace H₂O in the PIL dimethylethylammonium trifluoromethanesulfonate, [dema][TfO], leads to the coverage of Pt electrodes with an adsorbed oxide film at positive potentials. The onset potential for oxide formation is considerably higher than that observed in aqueous systems. Not only that, the potential at which oxide forms is highly temperature dependent. These observations have significant implications for electrocatalysis of both the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) in PIL-based fuel cells. Using a combination of cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy, we have studied the ORR and HOR in [dema][TfO] at Pt in the temperature range 25-160 °C. These measurements show that, when the Pt surface is covered with an oxide adlayer, the ORR only occurs when the Pt surface is reduced. Interestingly, when the Pt surface is not covered with an oxide adlayer, a significant positive shift in the ORR onset potential is observed, which demonstrates that the use of PIL electrolytes could lead to the development of highly efficient fuel cells. The implications of these results for fuel cell fabrication and uptake will be discussed.

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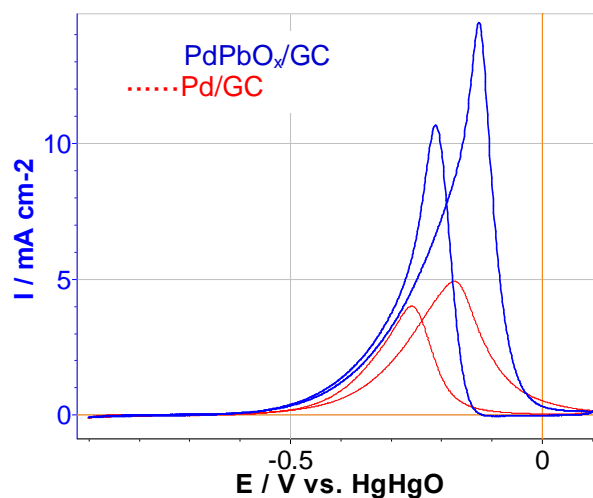
Highly active PdPbO_x nanoelectrocatalysts for alcohol oxidation

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Direct alcohol fuel cells (DAFCs) have attracted much attention due to their potential application as power supply for portable devices and vehicles. To date, majority of the research has been carried out in acidic media using proton exchange membrane as the separate for anode and cathode and thus limited the use of catalysts to Pt and Pt-based noble metal catalysts. The invention of anion exchange membrane has made it possible to operate under alkaline media and thus to use non-Pt catalysts, together with a wide range of metals and metal oxides as support or promoter. Pd has been identified as a promising catalyst for alcohol oxidation in alkaline solution although it exhibits low activity in acidic media. Some oxides, such as NiO and SiO₂, have been investigated as effective promoters to Pd for alcohol oxidation. Similar to SnO₂, PbO_x shows strong tendency of adsorbing H₂O and/or OH, and thus we propose that it could be a good promoter to Pd catalyst for alcohol oxidation.

In this work, we have prepared PdPbO_x by various methods, including electrochemical co-deposition followed by heating and potential scanning to generate optimum PdPbO_x. The SEM images show the as prepared catalyst surface was covered by quasi-homogenously dispersed nanoparticles with average size ca. 10 nm. The composition determined by XPS shows an atomic ratio of 60:40 (Pd:Pb). The Pb component was found all in oxidation states, 76% of PbO₂ and 24% of Pb₃O₄. The reactivity towards a range of alcohols electrooxidation has been carried out on PdPbO_x/GC in alkaline media by both cyclic voltammetry and chronoamperometry (CA), and remarkably higher current density was observed for all the four alcohols investigated, in comparison with Pd nanoparticles prepared under the same condition. The activity, indicated by the peak current at anodic scan, of the 4 alcohols studied was given in the following order: ethylene glycol > ethanol > glycerol > methanol. Very promising data have been obtained from the optimum catalysts for the targeted fuels, and these will be reported.



Cyclic Voltammograms obtained from ethanol oxidation on PdPbO_x/GC and Pd/GC, respectively. Solution: 1 M ethanol/NaOH.

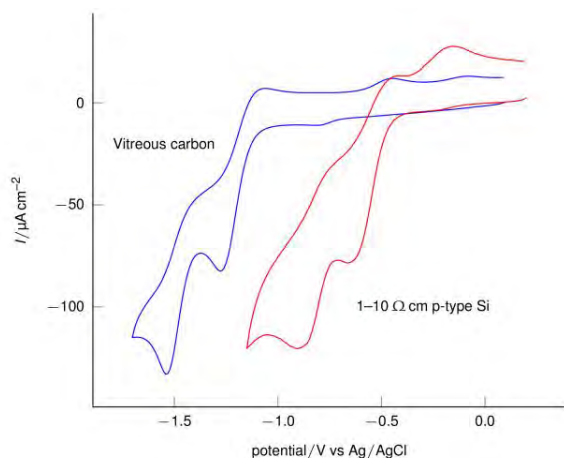
Solar fuels. Visible light driven generation of dihydrogen at p-type silicon electrocatalysed by a molybdenum hydride

Lee R. Webster, Saad K. Ibrahim and Christopher J. Pickett

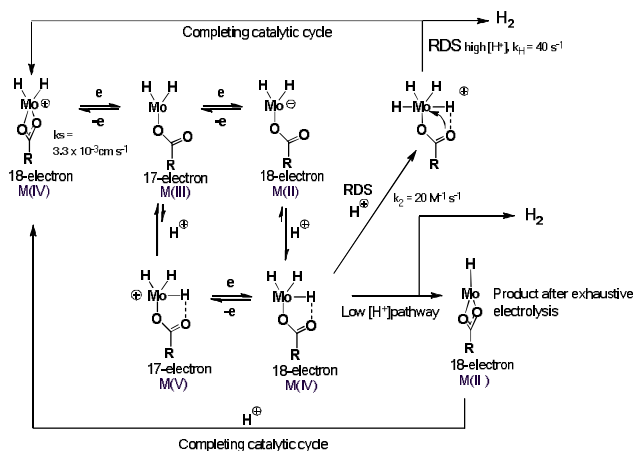
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Visible light driven photoelectrochemical conversion of protons to dihydrogen is a half-cell reaction of relevance to the generation of H_2 as a clean energy vector^[1], a solar fuel. By far the most advanced technology for converting light to electrical energy is based on semiconducting silicon. These readily available and well characterised photovoltaic materials can also provide a means of directly converting solar energy to stored chemical energy in a photoelectrochemical device^[2].

We show that a robust molybdenum hydride system can sustain photoelectrocatalysis of a hydrogen evolution reaction at boron-doped, H-terminated, p-type silicon^[3]. The photovoltage for the system is ca. 600-650 mV and the current densities which can be sustained at the photocathode in non-catalytic and catalytic regimes are similar to those at a photoinert vitreous carbon electrode. The kinetics of electrocatalysed hydrogen evolution at the photocathode are also very similar to those measured at vitreous carbon, evidently visible light does not significantly perturb the catalytic mechanism. The p-type Si we have employed optimally harvests light energy in the 600-700 nm region and with 37 mW cm^{-2} illumination in this range, the light to electrochemical energy conversion is estimated to be 2.8%.



Scheme 1. Proposed pathways for hydrogen evolution $[\text{MoH}_2(\text{O}_2\text{CMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ complex in 0.1 M $[\text{NBu}_4][\text{BF}_4]$ -MeCN at a dark and an illuminated 1. 10δ cm p-type Si electrode: The scan rate is 100 mV s^{-1} .



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SLRR-based deposition of platinum for dye sensitized solar cell counter electrodes

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The mass production of photovoltaics, such as dye sensitized solar cells (DSCs), is of great interest to the renewable energy generation industry. DSCs are low cost, photoelectrochemical devices that use sensitized-TiO₂, to generate electricity [1], a schematic of a DSC can be seen in Fig. 1. The devices consist of a dye adsorbed to a TiO₂ semiconducting layer which, when illuminated, injects an electron in to the TiO₂ network. This electron migrates to the external circuit where it is returned to the excited dye by a redox catalyst on the counter electrode (CE). This catalyst facilitates the return of injected electrons from the external circuit to the excited dye through the reaction pathway, $I_3^- + 2e^- \rightarrow 3I^-$ in the electrolyte. Currently, platinum catalysts are produced by a costly thermal route on FTO-glass or by reduction of the precursor with NaBH₄, typically on polymeric substrates.

The aim of this poster is to present a highly controllable, fast, low cost platinisation process, leading to a viable in-line method of applying catalytic platinum. This method entails a Surface Limited Redox Replacement (SLRR)-based deposition of Pb onto FTO-glass followed by the redox replacement of lead by Pt ions in solution, which was adapted from previous method for Au(111) and Ag(111) substrates [2], [3]. A short deposition pulse time favours the nucleation of small Pb/Pt clusters or particles on the substrate. The growth step is achieved through the redox replacement of surface Pb by Pt. DSC were constructed with SLRR-based and thermally platinised counter electrodes. Electrochemical impedance spectroscopy (EIS) was used to obtain the charge transfer resistance (R_{ce}) of the thermally decomposed and SLRR platinised DSCs. The Nyquist plot in Fig. 2 shows that the R_{ce} (diameter of semicircle) of SLRR constructed devices rival that of the conventionally used thermal platinum catalyst.

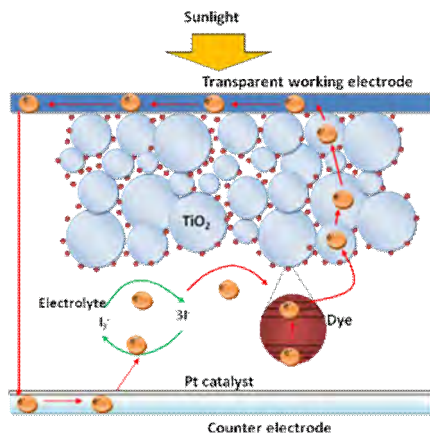


Fig. 1 . Schematic of a DSC

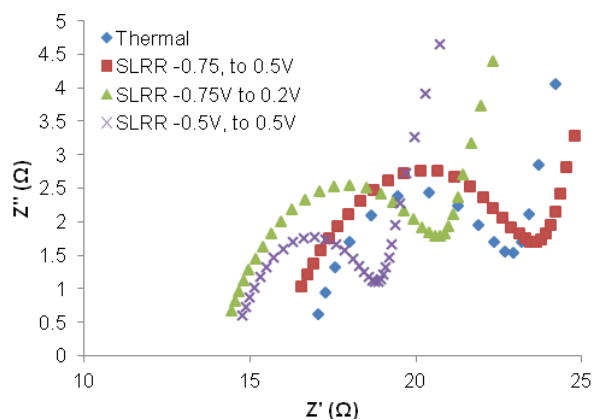


Fig. 2 . Nyquist plot showing comparison of Pt CEs

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Development of none-noble metal electrochemical cells based on OH⁻ conductive ionomer membrane

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Water electrolyzers efficiently store energy from renewable power sources, such as solar, wind, and hydroelectric powers, into chemical energy with hydrogen as the energy carrier. While in H₂-O₂ fuel cells, the chemical energy carried by hydrogen can be released to electricity, with large power densities and only producing water. Recently, there are accumulating interests on using OH⁻ conductive anion exchange ionomer membranes (AAEM) for these electrochemical cells. In a basic environment, the catalysts may be none-noble metals. This presentation would report two kinds of OH⁻ conductive polymethacrylate ionomers respective with quaternary ammonium and dialkylimidazolium functional groups. The M-doped Co₃O₄ (M= Li, Cu, and Mn) nanopowder catalysts were synthesized and characterized as with CV, SEM, TEM, and XRD. These spinel cobaltates exhibited good catalytic activity for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Membrane electrode assembly (MEA) using these catalysts was designed in catalyst coated on membrane (CCM) style and prepared with the polymethacrylate ionomers. The polarization performances of these MEAs in both water electrolyser mode and fuel cells mode were determined. With Cu_{0.7}Co_{2.3}O₄ catalyst the AAEM water electrolyser at 1.8 V voltage achieved 100 mA cm⁻² and 1000 mA cm⁻² current densities respectively in deionised water or in 1 mol dm⁻³ KOH solution. In the regenerative AAEM fuel cell using bifunctional Cu_{0.6}Mn_{0.3}Co_{2.1}O₄ catalyst, the peak power density was over 80 mW cm⁻² in fuel cell mode, and in electrolyser mode the onset voltage was about 1.55 V in deionised water. The fuel cell to electrolyser voltage ratio at 100 mA cm⁻² achieved c.a. 32%.

Development of a biosensor for HDL-cholesterol based on a novel electrocatalyst for hydrogen peroxide reduction

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Cholesterol is synthesized in the liver and transported in the blood in association with low density lipoprotein (LDL-C) and high density lipoprotein (HDL-C). HDL-C is a modifiable risk for coronary heart disease. Its routine measurement is recommended in the evaluation and management of hypercholesterolemia. In the past three decades, chemical precipitation methods, and more recently, homogeneous assays have been used to measure plasma HDL-C in clinical laboratories. Homogeneous assays were a major step forward in improving the precision of earlier precipitation methods.[1] The final step of measurement is typically based on the formation of hydrogen peroxide from cholesterol oxidase (ChOx). Novel methods for the electrocatalytic reduction of hydrogen peroxide have been developed.[2]

It has been shown that polyoxyethylene tribenzylphenyl ethers (Emulgen B-66) allow HDL-C to be selectively dissolved to allow the enzymatic catalysis of HDL-C alone.[3] This work is investigating the application of homogeneous cholesterol assay strategies to the measurement of HDL-C in combination with this novel electrochemical transduction methodology.

Printed electrodes with good catalysis of hydrogen peroxide at moderate reduction potentials were evaluated as the basis of the assay.[4] The effects of assay reagents such as buffer and surfactant on the electrode behaviour were assessed amperometrically in the presence of hydrogen peroxide solutions. Of three buffers evaluated, the electrodes showed a linear responses in 0.1M PBS (pH=6.8) with enhanced catalytic activity toward H_2O_2 in presence of Emulgen B-66.

The effect of other assay components such as cholesterol oxidase, cholesterol esterase and serum components were measured using the modified electrodes. However, the serum components showed a negative effect on electrode behaviour.

Amperometric responses in 0 to 2.5 mM HDL-C solutions were also measured. Non-specific signal contributions were observed from assay components. Further method development is to be performed to eliminate these interferences.

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Electrochemical fabrication and investigation of modified lead dioxide (PbO₂) electrode for persistent organic pollutants degradation

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PbO₂ as an electrode material is emerging as a potential candidate for the analytical investigations and for pollutant degradation because of its low cost, stability and efficiency. As nowadays water resources contamination by industrial effluents is the major problem faced by human being. So research have been focused for employing PbO₂ as an effective electrode for the degradation of persistent organic pollutants like phenols, pesticides and aromatic hydrocarbons.

To fabricate such a modified PbO₂ electrode which will degrade the persistent organic pollutants like phenolic compounds and can also be employed for the analytical purpose are the two main objectives of the present work. In this work PbO₂ was deposited galvanostatically at a current density of 10mA/cm² over the Pd substrate. Prior to the deposition the anodization of the surface of the Pd substrate at 10V was done to prepare the surface area and hence the loading capacity of the substrate towards PbO₂.

The semi-analytical studies of the PbO₂ deposited over anodized Pd substrate with the optimized deposition solution containing F⁻ ions and HClO₄ showed satisfactory electrochemical activity. Further investigations are needed to develop a low cost electroanalytical electrode with increased homogeneity and compactness of the deposited material.

The morphological studies of deposited electrodes by SEM revealed that nafion containing PbO₂ deposited over anodized Pd surface was the optimized electrode for the bulk electrolysis. 2-nitrophenol was completely and phenol was partially removed by bulk electrolysis at optimized current density of 20mA/cm² for 3 hours with the modified PbO₂ electrode having area of 4cm². In the case phenol fouling of electrode with polymeric compounds was observed which inhibited its further degradation ability. The degradation monitoring was contemplated by cyclic voltammetry, UV-visible spectroscopy and HPLC. The results found were good in agreement with each other. The percent degradation of phenol was approximately 50% and that of 2-nitro phenol was upto 99%.

Interfacial chemical reactions at disordered carbon surfaces

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Amorphous carbon materials are used for a vast range of applications, from catalyst supports to medical implantable devices and they have recently been shown to compare well to graphene electrodes in their electrosensing performance. Many of the applications of amorphous carbon rely on the ability to control surface chemistry and reactivity; the wide range of functions that can be modulated via surface chemistry has generated great interest in achieving a fundamental understanding of factors that control the surface reactivity of these materials.

Disordered carbons, such as amorphous carbon (a-C) and hydrogen doped carbon (a-C:H), however, present challenging surface chemistry problem since their bulk structure is heterogeneous. Although the surface chemistry of disordered carbons would be expected to range from graphite-like to diamond- or polymer-like, it is not yet clear to what extent surface reactions are affected by composition heterogeneity. We report on our progress towards developing structure/reactivity relationships for a-Cs. We have prepared a range of carbons with varying composition and used a combination of spectroscopic and electrochemical methods in order to understand the rate and yield of a benchmark surface reaction, the spontaneous attachment of aryldiazonium salts. We report, for the first time, in situ studies of the spontaneous adsorption of aryldiazonium cations at a-C substrates of varying conductivity and discuss the role that substrate electronic properties play in determining rate and yield of these surface reactions.

Electrical measurements at the solid/liquid interface using open loop Kelvin probe force microscopy

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Local ionic, electronic, and electrochemical phenomena at the solid/liquid interface are ubiquitous in physical chemistry and life processes. The small length scales at which these phenomena take place require techniques capable of probing the solid/liquid interface at the nanometer scale. Scanning probe microscopy (SPM) offers the potential for nanometer-resolution functional imaging, making it a powerful tool in light of such challenges. In the last two decades, an array of SPM techniques aimed at probing electronic, electrostatic, and electrochemical phenomena at the nanoscale have been developed, albeit under vacuum or ambient conditions. Here, we investigate novel open loop-Kelvin probe force microscopy (KPFM) methods for the characterization of electrostatic and voltage-controlled electrochemical dynamics in liquid. We perform measurements using dual harmonic (DH)-KPFM on graphene, under both liquid and ambient conditions. We also demonstrate spectroscopy measurements combining low frequency voltage sweeps and first-order reversal curve (FORC) measurements, allowing slow electrochemical dynamics to be explored and the hysteretic response of the electrochemical potentials to be investigated. Combined with insulated AFM probes we predict a bright future and a broad applicability of open loop liquid KPFM techniques for characterizing the solid/liquid interface at the nanometer scale.

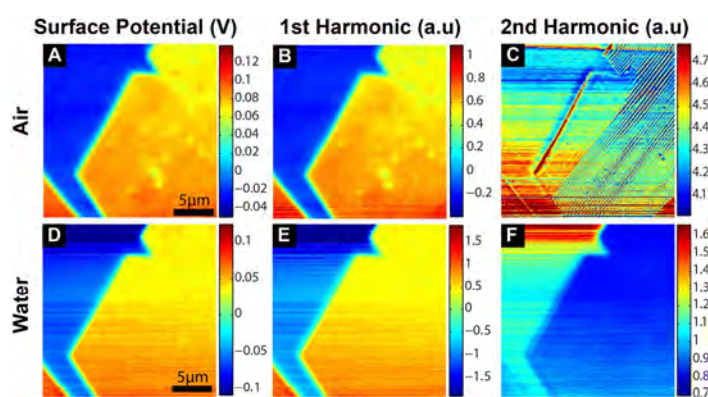


Figure 1 DH-KPFM surface potential measurements in ambient (A) and milliQ (D) of single layer graphene on CuO₂ substrate. Corresponding first (B, E) and second (C, F) harmonic amplitude response.

Non-oxidative electrochemical exfoliation method for the production of graphene

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For all potential future graphene applications, a scalable high yield/purity method of production is essential. However, current solution phase graphene production methods, whilst scalable, involve oxidative routes, since solution phase exfoliation proves difficult without the functionalisation/oxidation of the exfoliated flakes. Herein we present a viable non-oxidative production route to few layer graphene (40% yield, <5 layers) via the electrochemical intercalation of tetraalkylammonium cations into pristine graphite. Two forms of graphite have been studied as the source material: these yield slightly different results. Highly orientated pyrolytic graphite (HOPG) offers greater advantages in terms of exfoliate size but the source electrode set up introduces difficulties. Using a graphite rod source, few layer graphene (<5 layers) are formed directly (without the use of a sonication stage) although the flake sizes are currently no larger than 50 nm in diameter. Flakes have been characterised using Raman spectroscopy and atomic force microscopy (AFM).

Single cell manipulation and sensing: a multifunctional microgripper device

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This work presents tweezer like microgrippers (designed to manipulate cells) that have been modified to sense ion movement associated with the signalling response of the cell. The manipulation technology uses thermal actuation via a hot/cold arm principle to achieve this tweezer-like action. The device can grip objects and not fracture, even when subjected to a substantial applied tangential force. This is achieved by tailoring the microgripper tips at the mask design stage so that they best fit the item being manipulated. The combination of zero apparent damage with high levels of manipulation, sorting, isolation and positioning makes this microgripper a very competitive manipulation tool.

A fabrication route using MEMS (MicroElectroMechanical Systems) technologies has been developed to produce a high yield of operational devices. Photolithography enables control of the dimensions of the device, which can be resolved to a high degree of accuracy. The microgripper is mounted on a custom PCB, which allows an easy interchange of devices onto microscopes and standard macro-manipulation tools.

The functionality of the device is widened by the inclusion of a $300 \pm 50 \text{ } \mu\text{m}^2$ gold electrode protruding at one or both ends of the microgripper tips. This enables the device to be used as the working electrode in an electrochemical set up. The modification involves applying the process of adding the components that make up All Solid State Ion Selective Electrodes (ASSISEs). Detecting the changes in intra- and extra-cellular ion concentration associated with cell signalling has always been of great interest, with many different methods being utilised. Potentiometric sensors, such as ASSISEs, are particularly advantageous in this area due to their comparatively small size, portability, low energy consumption and low cost. A PEDOT:PSS film electrochemically deposited onto the gold electrodes at the microgripper tip can be coated with an ion selective membrane (PVC based) to enable specific ion sensing that allows real-time, local sensing of specific ion release from a manipulated species. Devices have been fabricated that are capable of sensing calcium ions at concentrations as low as $8 \times 10^{-5} \text{ M}$ with excellent Nernstian response (calibration slopes of $29.5 \pm 2.5 \text{ mV/dec}$). By interchanging the ionophore within the membrane, sensors to detect calcium, sodium and potassium can be fabricated. This creates a toolkit of sensors designed to detect specific ions in assorted real-life environments with a high degree of selectivity.

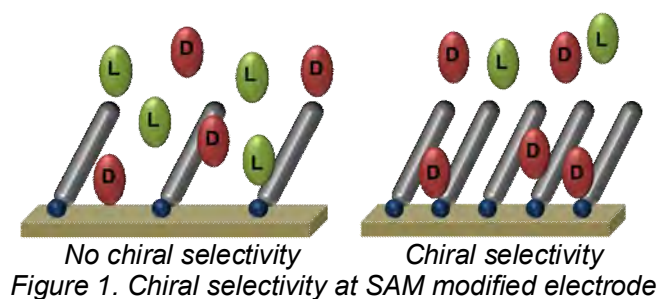
The ultimate potential of the microgripper will be realised in the determination of the change in specific ion concentration levels resulting from external electrical or physical stimuli of a manipulated cell. This can then be used in a feedback loop during manipulation to indicate the level of distress.

Electrochemical impedance for proline chiral discrimination

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The context of this research was the study of electrochemical analysis for chiral discrimination, as an alternative to standard chromatography techniques. This poster presents the demonstration of using a SAM-modified electrode for proline chiral discrimination, where the monolayer is characterised using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The gold electrode surfaces were modified with glutathione and cysteine, because of their preferential chiral interaction towards D-proline enantiomer identified in previous work¹. CV and EIS analysis conducted at the glutathione-modified electrode did not show any preferential enantioselectivity towards proline. However, impedance analysis showed how the cysteine monolayer modified electrodes exhibited different electron transfer rates of $K_3[Fe(CN)_6]$ in the presence of L- or D-proline. The charge transfer rate at the monolayer was almost twice as slow in the presence of D-proline ($9.50 \times 10^{-5} \text{ cm.s}^{-1}$) compared to L-proline ($2 \times 10^{-4} \text{ cm.s}^{-1}$). The slower electron transfer rates indicated the preferential interactions between the cysteine molecules and the D-proline enantiomer (Figure 1). This study also demonstrated that the packing of the cysteine molecules influenced the selective interactions taking place at the monolayer as no enantioselectivity was detected at a diluted monolayer.

These results indicate that electrochemical methods are a realistic alternative to chiral chromatography for the detection of chiral interactions.



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Fabrication and characterisation of bucky column electrodes for electroanalytical measurements

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Electrochemical measurements are applied to a wide range of different applications from industry settings to biological system. As such, the development of new materials capable of functioning as electrochemical sensors for practical sensor systems is a fundamental path to development new and innovative ways of examining different systems.

This work discusses a new manner of macro electrode formed by compression of carbon nanotubes to produce a solid disk of a Bucky columnq(BC)[1] which was then manufactured into a setup comparable to that of standard electrodes. This BC-based electrode has been characterised for its electrochemical properties in comparison to GC and BDD electrodes.

Interestingly, this BC-based electrode displayed fundamental differences to GC and BDD electrodes. These arose from the altered microenvironment the material provided and from minor expansion of the material in solution to produce an electrode with greatly increased surface area for its physical size.

The behaviour towards trial species such as potassium ferricyanide, ammonium iron (II) sulphate and dopamine has displayed behaviour that significantly differs from standard GC and BDD electrodes. While each of these processes are diffusion controlled at standard electrodes, at a BC-based electrode these display surface confined redox reactions. The redox couple associated with $\text{Fe}^{2+/3+}$ is irreversible at both a GC and BDD electrode while it remains reversible at a BC-based electrode up to moderate scan rates. Similarly the oxidation of dopamine is irreversible and produces by-products that be observed electrochemically are capable of fouling these electrodes, while at a BC-based electrode the redox couple of dopamine is clearly visible as a reversible process.

In terms of electrode fouling a BC electrode displays greater resistance to fouling than either a GC or BDD electrode. For a GC or BDD electrode fouling due to the oxidation by-products of dopamine suppresses the electrochemical response at the respective electrode renders any meaningful activity indistinct by ~3-4 minutes, depending on the specific electrode, of usage and at times >10 minutes even the background currents are reduced dramatically as access by solution species to the electrode surface is significantly blocked. In contrast a BC electrode displays a well-defined redox couple for dopamine for extended periods. Initial loss of the current response is logarithmic with the bulk of the loss occurring within 4 minutes reaching ~49% of its initial value further fouling up to ~22 minutes only reduced the response to ~40%.

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Redox potential and antioxidant activity monitoring for complication diagnosis in patients with kidney transplants

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It is well known that an imbalance of pro- and antioxidants can be an indication of certain pathological processes taking place in the organism. The use of redox potential monitoring of blood serum for diagnosing certain complications in patients following kidney or liver transplantation was previously developed [1], as the redox potential of biological media is an integral value, indirectly reflecting the pro- and antioxidant balance [2]. Synchronous measurement of redox potential and antioxidant activity in blood serum was proposed as a way to make the monitoring more comprehensive.

Since state-of-the-art methods of antioxidant activity measurement in biological media are quite expensive and relatively slow, a new electrochemical method was developed that measures antioxidant activity by cyclic voltammetry in blood serum added to aqueous benzoquinone mediator (Fig. 1). Antioxidant activity level was determined relative to quercetin.

Synchronous monitoring of redox potential and antioxidant levels in blood serum was performed in patients with kidney transplants. As the data in Fig. 2 show, redox potential and antioxidant activity levels have similar time dependences. Decreases in antioxidant levels correspond to positive shifts of redox potential, while increases correspond to redox potential negative shifts. These observations demonstrate that similar conclusions are reached based on either method.

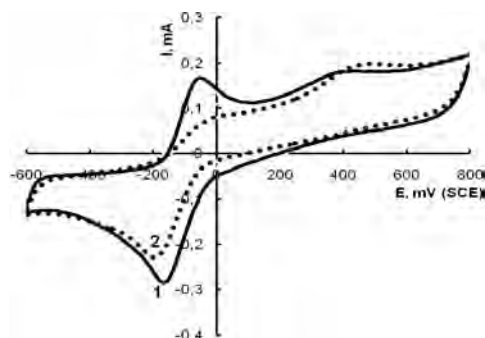


Fig.1. Cyclic voltammogram of benzoquinone without (1) and with blood serum (2) on Pt.

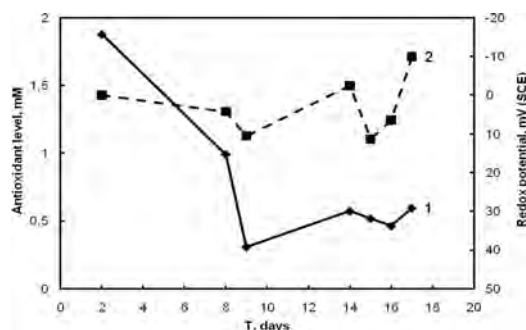


Fig.2. Monitoring of redox potential (1) and antioxidant level (2) of blood serum

However, sometimes no correlation was found between the two methods. For instance, sharp redox potential shifts (>30 mV) are known to indicate inflammatory complications, but are not reflected in the antioxidant level data. This absence of correlation may suggest that corrections in the course of treatment are needed.

Thus, synchronous monitoring of redox potential and antioxidant levels may possibly be used for assessment and adjustment of the medicinal treatment in patients with organ transplants.

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Mediated electron transfer using lignosulphonate modified electrodes

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Enhancement of electron transfer kinetics using inexpensive mediators. Such a statement sounds too good to be true but there is a class of compound that *is* relatively cheap and shows some promise of being an effective mediator: lignosulphonates [1].

Lignosulphonates are obtained from lignin, which is found in plant material and binds together cellulose fibres. After cellulose, lignin is the second most abundant biopolymer. Thus, compounds derived from lignin are quite cost effective for various applications, in this case mediated electron transfer.

The work presented herein focuses on how carbon electrodes modified with a lignosulphonate layer affect the electron transfer kinetics of a range of probes- such as ferrocyanide and probes in the ferrocene series- in a variety of conditions.

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Voltammetric behaviour of lead using a microband screen-printed carbon electrode and its trace determination in plants by stripping voltammetry

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The aim of this study was to determine trace Pb concentrations in sap obtained from plants via differential pulse anodic stripping voltammetry (DPASV) using a microband screen-printed carbon electrode (μ BSPCE). Cyclic voltammetry was employed to study the electrochemical behaviour of Pb^{2+} at these electrodes in a variety of supporting electrolytes. The anodic peaks obtained on the reverse scans showed that Pb had been deposited as a thin layer on the surface of the μ BSPCE. The anodic peak of greatest magnitude was obtained with 0.1 M pH 4.1 acetate buffer containing 13 mM NaCl. The conditions for DPASV were optimised; in quiescent solution, an accumulation time of 960 s, an accumulation potential of -1.3 V, pulse height of 50 mV and scan rate of 50 mVs^{-1} were found to be optimum. The sap was extracted from each of the plants and stored individually in vials. Analysis was carried out by DPASV following suitable dilution with the electrolyte described earlier. The performance characteristics indicate that reliable data has been obtained for this electrochemical assay which could be applied as a generic method for determining toxic levels of lead in plants.

Keywords: microband screen-printed carbon electrodes; lead stripping voltammetry; microband electrode; chloride ions; plants.

Chiral interaction and sensing at liquid|liquid interface

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The investigation of interactions of drugs, particularly chiral drugs with plasma proteins, is of fundamental importance for drug efficacy and toxicity studies. In this work, the interaction between propranolol, procaine and lidocaine hydrochloride with a chiral acute phase plasma protein, α_1 -acid-glycoprotein (AGP) at a micro liquid-liquid interface was studied. The binding of these basic drugs to the protein was studied using electrochemical techniques such as cyclic voltammetric (CV) and differential pulse voltammetric (DPV). The interaction between the AGP and the drugs was shown as a decrease in the CV and DPV current responses, corresponding to the decrease in the transfer of the drugs at the liquid|liquid interface. The uncomplexed/unbounded drug is able to diffuse through the interface into the organic phase, whereas the bound one is retained by the protein (Figure 1). The bound concentration of propranolol (R- and S- enantiomers), procaine and lidocaine to AGP was estimated based on the responses obtained in the presence and absence of the protein. Scatchard analysis was employed to calculate the association constant and the number of binding sites of the drugs with AGP. It was proved that AGP has different affinity for different basic drugs which was reflected in the calculated association constants $2.7 \times 10^5 \text{ M}^{-1}$ for S- and $1.3 \times 10^5 \text{ M}^{-1}$ for R-propranolol, $1.2 \times 10^4 \text{ M}^{-1}$ for lidocaine and $8.4 \times 10^3 \text{ M}^{-1}$ for procaine.¹

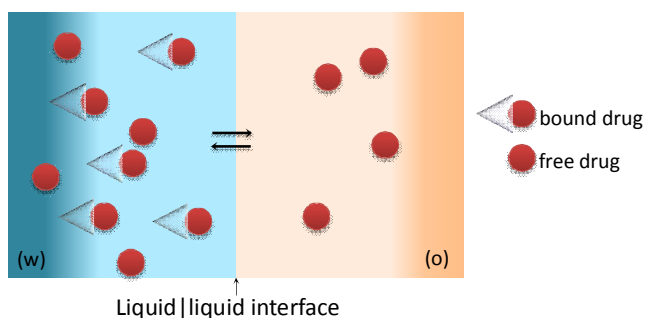


Figure 1 . Schematic representation of the drug-protein equilibrium at the liquid|liquid interface.

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Surfactant-mediated electrodeposition of bismuth telluride films and its effect on microstructural properties

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Thermoelectric Devices

Power harvesting from thermoelectric (TE) devices is seen as a highly promising route towards sustainable energy, as electricity can be generated from waste heat. This is, however, contingent on fabricating materials with higher TE efficiencies than currently available, as it cannot always be assumed that large thermal gradients will exist. Bismuth telluride-based alloys are currently the best commercially available TE materials for applications at room temperatures. Theoretical calculations predict that low-dimensional nanostructures of these materials can spectacularly enhance the figure of merit (a measure of the goodness of TE materials) from currently ~1 to higher values of up to 14 [1].

Electrochemical Fabrication

Whilst a wide range of fabrication techniques exist, such as single crystal growth, thin film technologies (MOVPE deposition, molecular beam epitaxy (MBE) including liquid phase epitaxy) and bulk powder syntheses, for the production of bismuth telluride compounds, these have proven to be quite costly and/or difficult to realise. Electrochemical deposition provides an attractive low-cost, room temperature and scalable route to the fabrication of high-quality TE materials such as bismuth telluride alloys [1,2].

Microstructural and Physical Properties

The correlation of microstructural properties with TE properties is still a mandatory challenge in order to achieve further progress in this emerging technology and has surprisingly received very little attention. The work presented here focuses on a detailed and systematic investigation of the microstructural properties (morphology, chemical composition, crystallinity and grain size) and physical properties (Seebeck coefficient, Hall coefficient, electrical resistivity, Hall mobility and carrier concentration) of electrochemically deposited bismuth telluride films in the presence and absence of levelling agents. Well adherent and high-quality n-type bismuth telluride films with a preferential (1 1 0) orientation, as determined by XRD, and close to stoichiometric composition were obtained in this way and preliminary transport property measurements indicate that these films show promising TE properties as well.

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Non-polar oil microdroplet detection using electrogenerated bromine as a molecular probe

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Oil droplet-modified electrodes have been employed for the study of ion transfer and photo-electrochemistry at three-phase junctions.^{1,2,3}

To date the vast majority of electrochemical studies have involved oils that are polar in nature and/or electroactive.⁵ The use of a non-polar oil complicates electrochemical measurements at the oil/water interface as it is extremely difficult to find a suitable supporting electrolyte to incorporate into the oil phase. However, although direct measurement of a redox active species in the oil phase presents a challenge, indirect measurement of molecular transport across this interface is possible using an aqueous phase electrogenerated species which partitions into the non-polar organic phase. One suitable redox couple is bromide (Br^-)/bromine (Br_2), as the electrogenerated aqueous phase product, Br_2 , is soluble in both phases. It has previously been shown that by using double potential step chronoamperometry (DPSC) in a generation-collection mode, interrogation of a liquid/liquid and liquid/gas interfaces via the partitioning of electrogenerated Br_2 was possible.⁶

In this study we investigate partitioning of electrogenerated Br_2 (from Br^-) across the non-polar oil (dodecane) droplet/ aqueous solution interface, using DPSC on a platinum nano-particle functionalized polycrystalline boron-doped diamond (PtNP-pBDD) electrode, employing an arrangement where the droplet sits on (but does not cover) the electrode surface (Figure 1A). We show both experimentally and through finite element simulation how the current-time profile for collection of the diffusion-controlled electrogenerated bromine not only depends on the size and number (Figure 1B) of the droplets on the electrode surface but is also very sensitive to the time period of the generation step.

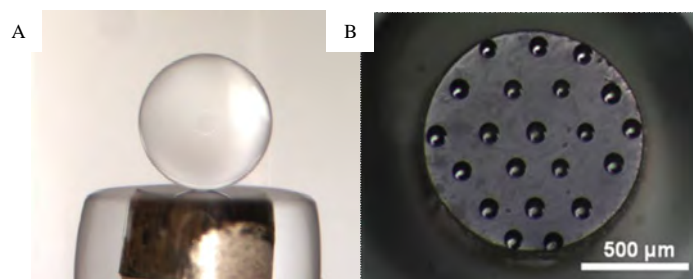


Figure 1: (A) A single 400 μm diameter dodecane droplet (side view) and (B) an array of ~ 100 μm diameter dodecane droplets (viewed from above), with an approximate spacing of ~ 120 μm i.e. 21 droplets on a 1 mm diameter PtNP-pBDD macrodisc electrode.

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Redox monitoring of HepG2 cells on carbon electrodes using resazurin dye

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The aim of this investigation was to explore the possibility of interrogating the redox status of mammalian cells using resazurin in conjunction with screen-printed carbon electrodes (SPCEs). One of the goals is the development of a biosensor system for drug/environmental toxicity testing.

Preliminary studies established that a density of $1-2 \times 10^4$ HepG2 cells per well of a 96 well plate produced a maximum dye fluorescent signal and, together with trypan blue exclusion viability testing, showed that cells maintained viability in the presence of the electrode materials and grew successfully on both uncoated and collagen-coated surfaces. Electron microscopic examination of gluteraldehyde-fixed surfaces showed that the cells had formed even monolayers.

Bioassay chambers were prepared by fixing cylindrical well sides onto Valox polymer bases bearing circular SPCEs. These chambers were sterilised and seeded with cells. As a measure of the cellsq metabolic activity and redox status, their ability during the final 4 h of incubation, to convert resazurin dye from its oxidised (blue) to its reduced (fluorescent) resorufin form was recorded using a plate fluorimeter. Dye conversion results showed that the cells in the chamber(s) remained viable; furthermore, the presence of collagen facilitated a 2.5-fold increase in dye conversion.

The voltammetric examination of resazurin at these SPCEs focused on the redox couple occurring between -0.5V and 0V: a pH study indicated that maximum current responses were obtained at pH 7 and calibration studies demonstrated good linearity ($R^2 = 0.995$) for both oxidation and reduction peaks, with detection limits down to at least 30 microMolar.

The results of these and further investigations into exploiting this system to develop an electrochemical biosensor device for monitoring cell metabolic status will be presented.

Investigation of the patterning of a lyotropic mixture onto silver paste electrodes via ink jet printing and its effect on the electroreduction of hydrogen peroxide

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Detection of hydrogen peroxide is widely used in a range of applications, from pharmaceutical to clinical and food industry, as well as environmental analysis. Peroxide is generated during many biological reactions and its concentration can be stoichiometrically related to the concentration of the analyte of interest.

Recent work has demonstrated that enhanced electrocatalytic reduction of hydrogen peroxide has been observed at silver paste electrodes when modified with solution of dodecylbenzene sulphonic acid (DBSA)/KCl which brings about modification of the surface with a liquid crystal-like lyotropic layer.^{Ref} However, modification of the surface also leads to the enhancement of the double layer capacitance. These layers have also been deposited using inkjet printing.^{Ref}

Microelectrodes are widely used in electrochemical analysis due to their reduced ohmic drop and charging current. These characteristics allow for lower detection limits and greater sensitivities in comparison to macroelectrodes. To overcome the disadvantage of the very small currents generated, microelectrode arrays are employed which have increased faradic currents while still having low charging currents.

In this study, we evaluate the effect of patterning of the DBSA/KCl solution onto the electrode using ink jet printing. The parameters of spot size, spot volume and spot spacing were investigated across the range of drop spacings from 20 μm to 250 μm .

The array structures were characterised using cyclic voltammetry and amperometry in the presence of hydrogen peroxide and in comparison with unmodified electrodes and electrodes completely covered with DBSA/KCl. Scan rate studies and determination of signal to noise were used to determine whether patterning was capable of enhancing the limit of detection of the electrode to hydrogen peroxide.

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Simultaneous determination of tyrosine and epinephrine using CeO₂ nanoparticles modified carbon paste electrode

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CeO₂ nanoparticles in the range of 3 nm were prepared by the precipitation method using two anionic surfactants of sodium dodecylbenzenesulfonate and sodium dodecyl sulphate. Their structural features studied by X-ray diffraction pattern (XRD), Scanning electron microscopy (SEM) and dynamic light scattering (DLS). The CeO₂ nanoparticles are proposed as a sensor for the rapid, sensitive and highly selective determination of trace amounts of tyrosine and epinephrine simultaneously in 0.1 M phosphate buffer solution (pH 7.3). The response peak current increases linearly with the tyrosine concentration ranging from 1×10^{-6} M to 4.5×10^{-5} M and 65×10^{-5} M to 1×10^{-4} M. The detection limit (S/N=3) for tyrosine was found to be 2×10^{-7} M. Epinephrine does not interfere with the determination of tyrosine. The method exhibits a high stability, selectivity and sensitivity. It is excellent for the simultaneous determination of tyrosine and epinephrine in real human blood serum.

Combined electrochemical and optical imaging of polymeric microcapsules using photocurrent measurements at electrolyte/insulator/ semiconductor field effect structures

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It will be shown that the electrolyte/ insulator/ silicon structures employed for Scanning Photo-induced Impedance Microscopy (SPIM) and Light-Addressable Potentiometric Sensors (LAPS) cannot only be used to produce images of local impedance and potentials but are also very sensitive fluorescence detectors and detectors of thermal radiation generated by gold nanoparticles. Electrochemical images were measured using single-photon excitation of photocurrents at 405 nm, while optical images were measured using two-photon excitation at 1250 nm. The latter resulted in a significant increase in the local photocurrent when microcapsules labelled with gold nanoparticles or fluorescence dye were present on the insulator.

Good lateral resolution of photocurrent measurements was achieved by using silicon-on-sapphire substrates. To improve the sensitivity of LAPS and SPIM, the traditional insulator was replaced with an undecylenic acid monolayer that was bound to hydrogen terminated silicon. Hollow microcapsules labelled with gold nanoparticles or fluorescence red 633 were prepared by layer-by-layer (LBL) coating of oppositely charged polyelectrolytes (PAH/PSS) on a sacrificial template (PMMA). The capsules were attached onto the insulator surface through the electrostatic interaction between the PAH polycation and COO⁻ terminal group.

To compare the impedance and optical images of light sensitive polymeric microcapsules, two different lasers (405 nm, 1250nm) were focused onto the 1 μ m thick silicon layer through the same microscope objective and scanned across the sample (Figure 1).

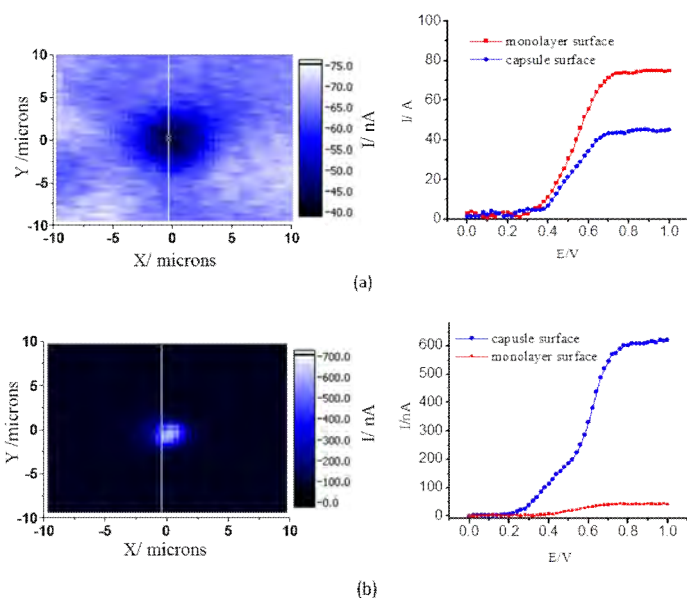


Figure 1 photocurrent images and photocurrent-voltage curves of capsules labelled with gold nanoparticles (a) 405 nm laser (b) 1250 nm laser

At 405 nm, all light is absorbed by the silicon resulting in a pure LAPS/SPIM image. Places where microcapsules adhered to the surface showed lower photocurrents than the bare organic monolayer due to the additional impedance of the polyelectrolyte shell.

When a 1250 nm femtosecond laser was employed, relatively low photocurrents were generated for bare monolayer surface by two-photon absorption in the silicon. However, in places where microcapsules adhered to the surface, the photocurrent was greatly enhanced due to the two-photon excitation of surface

plasmon resonance in gold nanoparticles resulting in the local production of heat. Similar results were obtained with microcapsules modified with fluorescent red 633. In this case, the two-photon absorption by the dye resulted in the emission of visible light thereby exciting much larger photocurrents than obtained by two-photon excitation in silicon. This technique has potential applications in cell imaging.

Fabrication and characterisation of nanostructured ZnO thin films grown on organic based ITO-PEN flexible substrates by electrodeposition routes

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Solar energy the most abundant but a least exploited sources of renewable. Recently, the development in the field of photovoltaics has been really extensive, fascinating and progressive. A significant amount of work has been conducted in order to fabricate morphologically controlled semiconducting materials and the use of such materials in photovoltaics having acceptable energy conversion efficiencies. Photovoltaic devices are used to harvest solar energy into electricity but the energy obtained in this way is about 0.04% of the global consumption (~ 15 TW in 2008, increasing 5%). Now it is the fastest growing sector for pursuing clean, renewable and cost effective way to get energy from sunlight [1].

Due to our complex life style today, the mobile power needs have become an essential element in day-to-day activities. The demand for flexible and efficient photovoltaics is rising rapidly as a wide range of new applications are emerging. Hence, there is a growing interest in the plastic electronics including the flexible photovoltaics [2]. Flexible photovoltaics construction involves processing materials at low temperature. Electrodeposition can play a significant role in the construction of such devices. Recent advances in the electrochemical deposition methods are really promising and allow construction of ordered semiconductor structures in the nano- and meso- scale which are capable of separation and collection of photogenerated charge carriers efficiently [3].

This work is focused on deposition of semiconductor material thin films on flexible substrates by electrodeposition routes and studies of their photoelectrochemical properties. Initial work has been conducted to grow ZnO nano rods on indium doped tin oxide (ITO) coated polyethylene naphthalate (PEN) flexible substrate. All the steps in the device formation have been performed using atmospheric, low temperature solution based conditions ensuring the stability of the plastic substrate. The seed layer has grown by electrodeposition using $\text{Zn}(\text{NO}_3)_2$ solution by varying the deposition parameters such as applied voltage, current density, deposition time, solution concentration etc. in order to optimise the process. After the seedling the electrodes are subjected to chemical bath deposition (CBD) for different time intervals using NaOH and $\text{Zn}(\text{NO}_3)_2$ at 80 °C [3]. The PEC performance of the electrodes has been evaluated after controlled annealing. The electrodes were subjected to the conventional heating, microwave irradiation and hybrid heating in order to ensure the stability of PEN during the thermal processing step [4]. The PEC properties of as-deposited and the treated electrodes are evaluated using standard protocols. The electrodes have been subjected to XRD and FEG-SEM studies to ensure the thin films contain the desirable material properties.

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Synthesis, characterization and electrochemical investigation of hybrid materials based on polyoxometalates and ionic liquids

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Early transition metals such as W, V, Mo, Nb and Ta are capable of making metal-oxide cluster anions in their highest oxidation state, and are generally referred as polyoxometalates (POMs). The structural and compositional diversity among this class of compounds have enabled them to be promising candidates for a wide range of applications across material science, medicine, biotechnology, nanotechnology and catalysis¹. Ionic liquids are considered as salts with low melting point usually below 100°C. They exhibit attractive properties like high thermal stability, non-volatile nature, high conductivity and wide electrochemical window. They are also employed in catalysis, synthesis of new materials and separation^{2,3}. In this work hybrid materials based on well Dawson $K_6[P_2W_{18}O_{62}] \cdot 14H_2O$ and vanadium substituted mixed addenda $K_8[P_2W_{17}V^{IV}O_{62}] \cdot 10H_2O$ POMs and ionic liquid 1-butyl-3-methylimidazolium bromide [BMIM][Br] were synthesized and characterised by spectroscopic and electrochemical techniques. Micro-crystals of these hybrid materials were adhered to the glassy carbon electrode surfaces and their redox properties were studied in contact with the ionic liquids [BMIM][BF₄] and [BMIM][PF₆]. A series of monoelectronic redox processes associated with tungsten-oxo framework of the POMs was observed. These POMs were also incorporated into conducting polymer polypyrrole and redox properties associated with the POMs and polymer were explored in ionic liquid media. Monoelectronic redox couples associated with W-O framework of POMs were accessible within the film. Polymeric films with different surface coverages were studied and thin layer behaviour was observed for up to 100mV/s.

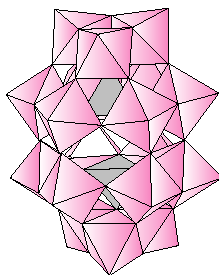


Figure: Well Dawson $[P_2W_{18}O_{62}]$ where pink octahedra present WO_6 units and grey colour presents PO_4 units.

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Formation and characterisation of three-dimensional macroporous copper structures

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Three-dimensional porous films have attracted much attention in recent years as they exhibit increased potential for rapid electrochemical reactions due to their considerably large surface areas. These films have potential applications in sensors, diagnostic devices, batteries and fuel cells.

In this study, three-dimensional macroporous copper films were generated using a hydrogen bubble templating method on gold electrodes. These films exhibited an ordered three-dimensional structure with interlinking branches surrounding micron-sized pores which were formed as hydrogen gas evolved at the electrode surface during copper electrodeposition, shown in figure 1. The micro-sized pores were approximately 50 μm in diameter, while the branches varied from 30 to 50 μm in diameter.

Additives were incorporated into the electrodeposition baths to control the film morphologies such as pore size and wall structure. By lowering the hydrophobicity of the hydrogen gas evolving at the electrode surface and by catalysing the copper deposition, the pore and branch diameters were successfully modified. These films were used for the detection of glucose in alkaline media.

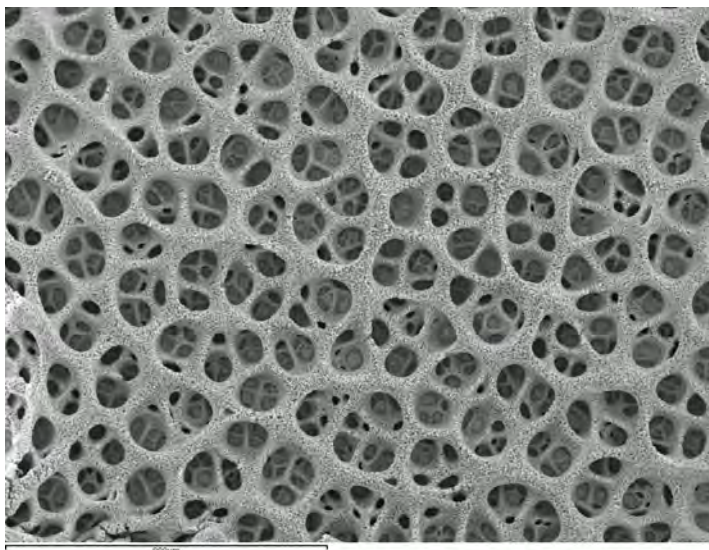


Figure 1: Macroporous copper structures

The use of metallocenes as redox probes in supercritical fluids

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Supercritical fluids have received increasing attention recently due to their unique properties, low viscosity leads to increased mass transport properties to and from the electrode surface. The solvent properties are also easily tuneable by changing pressure and temperature. Due to the specialised equipment needed for supercritical chemistry conventional reference electrodes cannot be used, this means that redox species need to be used in conjunction with a quasi-reference electrode. Redox species have a set redox potential which can be used as an internal reference. The most common of these are metallocenes such as ferrocene which has been well studied in both aqueous and non-aqueous media. A range of metallocenes have been studied in supercritical carbon dioxide (scCO₂) using acetonitrile (MeCN) as a co-solvent and tetrabutylammonium tetrafluoroborate (TBATFB) as a supporting electrolyte. These metallocenes include decamethylferrocene, ferrocene, decamethylcobaltocene and cobaltocenium hexafluorophosphate. Ferrocene redoxes occur at positive potential and cobaltocene redoxes occur at negative potential, when used together they can give a set potential between the two species. This set potential can be used as the internal reference for supercritical chemistry. The range of charges and sizes of these metallocenes will be used to study the properties of nanopores in supercritical conditions. This will lead to increased knowledge of how electrolytes and metal complexes behave inside and out of nanopores, allowing us to further understand deposition in supercritical conditions.

Magnetic properties of pulse DC electrodeposited ni nanowires

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Highly ordered nanoporous alumina templates have fabricated by a two-step anodisation process in 0.3M oxalic acid at 17 °C. Nickel nanowires of 30 nm diameter were grown in the pores of the templates using a series of 1 ms long half sinusoidal 8V potential pulses at a frequency ranging from 10-100 Hz. The electrolyte pH was adjusted to 4, 5 and 6 by adding sodium hydrogen carbonate. The effects of pH and off-time between pulses on the magnetic properties of Ni nanowires were systematically investigated. Coercivity of the nanowire arrays was greatest-85 mT, (Fig. 1)- when the off-time between pulses was 50 ms. Squareness was best, ~91%, (Fig. 2.) for the nanowires fabricated at pH~6. The magnetic easy axes of the nanowires are almost parallel to the wire axes. Changing the off-time between pulses changes the pH at the bottom of the pores optimising the electrodeposition condition hence affecting the microstructure and magnetic properties of the as deposited wires. The method is the most rapid, reliable and reproducible way to produce high quality nickel nanowires of this diameter.

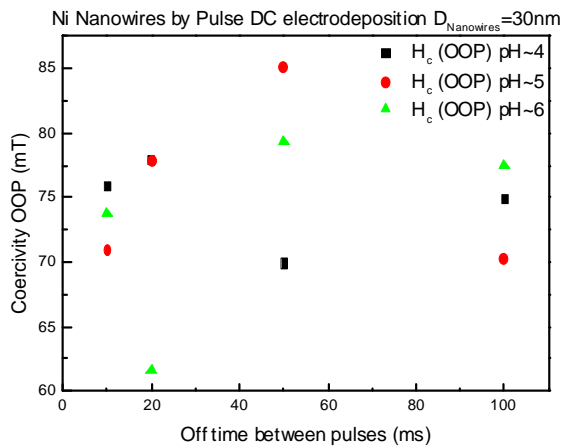


Fig. 1.

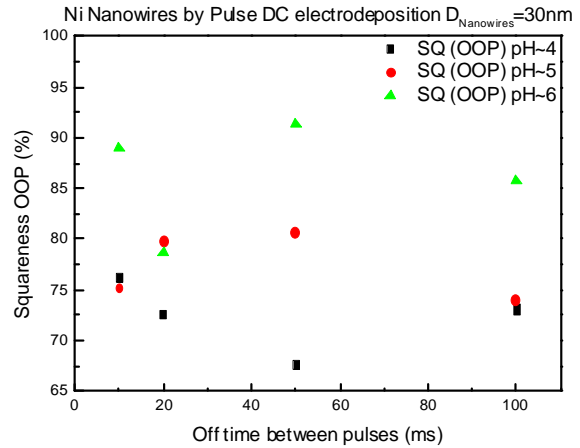


Fig. 2.

The interaction of iron-sulphur nanoparticles with carbon dioxide: electrochemical and surface processes implicated in the origins of life

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Iron sulphide materials are ubiquitous in the environment and include pyrite, mackinawite, pyrrhotite and greigite [i]. Redox processes involving CO₂ at the surface of iron sulphide materials have been implicated in the iron-sulphur world theories of the Origins of Life. There are two related theories - the pyrite-pulled mechanism of Wachterhauser [ii] and the iron-sulphur membrane theory of Russell [iii] . and both rely on the ability of naturally formed metal sulphide materials to reduce the CO₂ molecule. This electron transfer process is posited as the first step towards the formation of small organic molecules, which then undergo further reactions to form more complex molecules and eventually self-assembly into the first cellular organisms. The inspiration for these theories comes from the ubiquity of these materials in the natural environment, particularly in oxygen-deficient environments [iv]. Another argument for the role of iron sulphur materials is the almost universal incorporation of small FeS clusters (ferredoxins and rubredoxins) as electron transfer agents within enzymes. It is suggested that early metabolic processes must have made use of minerals related in structure and function to these now highly evolved enzyme active sites [v].

This presentation will discuss our recent work to understand how CO₂ interacts with the surface of Iron Sulphide Nanomaterials using electrochemical approaches and in situ and ex situ Raman spectroscopy, IR spectroscopy and XANES and XAFS measurements.

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Formation mechanism of nanoporous n-InP

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The anodic formation of porosity in semiconductors has received considerable attention, due to the fundamental insight it offers into semiconductor etching properties and its wide range of possible applications [1]. Although a number of models have been proposed to explain the formation of porosity in semiconductors [2-5], none as yet can explain the complete range of structures which have been formed in different semiconductor-electrolyte systems.

The anodic etching of n-type semiconductors in the dark is limited by hole supply at the semiconductor surface. It is generally accepted that this limited hole supply is what causes the initiation and propagation of porous etching, with hole supply being enhanced (and hence, porous etching initiated) at defect sites at the surface [6]. The newly formed pore tips then act as sites for preferential hole supply [5]. However, the variation in feature size, as well as the morphology observed as experimental conditions are varied cannot be so readily explained.

We have developed a new model to explain the formation of porosity in semiconductors based on a three-step process of charge transfer from the semiconductor to the electrolyte. The model is used to explain the characteristic width of the pore structures, and their directional preference, by considering the diffusion of holes at the semiconductor/electrolyte interface, and their interaction with the active species in solution.

The predictions of the model will be shown to be in agreement with the results obtained for the formation of porosity in n-InP in KOH [7-8]. The model will be shown to account for the formation of truncated tetrahedral CO porous domains by the preferential supply of holes to the {111}B surface states. The resulting pore growth and branching along <111>A directions leads to the characteristic tetrahedral domain shape.

The model also accounts for the formation of CLO pores in KOH under specific experimental conditions, as well as the measured dimensions of both the CO and CLO structures under a range of different formation conditions. The model can also be used to explain a large range of other pore morphologies that have been observed in other semiconductor-electrolyte systems.

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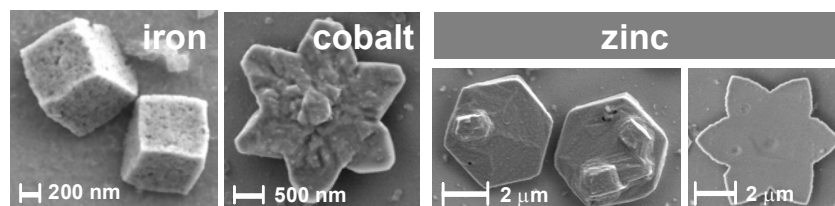
Electrosynthesised magnetic and non-magnetic microcrystals

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The electrodeposition of metals on cathodes coated with resistive electrosynthesised polymers produce particles instead of uniform films. Their morphology is modified by the electrochemical parameters employed during the deposition and the acid employed to dope the polymer.¹⁻³

In this work, submicron to micron size crystals of iron, cobalt and zinc are produced potentiostatically from solutions of variable ion concentration. We analyse the thickness of PANI on the particle size distribution and the effect of gravity, overpotential and the presence of acetic acid in the bath on the crystal shape. Their morphology reflects their crystal structure: *bcc* iron crystals grow in a cubic crystal habit with the 110 direction parallel to the substrate when acetic acid is present in the electrolytic bath, but the deposits in boric acid are hemispherical. *hcp* cobalt and zinc either grow as hexagonally shape crystals or in flower shapes with a six fold axis. In both cases the [001] direction is perpendicular to the substrate. The form depends critically on the concentration and conditions of convection.



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Surface adsorption and conformational changes of redox enzymes on graphene

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Enzymatic biofuel cells offer a battery-free way to meet the increasing power demands of miniature electronics. Biofuel cells use enzymes as catalysts for thermodynamically efficient conversion of fuels. They offer several benefits over fuel cells with conventional catalysts based on precious or toxic metals such as: higher efficiency, lower overpotentials and reactant specificity. However, when removed from a biological environment, their ability to maintain their functionality becomes extremely dependant on the surrounding conditions. We aim to combat this by working at ambient temperatures and use of buffers to maximise effectiveness.

Multicopper oxidases (MCOs) are a class of enzyme that catalyses the four-electron reduction of dioxygen to water. To exploit them in fuel cells, enzymes are immobilised on surfaces to create recyclable heterogeneous catalysts, although this can lead to enzyme function often changing when it is adsorbed. The overall aim is to improve our understanding of how these enzymes attach to surfaces to make efficient use of them as catalysts. We use the commercially available bilirubin oxidase from *Myrothecium verrucaria* (MvBOx) as our model MCO. We are investigating how MCOs attach onto the two-dimensional carbon material graphene, how they are stabilised and how their structural confirmations change. Proteins can absorb readily onto carbon surfaces, but there is little understanding regarding how proteins attach to defect and edge sites of single layer graphene.

A quartz crystal microbalance (QCM) and dual polarization interferometry (DPI) are used to give real-time analysis of enzyme-graphene interactions. We used these techniques to allow us to quantify mass adsorption, surface coverage, density and layer thickness. We combined these techniques with amperometric measurements to assay the activity of the enzymes and the degree of electronic connectivity between the enzyme and the sensor surface.

We have formed a graphene film on a silica-coated QCM crystal using a solution deposition technique. These films have been characterised by Raman and SEM to be graphene flakes composed of fewer than five layers with sizes ranging from 1.3 μm . DPI showed that MvBOx, which has a radius of 5.6 nm, forms 1.5nm-thick film on uncoated silica sensors. QCM data show a lower saturation level for enzyme adsorption on graphene-coated sensors than unmodified. Further work is to investigate any structural change and resulting activity of the enzyme upon adsorption and interaction with the graphene film.

Modulation of the luminescence and electronics of derivatised polyanilines with a novel ruthenium (II) phenanthroline luminophore

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Polyaniline (PANI) and poly(8-anilino-1-naphthalene sulfonic acid) (PANSA) were electrosynthesised on indium tin oxide (ITO) glass electrode and doped *in situ* with **ruthenium (II) (bis-2,2-bipyridyl)-2(4-carboxylphenyl) imidazo[4,5-f][1,10] phenanthroline** {[Ru(bpy)₂(picCOOH)]²⁺.(ClO₄)_{2n}} (RuBP) during the electropolymerisation process. PANSA showed a decrease in band gap and an increase in conductivity compared to PANI, which makes PANSA a more suitable material for plastic electronics and organic light emitting diode (LED) applications, since valence bond electrons can easily be excited to the conduction band of the polymeric materials. Electrochemiluminescence studies indicated an enhancement of the luminescence of PANSA-RuBP in comparison with that of RuBP. Also the molecule (PANSA-RuBP) did not exhibit the usual excimers associated with organic LED materials. This was confirmed by co-reactant of PANI-RuBP and PANSA-RuBP using tri-n-propylamine (TPA) which showed that PANI-RuBP was in the pernigraniline (P) state and PANSA-RuBP in the leucoemeraldine radical cation (LRC) state. The P state gives higher ECL signal than LRC state. This can be very useful in the application of electroactive polymers in the construction of ECL detectors which are the detectors of choice for most medical diagnostic instruments.

Synthesis, functionalisation and characterisation of nitrogen functionalised thin pyrolytic carbon films

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Conducting carbon materials have been shown to be of great interest for sensor and energy applications 1). Besides nanostructured CVD-grown materials such as nanotubes and graphene, pyrolytic carbon films (PyC) also show great promise 2). The later is accessible via a reproducible non-catalysed CVD process 3). In particular, the functionalisation and doping of these structures with nitrogen is of interest for various applications. This work details the surface nitrogen functionalisation of pyrolytic carbon films via a reliable ex-situ treatment with ammonia plasma. The carbon films were characterised with Raman- and IR- spectroscopy, scanning probe and scanning electron microscopy and contact angle measurements.

Electrochemical characterisation shows enhanced performance of these nitrogen functionalised PyC films in the ferri/ferro-cyanide redox probe when employed as the working electrode. The electron transfer kinetics of functionalised films is shown to more facile than that of as-grown pyrocarbon films and is attributed to both an increase in the proportion of edge plane graphitic carbon sites through surface roughening and the presence of heteroatoms in the carbon structure.

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Enhancement in photoelectrochemical properties of microwave treated Zn(OH)_2 , TiO_2 and Fe_2O_3 electrodes

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Low temperature deposition techniques such as electrodeposition, hydrothermal synthesis, chemical and physical vapour depositions are widely used to obtain various high quality nanoporous electrodes for electrochemical devices. In contrast with other techniques, the electrodeposition route provides many advantages, for example, it is usually carried out below 100°C and the film thickness and composition can be easily manipulated. The texture of electrodes can be altered in the electrodeposition process (i.e. pulsing) and typically such electrodes adhere strongly on the substrate. Various metal oxides, such as TiO_2 , ZnO , In_2O_3 , and ZrO_2 , have been successfully electrodeposited [1]. However, these methods generally involve a post-deposition annealing process. One of the major drawbacks of post-annealing is the particle growth and consequent collapse of the nanostructure during annealing. It reduces the porosity and effective surface area which will in turn affect the device performance (i.e. sensitivity in sensors, photocurrent in solar cells).

Microwave irradiation has shown great potential for the processing of different inorganic solids such as metal oxides (TiO_2 , ZnO and iron oxides etc.) and metal hydroxides. [2] Contrary to conventional heating, microwave treatment on metal oxides and hydroxides does not change the nanostructure of the material being heated which improves the crystallinity and inter-particle necking properties. Microwave irradiation has shown a significant potential to process not only metal oxides but also open up for processing of metal hydroxides in order to convert them into their metal oxides for various electronic and optoelectronic applications.

The effect of different heat treatments on the conversion of Zn(OH)_2 into their oxide is demonstrated in this work. The electrodeposited Zn(OH)_2 films are treated under microwave, hybrid and conventional heating and their photoelectrochemical (PEC) performance has been evaluated. It is found that there is a significant enhancement of the PEC performance in microwave treated electrodes comparatively. The microwave effect of PEC performance of metal oxides such as TiO_2 , Fe_2O_3 has been studied and it has found a 3-fold increase in the photocurrent after 100% microwave irradiation (Figure 1). [3] The results demonstrated that the microwave treatment of Zn(OH)_2 , TiO_2 and Fe_2O_3 showed superior PEC performance compared to that of the conventionally annealed samples. This presentation provides an insight of our present work in this area to date.

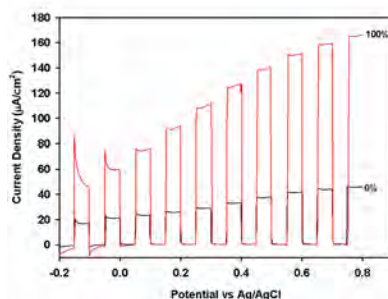


Figure 1. Chopped current-voltage characteristics of TiO_2 electrodes fabricated by AACVD at 400 °C with and without microwave irradiation (2.45GHz). Illumination intensity is AM 1.5 spectra.

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Controlled synthesis of Au/Pt/AuPt nanowires and dendrites by electrochemical routes and their SERS applications

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Au and Pt have been the focus of passionate research both from a chemical and electrochemical perspective due to their potential applications in surface enhanced Raman spectroscopy (SERS) sensing and fuel cell relevant electro catalytic reactions. Furthermore, bimetallic nanostructures, in particular, Pt-based nanostructures have been reported to exhibit good performance as electro catalysts in liquid fuel cells and are regarded as an alternative to commercial catalysts. Recently, dendrite shaped nanostructures have also received particular interest because of their large surface area and high specific activity owing to availability of edges, corners and stepped atoms on the branches. However, their synthesis approach usually involves specialist equipment, high temperature, high pressure conditions and noxious additives.

Here we prepared Au and Pt nanowires (~ 200 nm (d) \times ~ 3 -4 μ m (l)) using electrochemical deposition (chronocoulometry or potential sweeping) from metallic salt solutions. Porous alumina membrane templates (pore size 200 nm, 60 μ m thickness and 25 mm diameter) were employed as a substrate for nanowire formation with a thin layer of sputtered carbon or Au/Pd serving as electrical contact. A systematic study showed that the potential limits, scan rate and charge passed had a significant influence on the nanostructures formed in terms of shape and quantity. Under certain conditions, a three dimensional (3D) Au and AuPt nanodendrite network structure was also created by potential cycling. The growth of such AuPt dendrites was realised by electrodepositing Au initially followed by Pt over the range -0.2 to 1.4 V vs. Ag/AgCl at 0.1 V/s.

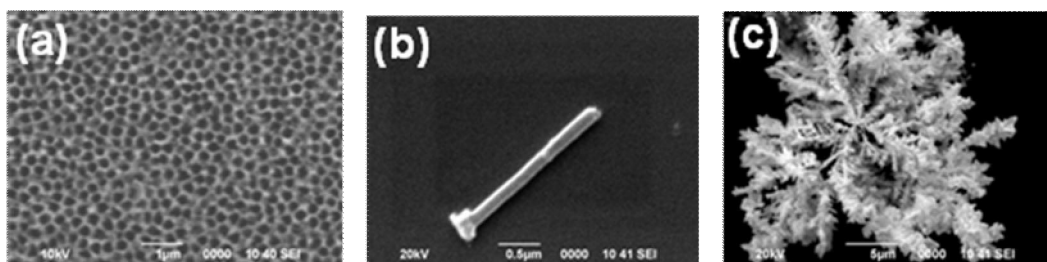


Fig. (a) Porous alumina membrane (b) & (c) SEM of the typical Au nanowire and Au dendrite structures, respectively.

Confirmation of the presence of the material was achieved using cyclic voltammetry while SEM/EDX was employed in order to examine the morphology and structural composition. Free standing nanowires and nanodendrites were obtained by dissolving the alumina template in 3M NaOH for 30 minutes. The Au dendrite structures resulted in a significant enhancement of Raman scattered signals as demonstrated by analysing the enhanced Raman signature of malachite green molecules on a Si substrate coated with nanodendrites. Our results indicate that these nanostructures can act as efficient probes for SERS and show great promise as an analytical platform especially in biological systems.

Polypyrrole nanowire modified membranes: remediation of hexavalent chromium

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Chromium exists in nine oxidation states, but trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are of primary interest due to their stability in the environment. Cr(VI) is a restricted hazardous substance (EU 2002/95/EC); it is 100 times more toxic, 1000 times more mutagenic¹ and much more mobile than Cr(III). Both substances are discharged into the environment as waste products from sources such as leather tanning, wood preservation and electroplating and increasing amounts are being found in the natural environment. The contamination of ground water supplies by the readily soluble Cr(VI) lead to two exposure pathways: dermal contact with, and ingestion of contaminated water. A common form of Cr(VI) is the chromate form, CrO_4^{2-} , which can enter the blood stream through skin lesions, causing destruction of red blood cells².

We have developed a conducting membrane modified with polypyrrole nanowires. The nanowires are synthesised electrochemically, at a gold plasma coated nylon membrane surface, in the presence of weak-acidic phosphate and non-acidic perchlorate anions. The morphology of the nanowires has been examined using SEM. It has been found that a gold coating of thickness 70 nm confers sufficient conductivity while maintaining porosity of the membrane. Applied potential is one of the key factors in attaining nanowire morphology, with nanowires forming between (0.75 . 0.85 vs. SCE). Varying growth potential and polymerisation time also influences the dimensions and abundance of polypyrrole nanowires.

When placed in a solution of acidified Cr(VI), the reduced nanowires will remove up to 99% of the Cr(VI) within 48 hours, with up to 25% removal occurring in the first 90 minutes. The formation of nanowires greatly increases the polymer surface area and thus its efficacy. Similar results have been obtained for real water samples spiked with Cr(VI). In order to understand the mode of Cr(VI) remediation, studies have been carried out using open circuit potential measurements on the reduced nanowires when placed in the solution containing Cr(VI). In addition EDX measurements have been carried out on the nanowires after the Cr(VI) remediation experiment is completed. It would appear that the mechanism for removal is a combination of adsorption and the reduction of Cr(VI) to the much less toxic Cr(III). As the membrane maintains its conductivity, this will be exploited to reduce the adsorbed Cr(VI) to Cr(III), removing the presence of Cr(VI) contaminated waste, and allowing for the successful recycling and reuse of the modified membrane.

¹ Nguema, P.F. and Luo, Z. *Ann. Microbiol.* 62, 41-47 (2012)

² Chromium(VI) Handbook, Independent Environmental Technical Evaluation Group (IETEG), edited by J. A. Jacobs, J. Guertin, C. Avakian. CRC Press, 2004.

Excellent (inside/outside) nanoparticle (Pt and PtM, M= Au, Cu) decoration of carbon nanofibers: a strategy to improve utility of Pt and nanofibers for fuel cell applications

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Pt based monometallic (Pt/CNF) and bi-metallic (Pt₂Au/CNF and Pt₂Cu/CNF) nanomaterials were synthesised using carbon nanofibers as a supporting matrix with overall target to improve the Pt utility targeted for fuel cell applications. Excellent Pt nanoparticles dispersion and decoration (inside/outside) of functionalised carbon nanofibers (f-CNF) were achieved. The surface morphological, compositional and structural characterisations of the synthesised nanoscaled materials were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM/STEM/DF-STEM), energy-dispersive X-ray spectrometry (EDX), thermogravimetric analysis (TGA/DTG) and X ray diffraction. Cyclic voltammetry (CV) was used to confirm the metallic electrochemical responses of the nanomaterials as well to check the catalytic potential for low temperature fuel cell (DMFC/DFAFC - methanol/formic acid electro-oxidation studies) applications. Overall the bimetallic materials showed excellent response in terms of per mg Pt activity and peak potential as well as showed advantages over their monometallic counterpart Pt/CNF. The proposed catalysts are excellent alternatives in reducing the precious Pt and in improving the electro-catalytic response. Bimetallic combinations showed better response (in terms of per mg Pt activity) compared to the monometallic counterpart Pt/CNF and signified the effect of secondary metals Cu and Au in modifying the properties due to associated ensemble/electronic effects. The target was to improve the utility of both the precious Pt and support material (using both side nanoparticle decorations of nanofibers) for methanol/formic acid electro-oxidation studies. The effective utilisation of the inner nanofiber surface together with the modified surface characteristics enables excellent decoration, effective dispersion and efficient impregnation of Pt/PtM nanoparticles all along the nanofibers. Electro-catalysts exhibit excellent I_f/I_b values, indicating the exceptional antipoisoning strength and great potential to be used in fuel cell conditions. The improved carbon surface area using inner/outer surfaces of nanofibers and excellent nanoparticle dispersion/decoration together with the presence of functional groups provided strong interactions and stability which resulted in excellent catalytic performance. The decorated nanoscaled materials are capable of large scale production and are of great potential/promise to be used in fuel cell industry.

Hollow carbon nanospheres/alloying metal anodes for lithiumion batteries

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Although the energy density of commercial Li-ion graphite based negative electrodes is relatively high, the slow intercalation of the lithium ions through the graphene layers limits the rate capacity and the power density.¹ Furthermore, the low temperature performance of Li-ion batteries is significantly degraded from that at room temperature. Rate capability, capacity and cycle life can all be substantially reduced as the temperature is lowered. Lowering the temperature of the batteries reduces the ionic diffusivity of the electrodes, so there is a need for a reduction in the physical dimensions of the active material to shorten the diffusion distances.

Hollow carbon nanospheres (HCNS) consist of concentric graphene layers, like graphite but curved into ~40 nm spheres. The small size of these carbonaceous species allows for electrode with significantly reduced diffusion distances as compared to graphite and the possibility of high rate capacity. We have found that negative electrodes for Li-ion batteries made with HCNS cells can be cycled at extremely high rates (>100C, charge and discharge) over multiple hundreds of cycles with little capacity fade.

In addition, HCNS are extremely robust, allowing them to cycle at high rates for more than 1000 cycles without capacity fade or in electrolytes that have good low temperature characteristics but are incompatible with graphite (e.g. PC). This gives HCNS excellent low temperature performance down to . 50 °C at moderate to high rates with excellent capacity retention.

One disadvantage of HCNS anodes is that their capacity is somewhat less than graphite, achieving only 220 mAh/g. One possible solution to this issue is to embed Sn or other alloying metals into the HCNS. Optimally, the Li alloying metal will provide higher capacity while the HCNS provides an electrically conduction, porous scaffold which is unaffected by the expansion and contraction of the alloy, mitigating the failure mechanism of alloy anodes. We have found this scheme to be effective with HCNS/Sn based electrodes retaining 94% of their initial capacity after 200 cycles at a C/2 rate. We will present the details of our investigations of HCNS/alloying metal anode performance.

Activity enhancement of tetrahexahedral Pd nanocrystals by Bi decoration towards ethanol electrooxidation in alkaline media

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Direct ethanol fuel cell (DEFC) has attracted increasing interests since it is considered as a promising alternative for the electricity power supply of portable application. In this work, we have developed a suite of novel size and shape controllable nanocatalysts and here we report one of the systems, e.g., tetrahexahedral (THH) Pd Nanocrystals (NCs), with and without Bi-decoration, towards ethanol electrooxidation in alkaline media. It has been found that Bi-decorated THH Pd NCs with low coverage exhibits superior catalytic activity in comparing with that of bare THH Pd NCs.

THH Pd NCs were prepared by sophisticated electrodeposition on a GC electrode. Bi decoration on THH Pd NCs was carried out in a dilute solution containing Bi salt. The Bi coverage is evaluated by the degree of blockage of hydrogen adsorption charge and is defined as

$$\theta_{Bi} = 1 - \theta_H = 1 - \frac{q_{H,Bi}}{q_{H,unm}} \quad (1)$$

Figure 1a shows the SEM image of bare THH Pd NCs, it can be seen that an average size of about 50 nm and a shape based upon a cube with a pyramid atop each of the six faces, indicating a typical tetrahexahedral shape of Pd nanocrystal. The reactivity of pure and Bi-modified THH Pd NCs towards ethanol electrooxidation has been studied, and the data obtained from cyclic voltammetry are shown in fig. 1b, whilst the data of current density at -0.3V are also displayed in fig. 1a. These data show clearly that Bi-modified THH Pd nanocatalyst with an optimum Bi-coverage gives a significant enhancement in the activity towards ethanol electrooxidation.

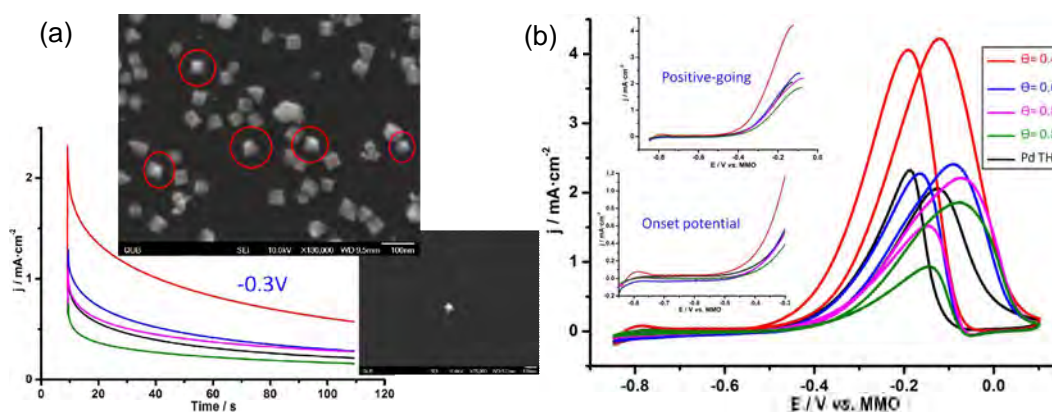


Figure 1 (a) SEM images of THH Pd NCs and current transients recorded at -0.3V for ethanol oxidation on bare and Bi-modified THH Pd NCs with various Bi coverages; (b) cyclic voltammograms (CVs) of THH Pd NCs with different Bi coverage, insets show the CVs of positive-going and the onset potential, solution: 0.1M EtOH + 0.1M NaOH, scan rate of 50 mV s⁻¹.

Novel ionic clusters catalytic enhancement by nanoparticle doping

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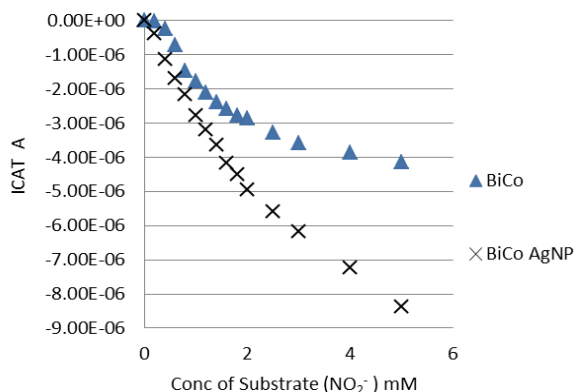
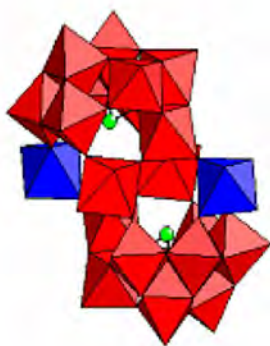


Figure 1.(Above Left) Krebs-type polyoxometalate, $[X_2W_{20}M_2O_{70}(H_2O)_6]^{n-}$ (Bi or Sb, M = Fe, Co or Cu) green represents the central heteroatom (X), blue octahedra represent the substituted transition metal (M) and red octahedra represent the WO₆ units of the metal oxide framework (1). Figure 2. (Above Right) Catalysis of $[BiCo]^{10-}$, PDDA, AgNP multilayer on glassy carbon disc electrode Ag/AgCl reference electrode (1M KCl), Pt Counter Electrode, electrolyte pH 2.5 0.5MNa₂SO₄ scan rate 10mVs⁻¹

Recent progress in technology has led to much interest in Polyoxometalates, the large cage transition metal oxides which demonstrate reversible electrochemistry and efficient, clean electrocatalytic effects and potentially have many other applications.

The Krebs type Polyoxometalates with the general formula $[X_2W_{20}M_2O_{70}(H_2O)_6]^{n-}$ (X=Bi or Sb, M=Co²⁺ or Cu²⁺) were investigated previously in homogeneous solution and in solid state for their catalytic properties (1). Due to the solubility of the POMs, recovery from solution would be difficult, this makes film-based catalysis the more viable prospect. This study utilises the layer by layer (LBL) technique to investigate the catalytic effect of doping the layers with silver nanoparticles for NaIO₃ and NO₂⁻ catalysis.

Nitrite is used as a preservative in meat, it is also a product of broken down nitrate which occurs in various foodstuffs. Iodate can be used to characterise new mixing processes and as a catalytic indicator. On oxidation, Iodate forms periodate which can then be used as a strong oxidiser in chemical reactions.

The study has shown that the addition of silver nanoparticle to the multilayer structure has a catalytically favourable effect to the catalytic current by a significant amount.

(1) AF Murphy, *Investigations into Polyoxometalate Based Solid-State Materials*, 2010

High selective tramadol sensor based on modified molecularly imprinted polymer–carbon paste electrode with multi walled carbon nanotubes

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Here we describe a novel method to determine the tramadol in physiological sample without needing a sample treatment. Recently in many researches, carbon paste electrode (CPE) and glassy carbon (GCE) have been applied for the determination of tramadol. As far as we know, these electrodes do not show a suitable selectivity for determination of tramadol. Usually, the determination of tramadol is performed at very high applied potentials, i.e, 1 V, where many other drugs can be either reduced or oxidized at this voltage [1-3]. In attempt to overcome this issue, we propose a new method in which tramadol is firstly extracted from the sample into the sensor and subsequently the extracted amount is determined by differential pulse voltammetric method.

Molecularly imprinted polymer (MIP) is used as a recognition element in the carbon paste electrode structure. A highly selective molecularly imprinted polymer (MIP) for tramadol hydrochloride is prepared by a bulk polymerization technique. In the polymerization step, we use tramadol as the template, MAA as functional monomers and EGDMA as the cross-linker in chloroform as solvent. This polymer is characterized on the basis of FT-IR and thermal analysis (TGA, DTA). The obtained polymer block is ground and sieved then tramadol is removed from the polymer particles by leaching with methanol/acetic acid (9/1) three times which leaves a cavity in the polymer particles. The adsorption/desorption cycle of tramadol in the polymer sites is investigated and followed by UV spectroscopy at λ (max) of 272 nm [4, 5].

To improve the conductivity of CPE, the multi wall carbon nanotubes (MWCNTs) are incorporated in the structure of CPE. The carbon paste electrode is prepared by mixing the MIP particles, MWCNTs, graphite powder and paraffin. Effect of the MIP-CPE composition on the characteristics response of the tramadol electrodes is investigated. The studied parameters include the amount of the MIP particles, MWCNTs, graphite powder and paraffin [6]. The sensor is fully characterized in terms of composition then extraction step is optimized with changing the pH and sample matrix. The electrochemical behavior of tramadol is also investigated by cyclic voltammetry (CV), square wave voltammetry (SQW) and differential pulse voltammetry (DPV). An optimum electrochemical response is obtained for DPV method in the phosphate buffered solution at pH 7.4.

Finally, the proposed electrode is used for the determination of tramadol in urine and medicinal tablet. The electrode shows a wide dynamic linear range for tramadol from 5×10^{-7} to 10^{-3} mol L⁻¹. The observed detection limit is 10^{-8} mol L⁻¹. The obtained result agrees with the UV results for the standard solution, but it is not possible to carry out the UV spectroscopy for real samples due to interfering species in the real matrix. Overall, this methodology shows some several practical advantages such as simple preparation method, high selectivity and sensitivity, long-term stability, ease of preparation, fast response and good reproducibility.

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Construction and characterisation of an electrochemically pre-treated glassy carbon electrode modified with calf thymus DNA

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An electrochemical DNA biosensor based on an immobilised layer of DNA on a glassy carbon (DNA-GC) electrode has been developed. Potentiostatic activation of the surface is carried out to create a carbonyl functionality to improve the coupling reaction of *N*-hydroxysuccinimide (NHS) and 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC). The 5'phosphate group of DNA is conjugated to a NHS through an amide bond, which is then covalently immobilised to the GC using EDC cross linker. Fabrication of the electrode using EDC-NHS improves the success of the DNA drop cast.

The efficacy of new potential anti-cancer drugs can be assessed by monitoring drug-induced DNA damage caused by direct association of DNA-GC electrodes with known DNA intercalators and short-lived radical species. The damage caused to the DNA-GC electrodes can be monitored, through the enhancement of peak currents due to increased exposure of electro active DNA base pairs to electrochemical oxidation, using the following relation:

$$\% \Delta i = \frac{i_{\text{modified}} - i_{\text{bare}}}{i_{\text{bare}}} \times 100$$

DNA modified electrodes have applications in nucleotide sequencing and can be utilised as rapid analysis tools for biological warfare agents, forensics, disease diagnostics, environmental testing and medical research of genomic material.

Complications in observing electrochemical processes involving serotonin in different biological matrices

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Serotonin is an important neurotransmitter that plays important biological roles in various areas of the body; serotonin is known to influence key neurological traits, such as anxiety, but also plays a key role in driving gastrointestinal motility and platelet aggregation. As such monitoring the activity of serotonin and relating it to observed processes is a key step in understanding these various different metabolic processes it is involved in. Electrochemical measurements have proven to be the method of choice for *in vitro* and *in vivo* monitoring of neurotransmitters [1, 2]. During recordings the sensor sensitivity, selectivity and stability can reduce over time. The biological matrix components are well known to cause biofouling of the sensor, thus limit lifespan of the electrode [3]. However limited is known about the influence of different biological matrixes on the stability.

We investigated the performance of glassy carbon (GC) and boron-doped diamond (BDD) electrodes in different biological matrixes that mimicked the three areas serotonin is known to be found (blood, brain and intestinal tract). Electrochemical recordings were carried out in PBS buffer, 0.5 % w/v mucin and 5 % w/v albumin on the GC and BDD diamond electrodes. Repeated voltammetric measurements were carried out in each matrix over a period of 100 minutes.

During recordings of serotonin on the GC electrode, the albumin matrix was acting in a protective manner against electrode fouling in comparison to mucin, where experiments displayed an increased rate of electrode fouling. On the BDD electrode, mucin once again enhanced the rate of electrode fouling, however albumin did not alter the rate of fouling. This data suggests that all proteins cannot be considered to behave in a similar fashion for electroanalytical measurements and thus careful consideration on the matrix effect needs to be considered before biological monitoring.

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Application of a printed electrocatalyst for H₂O₂ to the development of biosensors

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Many enzymatic reactions, e.g. the oxidation of glucose or cholesterol by glucose oxidase (GOx) or cholesterol oxidase (ChOx), respectively, in the presence of oxygen release hydrogen peroxide (H₂O₂) as an end-product. Therefore, the determination of its concentration may be used as an indicator in the progress of the reaction. Many metal and metal alloys such as Pt, Pd, Ag, Pd/Au and Au/Pt have been employed in recent years in the manufacture of electrochemical sensors for H₂O₂ determination. However, its slow electrocatalytic kinetics at metallic electrodes and the need for high applied potentials have prevented it from being more widely used as the signalling molecule in biological systems.

Recently, our group has reported a significant enhancement in the catalytic activity of silver screen printed electrodes towards H₂O₂ reduction after exposure to a mixed surfactant/salt solution.[1] The electrodes modified with a dodecylbenzenesulphonic acid (DBSA) and KCl solution exhibited up to 80-fold higher responses when H₂O₂ was measured by amperometry at -0.1 V vs. Ag/AgCl. The use of inkjet printing during the modification process might improve the variability of the sensing devices found in previous manual modification procedures by enhancing the control of the reagent volume and exposure times.[2]

In the present work, DBSA/KCl modified silver screen printed electrodes were assessed for their ability to couple this electrocatalysis to the reduction of H₂O₂ generated from enzymatic reactions. First, a mediatorless glucose biosensor was fabricated by the immobilization of GOx onto the modified electrode. The deposition of a perm-selective membrane of cellulose acetate was required to prevent interferences at the electrode surface as well as to facilitate enzyme immobilization. Then, the capacity of the electrocatalyst to detect the H₂O₂ produced after the enzymatic reaction of cholesterol oxidase and cholesterol was evaluated. Analytical parameters of the biosensors such as LOD, sensitivity and reproducibility were measured. The device was shown to be capable of the quantitative determination of both glucose and cholesterol.

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Scanning electrochemical microscopy (SECM) study of microbial fuel cells (MFCs)

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A century ago, Potter [1] used microbes to generate power. Today, microbial fuel cell (MFC) technology has evolved to the point where real world applications are very possible. MFCs utilise the microbes as catalysts for the direct conversion of chemical energy, in the form of organic matter, to electrical energy. In today's world, with the effects of greenhouse gases and a non-sustainable dependence on fossil fuels; MFCs promise a carbon neutral energy source.

The power generation of MFCs is dependent on understanding the microbe-anode interaction; a vital process that makes it possible to use organic matter as electron donors. Electron transfer from microbes to the anode can occur directly or via a self-produced or artificial mediator. Suitable redox mediators act as electron shuttles being reduced by the microbe, and subsequently re-oxidised at the anode [2].

The focus of our investigation is to study the electrochemistry of a single and/or cluster of microbes in the presence of artificial mediators. The primary electrochemical technique employed is Scanning Electrochemical Microscopy (SECM) in Feedback mode, Generation/Collection (G/C) mode and Surface Interrogation (SI-SECM) mode, with the aim to evaluate rates of electron transfer and factors affecting the rate. All experiments were performed in deoxygenated phosphate buffer solution to avoid competition between oxygen and redox mediator, simulating conditions present in a MFC anode chamber. Initial studies have looked at the interaction of *Saccharomyces cerevisiae* (baker's yeast) with ferrocenemethanol. Cyclic voltammetry studies of the yeast (at different stages of growth) immobilised onto a boron doped diamond electrode show distinctive catalytic enhancement in oxidative current.

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Redox polymers and complexes for mediation of glucose oxidation in enzymatic fuel cells

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Combination of redox enzymes and redox mediators as thin films on electrodes can achieve efficient electron transfer between enzyme and electrode for oxidation or reduction of enzyme substrates, providing signals for use in biosensor and biofuel cell devices.

The variation in redox potential of mediators, for provision of enzyme electrodes for glucose oxidation by glucose-oxidizing enzymes, can be achieved by chemical synthesis of metal complexes with appropriate ligands (electron donating/withdrawing). Furthermore, tailoring of mediators for ease of co-immobilisation is possible by introduction of polymeric ligands, or ligands with tetherable functional groups.

We report here on tailoring redox mediators for preparation of enzyme electrodes capable of generating high current, stable for extended time periods, on bioelectrocatalytic oxidation of glucose. Increased currents, and stability of these currents, for glucose oxidation, are achieved by selection of mediator, enzyme, immobilization approach and electrode surface.

Optimised glucose-oxidising anodes combined with oxygen-reducing cathodes, based on blue multi-copper oxygenases, result in fuel cells providing almost 0.1 mW/cm² in 5 mM glucose at pH 7.4 over prolonged periods.

The formulation and characterisation of a polypyrrole-chitosan composite

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Incorporating a natural bioactive material with a synthetic, semi-conducting polymer is a well documented strategy for optimising biological activity in progressive biomedical materials. A consequence of this strategy is that the material properties can be altered. In this study, pyrrole was electropolymerised in the presence of chitosan (an insulator) to give a polypyrrole-chitosan composite. This composite material was characterised using traditional techniques, such as Scanning Electron Microscopy, Differential Scanning Calorimetry, Fourier Transform Infrared Spectroscopy and the electrical behaviour was characterised using Cyclic Voltammetry and Electrochemical Impedance Spectroscopy (EIS). The transmission lines obtained from the EIS spectra were analysed by constructing equivalent circuit analogues of each polymer to investigate the impedance response. The resistance contribution and capacitance values were derived from the equivalent circuits. The chitosan yields a resistance characteristic of an insulator and the polypyrrole yields a low resistance value characteristic of a semi-conductor, however, the polypyrrole-chitosan composite maintains a resistance characteristic of a semi-conducting material.

Phenanthrene degradation and concomitant electricity generation using a bioelectrochemical process

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Environmental pollution by petroleum hydrocarbons resulting from oil spillages, leaks or indiscriminate disposal is a serious problem. The hydrocarbons are toxic, posing serious threats to human health from contaminated groundwater and soils. While a number of approaches (e.g. biostimulation) are available to deal with the problem, many of them are expensive, ineffective, too slow or environmentally unfriendly. Recently, the use of bioelectrochemical systems (BES) for promoting the enhanced anaerobic degradation of petroleum hydrocarbons has been suggested. In this study, five different inocula (*S. oneidensis* MR1, *P. aeruginosa*, undefined mixed culture, co-culture of *S. oneidensis* and *P. aeruginosa*; and the co-culture + the undefined mixed culture) were evaluated for their potential in co-metabolic degradation of phenanthrene (a model petroleum hydrocarbon) in a microbial fuel cell (MFC).

All the five inocula showed very high potential for phenanthrene degradation with a minimum degradation efficiency of 95%. *P. aeruginosa* gave the highest degradation rate of 0.055mM/d with the *S. oneidensis* giving the lowest degradation rate of 0.027mM/d. These degradation rates are considerably higher than those observed for anaerobic degradation in a non-MFC reactor. The maximum power density of the MFCs was 1.1mW/m² obtained using a co-culture; the lowest, 0.19mW/m², was obtained using *P. aeruginosa*. Coulombic efficiencies for all MFCs was very low (range 0.4 -1.0%) perhaps due to electron diversion to methane formation or reaction with oxygen from the cathode to form water.

Adsorption studies revealed that the anode (carbon) electrode has a high affinity for phenanthrene with 90% of the solute adsorbed in less than 3h. This suggests the carbon electrode could be used in co-localising petroleum contaminants in the environment while they are being degraded by electrochemically active bacteria in the anode of a MFC.

This work highlights the possibility of using microbial fuel cells to achieve high degradation rates of phenanthrene through co-metabolism with concomitant electricity production and could potentially be utilised as an independent system or be integrated with other bioremediation technologies (e.g. pump and treat or permeable reactive barriers) to remediate petroleum hydrocarbons from contaminated subsurface environments or industrial effluents.

A membraneless and mediatorless high-power enzymatic H₂ fuel cell based on compacted mesoporous carbon electrodes

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This poster presents a membraneless and mediatorless high-power enzymatic H₂ fuel cell based on the compacted mesoporous carbon electrodes modified with O₂-tolerant hydrogenase and bilirubin oxidase. The power density of this enzymatic H₂ fuel cell reached 720 W cm⁻² at 0.69 V in a quiescent condition under a non-explosive hydrogen-air (78/22) gas mixture at 25 °C; to the best of our knowledge, this power density is the highest among the enzyme-based H₂ fuel cells. Moreover, the mechanism of the high power of this enzymatic H₂ fuel cell is also discussed in this poster. This method could be extended to other types of enzymatic fuel cells.

External resistance effect during MFC maturing period

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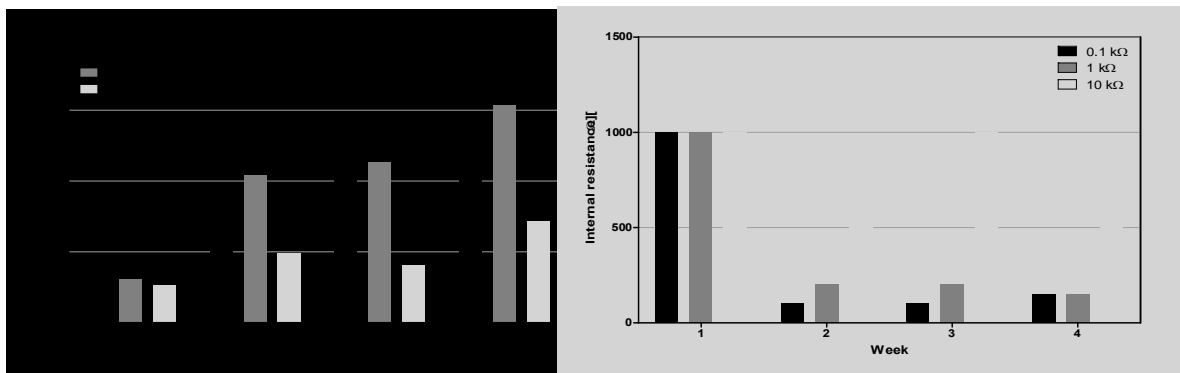
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Microbial fuel cells (MFCs) are devices that convert chemical energy of feedstock into electricity through the metabolic activity of microorganisms. In order to get maximum power output from MFCs, it is well known that the external resistance should match the internal resistance of the MFC system. With this in mind, there have been only a few studies, looking into the effects of external resistance loading on the length of maturing for MFCs [1]. By applying different resistance values, the microbial environment inside the anode could be selectively controlled. In this study, different resistances were loaded to find out the value that best allows maximum power output or shorten the maturing period.

Three different resistance values, 100 Ω , 1k Ω and 10k Ω , were connected to duplicates of MFCs, assembled with open-to-air cathodes and 25ml anodes, inoculated with activated sludge. The anodes and cathodes contained carbon fibre veil electrodes, with a total surface area of 270 cm². MFCs were fed with neat human urine. Polarisation experiments were performed using a variable resistor once every week.

Figure 1 shows the maximum power output recorded every week and the calculated internal resistance values for the MFCs loaded with different resistances. In the second week, maximum power density increased and internal resistance values decreased significantly from the first week, apart from the MFC with 10k Ω . This suggests that the maturing of the MFCs under 100 Ω and 1k Ω was accelerated. In the case of power generation, the MFC with the middle value resistance (1k Ω), showed the highest outputs.



Although it is still unclear what value of optimal external resistance might be optimal for different MFCs, it appears that lower external resistances accelerate the maturing period and enhance the MFC performance. Therefore external resistance value is a critical parameter to be considered, when setting-up MFCs.

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Acknowledgements: The authors would like to thank the EPSRC for the financial support of this work through the EP/I004653/1 project, Engineering and Physical Sciences Research Council, U.K.

Effects of different chloride ion concentrations on corrosion of mild steel in aerated environment

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The corrosion of mild steel in aerated solutions containing different chloride concentrations (0.0585, 0.3, 3.5, 5.85, and 10% NaCl) has been investigated using different electrochemical techniques such as linear polarisation resistance (LPR), potentiodynamic polarisation (PDP), and electrochemical impedance spectroscopy (EIS). The three techniques gave similar results that explained the combined effects of both oxygen and chloride ions in determining the mechanism and kinetics of corrosion of mild steel. Both potentiodynamic polarisation and electrochemical impedance spectroscopy confirmed that increase in chloride concentration increases the electrical conductivity of the solution which has direct impact on the corrosion rate of the mild steel. The results obtained with linear polarisation resistance showed an increase in corrosion rate as the chloride ions concentration increase up to the threshold chloride concentration of 3.5% NaCl with corrosion rate of 0.24mmpy which is marginally higher compared to 0.189 and 0.181mmpy for potentiodynamic polarisation and electrochemical impedance spectroscopy respectively but there corrosion rate follow the same trend, and decrease with further increase in chloride concentration. Since the rate-determining step for the electrochemical reaction (corrosion) is oxygen reduction as the cathodic reaction, it was established that there was decrease in oxygen solubility at higher chloride concentrations that resulted in low corrosion rate. This is important in understanding how the chemistry of seawater environments and the condensates, which may be formed on mild steel, affect its corrosion resistance, so as to determine the amount of corrosion inhibitors to be injected to protect the steel in chloride environment.

Electrochemical detection of fluoxetine using the boron-doped diamond electrode

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Fluoxetine (FXT), a well-known antidepressant, is a potent highly specific serotonin uptake inhibitor (SSRI), used to treat major depression, obsessive compulsive disorder, bulimia nervosa and panic disorder. After its releasing on the market in 1987, it became shortly a world wide very used drug, its presence being reported in the wastewater.

Electroanalytical techniques were applied in the quantification of fluoxetine in pharmaceutical formulations, the results being in good agreement with the official pharmacopeias. Good detection limits were obtained for dropping mercury electrode ($\text{LOD} < 0.099 \text{ M}$) [1], glassy carbon electrode ($\text{LOD} = 1 \text{ M}$) [2], and different chemically modified sensors ($5 \text{ Mn LOD} < 48 \text{ M}$) [3-5]. Recently, the boron-doped diamond (BDD) electrodes have become an important electroanalytical tool, due to they exhibit a large potential window and very low background current. This study aims to develop a BDD based electroanalytical method for fluoxetine determination from aqueous solution. Voltammetric methods, e.g., cyclic voltammetry, square-wave voltammetry, and differential-pulsed voltammetry, were applied to found the optimum methods in the relation with the best electroanalytical parameters (sensitivity and the lowest limit of detection). Square-wave voltammetric method allowed to reach the best performance for FXT detection under optimised conditions, like 0.05 V step potential, 0.2 V modulation amplitude and 75 Hz frequency (see Fig. 1). In addition, to elucidate some mechanistic aspects regarding the electrochemical oxidation of FXT on BDD electrode, the effect of the scan rate on CV shapes was investigated.

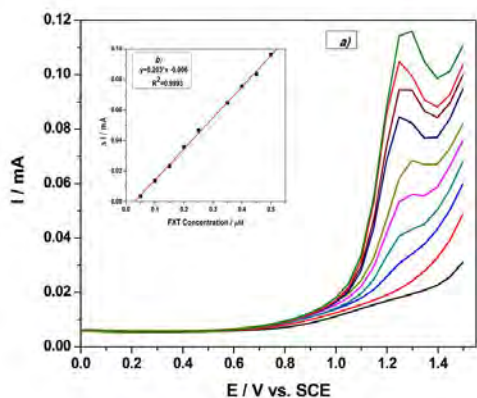


Figure 2 a) Square-wave voltammograms recorded on

BDD electrode with a modulation amplitude of 0.2 V , a step potential of 0.05 V , a scan rate of 5 Vs^{-1} in a potential range between 0 and $+1.5 \text{ V}$ vs SCE in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte in a concentration range: $0.05\text{--}0.5 \text{ M}$ of FXT; **b)** Calibration plot of the currents recorded at $E = 1.27 \text{ V/SCE}$ vs. FXT concentration

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Electrochemistry at the solid/gas interface

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To date, redox reactions in the gas phase (electron attachment or detachment) are commonly studied using photoelectron spectroscopic, or related techniques, in conjunction with mass spectrometry for analysis of products and/or reactants.¹ There are limited examples using plasmas as media to study redox reactions but no examples of voltammetry in the gas phase at true solid/gas interfaces.

We demonstrate, for the first time, the ability to control redox reactions at the solid/gas interface, by considering gaseous flame plasma as an electrolyte. An innovative method to perform potentiodynamic experiments in a liquid-free electrochemical system using flame plasma is described. Our novel approach can help apply the well-established foundations of electrochemistry developed almost exclusively in liquids, to the new context of gas plasma.²

Successful electrochemical measurements at the solid/gas interface are demonstrated by doping the flame plasma with metal oxide salts and recording distinct faradaic peaks at defined potentials in cyclic voltammograms. The voltammograms for three different metal oxides - tungsten oxide, molybdenum oxide and vanadium oxide - are all unique. Furthermore, we show that the size of the current peaks depend on the amount of the oxide in the flame. Whilst this is possible and routinely done in liquids, this is the first time to be shown in the gas phase.

The most significant innovation that made these measurements possible was the formation of a reference electrode. Extensive assessment of several materials has enabled the development and optimisation of a reference electrode that has enabled us to further extend the potential window and investigate scan rate dependence.³ After careful experimentation and appropriate control experiments, we conclude that the features observed are specific reduction processes at the solid/gas interface. We discuss the physical origin of these electrochemical signals measured in flame plasma and provide a framework of interpretation upon which a full mechanistic understanding can be based.

Liquid-free electrochemistry presents access to a plethora of redox reactions, which lie outside potential limits defined by the liquid. The prospect of new redox chemistries will enable new technological applications such as electrodeposition, electroanalysis and astrochemistry, which will have significant economic and environmental benefits.⁴

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Influence of different surfactants on the electroreduction of Zn^{2+} ions

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For the purpose of this study surfactants from multiple groups were chosen: neutral, anionic and cationic with similar particle masses. They were as follows: decano-N-methylglucamide ($\text{C}_{17}\text{H}_{35}\text{NO}_6$), sodium 1-decanesulfonate ($\text{C}_{17}\text{H}_{35}\text{SO}_3\text{Na}$) and octyltrimethylammonium bromide ($\text{C}_{11}\text{H}_{26}\text{NBr}$). The chosen surfactant concentrations were lower than their critical micellar point. A 1M NaClO_4 solution was used as the base electrolyte. The Zn^{2+} electroreduction studies were performed by means of differential pulse polarography (DPP). The introduction of an anionic surfactant to the Zn^{2+} ion solution caused a DPP peak rise along with its width reduction half way through but leaving the peak value virtually unchanged. This was a result of the anionic surfactant's accelerating properties on the electrons exchange between Zn^{2+} ions and the electrode. The remaining two surfactants were Zn^{2+} ions electroreduction inhibitors, but their inhibiting interaction depended on their concentration. The neutral surfactant indicated a higher activity in the lowest studied concentrations. Neutral and cationic surfactants inhibiting effect revealed by a DPP peak drop, an increase in its width half way through and the peak's virtually constant potential in the low concentrations. With relatively higher concentrations of these two surfactants, the peak potentials shifted in the direction of more negative values due to the blocking of the electrode surface by adsorbed surfactants and an over voltage increased on the Zn^{2+} ions electroreduction process. The height of the DPP peaks significantly rose in the highest studied concentrations of cationic surfactant.

Highly boron doped heteroepitaxial (100) single crystal diamond: a new electrode material

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Synthetic boron-doped diamond (BDD) grown by chemical vapour deposition (CVD) has attracted attention in electrochemistry because of attractive properties, such as a wide potential window, a low background current, resistance to fouling and chemical stability. The vast majority of the work has investigated polycrystalline BDD, in micro- or nano- crystalline forms, and it is believed that the presence of grain boundaries, and the highly anisotropic distribution of the B dopant which arises from the differing crystal orientations, both contribute to a significant degradation of the electrode properties. A very limited amount of work has been carried out on single crystal diamond grown homoepitaxially by CVD on diamond gem+substrates, but there is no practical application for such material because of the absence of cheap large area diamond gems.

In the presence work, we therefore explore a new type of single crystal diamond electrode, grown heteroepitaxially by CVD on Si (100) wafers. Although diamond heteroepitaxy is recognised to be extremely challenging, this can be achieved routinely in the present approach, using Ir and YSZ (yttria stabilised zirconia) buffer layers to control the diamond nucleation process. The electrochemical properties of this new electrode material have been compared to those of conventional microcrystalline and single crystal diamond. In the comparison, the heteroepitaxial diamond is shown to provide an improved potential window and lower capacitance; it also exhibits improved resistance to fouling by adsorption and more uniform lateral activity. The flat band potential is found to be lower than that for conventional diamond electrodes, due to an absence of oxygen functionalities and grain boundaries. Finally, characteristic features can be seen in electrochemical images obtained by SECM, which are absent in those for homoepitaxial diamond, which can be attributed to aspects which are characteristic of the heteroepitaxial CVD diamond growth process.

Electrodeposition and electrocatalytic properties of Pt-Au overlayers

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Bimetallic nanostructures represent a promising route to modifying the electronic and geometrical properties of catalysts, while lowering the noble metal content. A recent method for achieving atomic scale controlled growth of noble metal is known as the Surface Limited Redox Replacement Method (SLRR) [1]. The SLRR method has been successfully applied to the deposition of Pt overlayers on Au, using a Cu [1] or Pb [2] UPD layer as a sacrificial template.

Nanoscale platinum and gold are systems of current interest as powerful catalysts relevant in many fuel cell reactions [3, 4]. In this work, we will present the optimization of this method in single cell configuration using Pb UPD to design ultra-thin overlayers of Pt and Au. The developed bimetallic structures have been analyzed by electrochemical, STM, EDX and X-ray diffraction methods. The dependence on the electrooxidation of CO with Pt and Au thickness has also been determined. The observed trends in the onset potential for CO stripping have been rationalized by strain and ligand effects at the substrate-overlayer interface [5].

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Ion volume and polarisability effects on the behaviour of an electrolyte near a charged surface

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When a potential is applied to an electrode in contact with an electrolyte, the ions in the electrolyte respond by moving in opposite directions, leading to the formation of a charge separated region near to the electrode surface, known as the electric double layer. The resulting difference in the structure of the electrolyte in the double layer can be expected to have a strong influence on any processes which occur at the electrode surface compared to the same processes if the electrolyte structure remained the same as the bulk right up to the electrode-electrolyte interface.

For dilute electrolyte solutions and applied surface potentials up to the thermal voltage ($k_B T/e \approx 25\text{mV}$, at room temperature), the double layer structure is well described by the standard Guoy-Chapman-Stern (GCS) model, which assumes the charge density obeys a Boltzmann distribution with distance from the electrode surface. However, above this potential the model disagrees with experimentally measured properties such as the differential capacitance while also predicting surface ion concentrations which exceed the close packing limit.

In this work we use an approximate dynamic density functional theory to consider the structure of the double layer, how it forms and how it behaves under a time varying potential. The free energy functional accounts for ion volume effects, using a model of the form suggested by Bikerman [Philos. Mag. 33 (1942) 384-397], and also includes the effects of ion polarisability on the permittivity of the solvent, by assuming a linear variation of the permittivity with the concentration of the ions as described by Hasted *et al* [J. Chem. Phys. 16 (1948) 1-21]. The free energy functional is linked to the dynamics in the manner of the over-damped limit described by Archer [J. Phys.: Condens. Matter 18 (2006) 5617]. The resulting equations formed a modified Poisson-Nernst-Planck system which was solved numerically.

The model was used to show how both the excluded volume and polarisability have a significant impact on the double layer structure at equilibrium. Good agreement with differential capacitance curves can be achieved using the width of the Stern layer as a single fitting parameter, offering significant improvement over the GCS model.

The dynamic aspect of the model allows the way in which the double layer forms to be considered, with differences in the formation times occurring depending on the value of the charging potential relative to the peak in the differential capacitance. It also enables modelling of cyclic voltammetry, where expected behaviour at high frequency and low frequency is observed.

Electrooxidation of methanol within an alkaline fuel cell: Determination of the nature of the initial adsorbate

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Fuel cells, as an emerging clean energy technology for transportation, stationary power generation and portable power, have attracted global attention from the scientific community in recent years, thanks to their high energy efficiency and zero/low net emissions. Alkaline fuel cells have attracted particular interest due to their improved reaction kinetics^{1,2} and enhanced electrode stability. Within this context, the electrooxidation of methanol on platinum represents one of the most fundamental examples of fuel oxidation at the anode, complete oxidation to CO₂ generating a total of six electrons. Such a simple system is ideal for study by theoretical simulation, as a comprehensive understanding of one of the simplest systems can be used to improve the reaction in more complex systems. In determining any reaction pathway the importance of correctly identifying the nature of the initial adsorbed species in order to calculate the remainder of the reaction pathway is obvious. However, recent literature^{3,4} provides conflicting information on the first step in the methanol decomposition pathway.

This work sets out to establish what role the solution and the surface have to play in the initial adsorption/deprotonation process of methanol. Density functional theory (DFT) calculations, in combination with a cluster-continuum model approach, have been used to quantitatively resolve the nature of the adsorbing species. We show quantitatively that methanol is the dominant species in solution over methoxide, and also has a smaller barrier to adsorption. Interestingly, these results are catalyst independent by nature of their derivation and therefore applicable to any methanol alkaline fuel cell. The nature of the predominant surface adsorbed species on Pt(211) is revealed to be a stable methanol-OH complex regardless of whether the adsorbate is methanol or methoxide. Therefore, in order to more accurately model the real system, future theoretical studies should model the electrooxidation of this complex, as opposed to simply methanol or methoxide on the surface.

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Oxygen reduction and hydrogen evolution at the interface between two immiscible electrolyte solutions studied by scanning electrochemical microscopy

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Oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) at the interface between two immiscible electrolyte solutions (ITIES),¹ coupled to oxidation of decamethylferrocene (DMFc) present in organic phase were studied by Scanning Electrochemical Microscopy (SECM).² The studied biphasic system consists of acidic aqueous solution and tetrahexylammonium perchlorate or bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate solution in 1,2-dichloroethane. Two-electron ORR was studied using feedback mode SECM. Hydrogen peroxide generated at the ITIES was detected by electrooxidation at platinum microelectrode positioned in close proximity of ITIES. Oxygen produced at the microelectrode acted as an additional source of substrate for feedback process. Under oxygen free conditions, when more lipophilic salt was dissolved in the organic phase, the protons from acidic aqueous phase were reduced at the ITIES to hydrogen. Its flux was detected by potentiometric measurement at SECM tip.

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Choline chloride based ionic liquids – some answers, more questions

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Examples will be presented of electrochemical processes developed during EU RTD integrated project, IONMET (April 2005-December 2009) which had the objective of transforming the industrial electroplating and metal finishing sector by introducing a new range of ionic liquids based on choline chloride. This was a large project, with 33 partners and a budget of over " 12M.

- Stainless steel 300 and other non-ferrous alloys can be electropolished at higher anodic efficiency and using more eco-friendly conditions compared to traditional electrolytes.
- Immersion silver can be deposited on copper patterns on printed circuit boards with good thickness, 100 nm, pleasing appearance, good shelf life, reliable solderable finish and no problems with Cu-Ag intermetallics.
- Because of the novel redox behavior in choline chloride ionic liquids, mixed alloys, e.g. Zn-Sn, with higher Zn content can be deposited.

Some challenges must be considered to ensure the technical and commercial success and uptake of ionic liquids.

Protocols and routine analytical methods suitable for quality control must be developed.

Electrochemistry in aqueous solutions dates from the early 1800s and the reactions of metals in water are well known. Electrochemistry using ionic liquids is much more recent and there are still many unanswered questions about how metals react. There are a wide range of ionic liquids, each with varying chemical properties.

Aqueous electrochemistry is supported by such books as Marcel Pourbaix's, Atlas of Electrochemical Equilibria in Aqueous Solutions and by Frederick A. Lowenheim's, Modern Electroplating. In the third edition of Lowenheim's book, 1974, he has a dedication to Dr William Blum who was, he says, "primarily responsible for the transformation of electroplating from a mysterious and capricious art to a more or less exact science".

This presentation will suggest some areas which must be addressed in order to follow Dr Blum and to do the same for the use of ionic liquids in the metal finishing sector and to build a stronger theoretical and practical foundation.

Self-assembly and electrochemistry of graphite at the interface between two immiscible electrolyte solutions

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The electrochemistry of graphite is a well studied area, with much debate in the literature over the differing activities of the basal plane and edge planes. The recent interest in graphene has spread in to electrochemistry and has also re-ignited interest in graphite electrochemistry. The electrochemical studies of graphene undertaken thus far have been carried out by supporting the graphene on a substrate (usually a Si/SiO₂ wafer). Supporting the graphene in such a way is believed to dope the graphene and alter its electrical properties. Suspending graphene at the interface between two immiscible liquids and probing it using liquid|liquid electrochemical methods would be a way to circumvent the problem of substrate doping. In relation to this, the self-assembly of particles at liquid|liquid interfaces has been known as a phenomenon for over 100 years and such interfaces have been used to assemble graphitic materials, such as carbon nanotubes (CNTs) in the past. A few recent studies have attempted to incorporate liquid|liquid self-assembly into production routes for graphene, which may be compatible with liquid|liquid electrochemistry. From the point of view of this work, a key question which is as yet unanswered is how the presence of electrolyte in both liquid phases will affect the self -assembly of graphene at the interface.

Graphite flakes were dispersed in 1,2-dichlorobenzene (DCB) both in the presence and absence of bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) electrolyte. The dispersed flakes were subsequently characterised using optical microscopy and **Electrochem 2012 Poster Abstract** Raman spectroscopy. The dispersed graphite flakes were assembled at the water|DCB interface with and without electrolyte present in both phases, with the result that a greater proportion of the dispersed graphite flakes assembling at the interface when BTPPATPBCl electrolyte was present in the DCB phase (see Figure 1). To gain a further insight into the improved assembly in the presence of the DCB phase, the three-phase contact angle between graphite flakes, water and DCB was measured. The electrochemistry of the assembled graphite at the water|DCB interface was also investigated, using cyclic voltammetry and impedance spectroscopy. It was found that the capacitance across the interface increased in the presence of graphite, compared with the interface free of graphite. Raman spectroscopy. The dispersed graphite flakes were assembled at the water|DCB interface with and without electrolyte present in both phases, with the result that a greater proportion of the dispersed graphite flakes assembling at the interface when BTPPATPBCl electrolyte was present in the DCB phase (see Figure 1). To gain a further insight into the improved assembly in the presence of the DCB phase, the three-phase contact angle between graphite flakes, water and DCB was measured. The electrochemistry of the assembled graphite at the water|DCB interface was also investigated, using cyclic voltammetry and impedance spectroscopy. It was found that the capacitance across the interface increased in the presence of graphite, compared with the interface free of graphite.

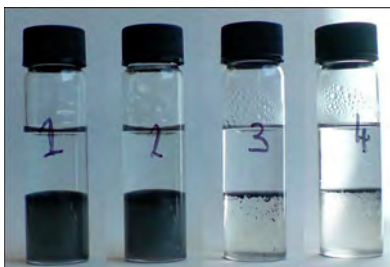


Figure 1. Graphite attached at the H₂O|DCB (A), 0.1 M LiCl(aq)|DCB (B), H₂O|10 mM BTPPATPBCl(DCB) (C) and 0.1 M LiCl(aq)|10 mM BTPPATPBCl(DCB) (D) interfaces.

Electrochemical impedance spectroscopy at recessed microelectrode arrays

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We report the fabrication and electrochemical response of gold microdisc and microband electrode arrays on silicon. These microelectrode arrays were fabricated by the combination of UV photolithographic and e-beam lithographic techniques. Three silicon nitride layer thicknesses (200, 300 and 500 nm) were chosen in this study in order to investigate the effect of recess depth toward the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Prior to that, visual inspection on the recessed microelectrode arrays was carried out by scanning electron microscopy (SEM). CV characterisation using a 1 mM ferrocenecarboxylic acid in phosphate buffered saline electrolyte solution, demonstrated steady-state voltammetric curves expected for recessed microelectrodes. This indicates that the hemispherical diffusion layers of the individual microelectrodes are not perturbed by the diffusion layers of the neighbouring microelectrodes. This characteristic is supported by a good agreement between experimental and theoretical data found for all recessed devices. The electrochemical impedance spectrum for microdisc electrode appears as a flattened semi-circle, confirming the steady-state behaviour. The calculated charge transfer resistance (R_{ct}) increased whilst the double layer capacitance (C_{dl}) per surface area decreased accordingly with the recess depth. The results are in good agreement with the simulation work done by Comsol multiphysics (version 4.2a). For microband electrodes, a semi-circle region followed by a straight line was observed. The linear part observed at the lower frequencies implies a mass-transfer limited process whereas the semi-circle region observed at high frequencies implies a charge-transfer limited process. The characterisation of micro-electrode array by EIS will help for the development of biosensors for odorants based on the immobilisation of olfactory receptors.

The authors gratefully acknowledge the European Commission (Bioelectronic Olfactory Neuron Device, Grant agreement N° 228685) for support for this work.

Ultrasound-assisted electrodeposition of nickel from a watts bath: effects of ultrasonic power on the structure and mechanical properties of thin deposits

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In this study, we have evaluated the effect of ultrasonic power on the electroplating of nickel by characterising the deposits produced by different methods. Nickel coatings from a Watts bath were produced under silent/still conditions, mechanical agitation at 300 rpm, and ultrasonic agitation at a frequency of 32-38 kHz and different powers: 0.011, 0.124 and 0.180 W/cm³. X-Ray Diffraction (XRD) and Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) analysis of the coatings was carried out to investigate the effects of ultrasound on the crystal orientation and structure of the deposits and to determine whether this was related to the measured microhardness.

XRD analysis showed that, under silent/still conditions, nickel deposits formed a mixture of crystals growing in both [100] and [211] directions. Mechanical agitation favoured the electrocrystallization in the [211] direction, while cavitation phenomena induced by ultrasonic irradiation counteracted this effect, leading to deposits growing in the [100] direction. This was most pronounced at an intensity of 0.124 W/cm³. The [100] orientation is commonly related to more ductile deposits with less brittleness [1] and is favoured for many industrial applications.

Crystals with [100] and [211] orientations were also clearly noticed in FIB-SEM images of the surface of the coatings deposited under silent/still conditions. The [211] orientation was predominant in the deposits plated under mechanical agitation, while the proportion of crystals growing in the [100] direction increased in the presence of ultrasound. The cross-section of coatings were further examined by FIB-SEM analysis, showing that ultrasound had modified the nickel deposit, resulting in a more fragmented, less columnar structure with refined grains.

This modification of the microstructure by ultrasound affected the mechanical properties of the coating. The deposits plated under silent/still conditions and mechanical agitation had similar hardness values of 282 and 288 HmV, respectively, while the deposits plated under ultrasound showed an increase of up to 360 HmV at 0.124 W/cm³.

In summary, Ni deposits plated in an ultrasonic field from a Watts bath presented a higher hardness and a greater proportion of crystals with the [100] preferred orientation, especially when an ultrasonic power of 0.124 W/cm³ was utilized. Such a combination of harder and more ductile nickel deposits is of interest for industrial applications of pure nickel coatings.

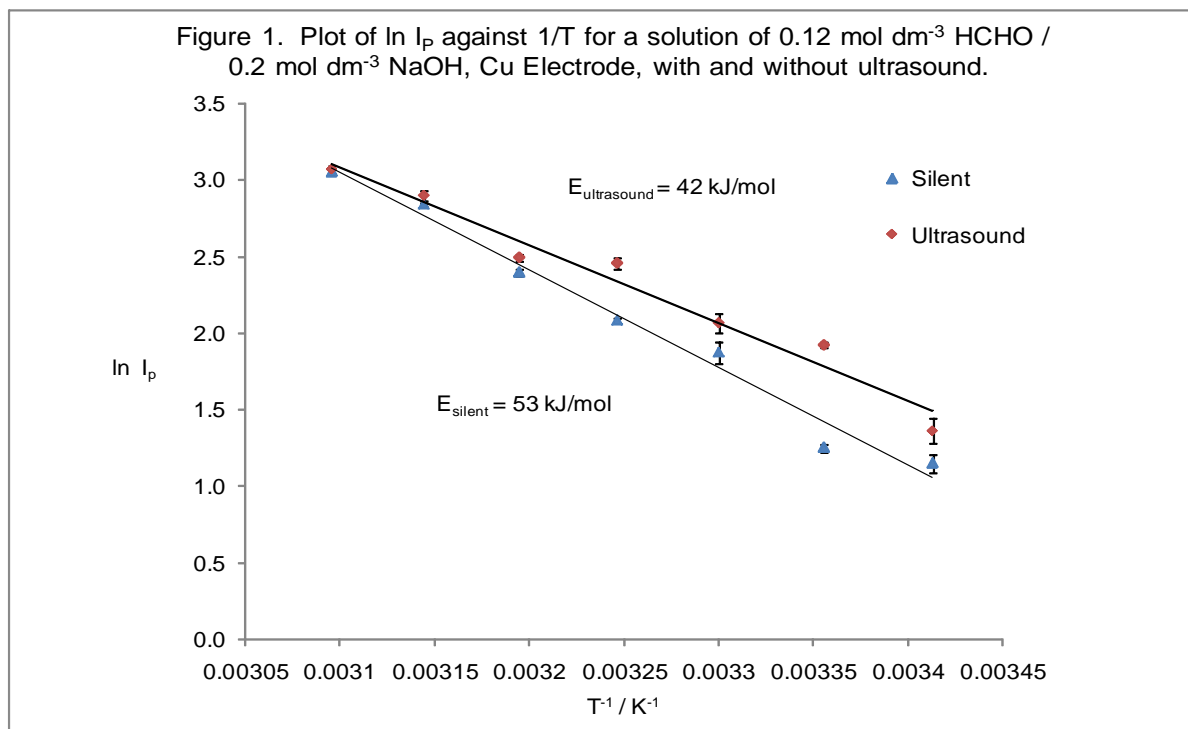
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An electrochemical study into the effect of ultrasound (40 kHz) on electroless copper plating

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Advanced manufacturing processes require electroless copper deposition to initiate on metals such as nickel and the reaction needs to continue on the freshly deposited copper (Cu) surface. The bath operating temperatures can be as high as 70 °C and with rising energy costs it is essential to investigate methods to reduce these whilst still maintaining product performance. In this study, an electrochemical mixed potential approach was used to investigate the effect of ultrasound (40kHz) on the oxidation of formaldehyde and the reduction of the Cu. EDTA complex at a range of temperatures. Mixed potentials and deposition rates were calculated from Tafel plots and the results compared with weight gain experiments. Activation energies for the two half reactions were also recorded for silent and ultrasonic conditions. It was concluded that electroless copper deposition was not limited by the transport of chemical species to the reaction site, but rather by the sensitivity of the formaldehyde oxidation rate to temperature. An apparent lowering of the HCHO activation energy was observed under ultrasonic irradiation, see Figure 1, and it is proposed that this is due to the energy released from cavitation. Unfortunately, this effect is localised and is too small to influence the overall rate of deposition at lower operating temperatures.



Electrokinetic remediation of a heavy metals contaminated soil from the mining district of Linares (Spain): Weak acid enhancement

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On another paper presented at this conference, we present the results obtained for the remediation of a soil from the mining district of Linares (Spain) contaminated by heavy metals, mainly by Pb. In that work, we used the electrokinetic remediation technique enhanced by the addition of a strong acid at the cathode compartment. Here a similar study is presented, but in this case the enhancement agent is a weak acid solution (acetic acid) instead of the strong acid solution (nitric acid) used in the abovementioned work.

As indicated, this Linares soil is a clay-loam soil (according to International Soil Science Classi, cation) with a very low hydraulic conductivity (below 10^{-10} m/s) and very high concentration of Pb, (45200 ± 700) mg kg⁻¹, besides others heavy metals. Acetic acid was selected as enhancement agent in these EKR experiments because more than 80% of the Pb present in the soil is recovered in the first step of the fractionation analysis of the heavy metals following the BCR sequential extraction procedure. The extractant solution that is used in the first step of the BCR method is an acetic acid solution. Thus, the acetic acid enhancement in these EKR experiments aims the exchange of the basic front that would migrate through the soil from the cathode toward the anode by and acetate front moving in the same direction. Since the hydronium ions generated at the anode are not neutralized, an acid front advances across the soil toward the cathode releasing heavy metals from the surface of soil particles. When this front meets the acetates front, the aqueous phase in the soil would be very similar to the one used in the first step of the BCR fractionation method, in which a large amount of Pb is extracted. In addition, it is avoided that the pH of the soil reaches values as low as those achieved when strong acid solutions are used as enhancement agent.

The experimental setup and procedure is the same described in the other paper: two methacrylate columns electrically connected in series that holds 15.5 g of water saturated soil, and which are crossed by a constant current density of 2 mA cm⁻². But in this case, an acetic acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value.

The recovery of Pb at the cathode is similar to that obtained with the strong acid enhancement (around a 30% of the Pb). Also the concentration profiles of Pb in the soil column are similar for the two types of enhancement. Nevertheless, the acid consumption rates at the cathodes are extraordinarily different. The acid addition rate acid for the acetic acid is more than fourfold higher than that needed with the nitric acid, and than the rate of charge circulating through the soil. On the other hand, the time required for the achievement of a similar efficiency in the clean-up is 2.5 fold higher for the nitric acid than for the acetic.

Acknowledgements: The authors thank Prof. Carmen Hidalgo Estevez from the Department of Geology/EUP Linares, University of Jaen for the localization of soils and acknowledge the financial support of the Ministerio de Ciencia e Innovación of Spanish Government through the project ERHMES, CTM2010-16824.

Electrokinetic remediation of a heavy metals contaminated soil from the mining district of Linares (Spain): Strong acid enhancement

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This work studies the feasibility of the remediation of a soil from the ceased mining district of Linares (Spain), using the electrokinetic technique enhanced by the addition of a strong acid at the cathode. The soil samples used in this study were collected at 10-30 cm depth, from a zone downstream from some slag heaps. The values obtained for the total concentrations of the most representative metals, in mg kg⁻¹, were Pb: 45200 ± 700, Mn: 2300 ± 200; Cu: 530 ± 16 and others in lower concentrations such as Zn, As, etc. Pb is the one that more clearly reveals a significant degree of contamination of the soil.

Among the different technologies for the remediation of soil contaminated by heavy metals, the *in-situ* soil flushing has been one of the most used at field scale for some years. Nevertheless, the very low value of the hydraulic conductivity of the soil from the mining district of Linares (below 10⁻¹⁰ m s⁻¹) makes this technique not feasible. In these cases, in which the soil is clayey, the in-situ soil electrokinetic remediation (EKR) should be considered. This innovative technique basically consists in the extraction of contaminants from the soil by means of an electrical field. Thus, when an electrical potential difference is applied between two electrodes inserted in the soil, the available ions in the pore aqueous phase (including the heavy metal ions) are mobilized by electromigration towards the electrodes where they are recovered and correctly treated. Frequently, water electrolysis reactions occur at the electrodes and generate two fronts: an acid one that migrates through the soil from the anode toward the cathode and a basic one that moves in the opposite direction. This basic front can cause the precipitation of the heavy metals in the soil and also a low electrical-conductivity zone can arise in the region where the acid and alkaline fronts meet, which will hinder the clean-up. In order to prevent these problems, an enhancement of the EKR technique consists in the addition of an acid to the cathode compartment. Thus, the basic front is avoided by the neutralization of the hydroxyl ions. This work evaluates the feasibility of the removal of Pb from the Linares soil using the EKR technique enhanced by the addition of a strong acid (nitric acid) at the cathode.

The electrokinetic experiments were performed in two small methacrylate columns (3.2 cm² cross section area and 2 cm length) that hold about 15.5 g of the water saturated soil each one. The two columns are electrically connected in series, thus assuring that the same electrical charge flows through both columns. All the experiments were performed at a constant current density of 2 mA cm⁻². Nitric acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value. Around a 27% of the Pb in the soil was recovered at the cathode whereas the concentration of Pb in the half of the soil closer to the anode was reduced below 10% of the initial one.

Acknowledgements: The authors thank Prof. Carmen Hidalgo Estevez from the Department of Geology/EUP Linares, University of Jaen for the localization of soils and acknowledge the financial support of the Ministerio de Ciencia e Innovación of Spanish Government through the project ERMES, CTM2010-16824.

Nanocellulose film electrodes in hydrodynamic and stationary modes

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Cellulose is the most common natural polymer and it has a wide range of applications in particular in analysis due to its properties such as water adsorption. Natural cellulose is a complex nano-structure which can be degraded to its nanofibril components. These can be employed in turn to form nanocellulose films for example on electrodes. These films have been used to protect the electrode surfaces or control the flow of reagents to and from the electrode [i]. The nanocellulose films have also been previously used as precursors to carbonised films on the electrodes [ii].

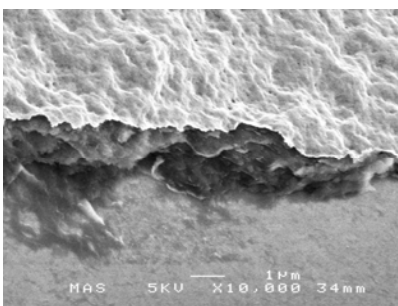


Figure 1. FESEM image of ITO slide with 5 layers of cellulose.

In this report new types of nanocellulose films on tin-doped indium oxide (ITO) electrodes are introduced. The hydrophilic properties of cellulose are utilised to produce an electrode which can be used with high sensitivity in hydrodynamic flow system as well as stationary in solution. Several redox systems are investigated. The concept of voltammetric analysis is introduced.

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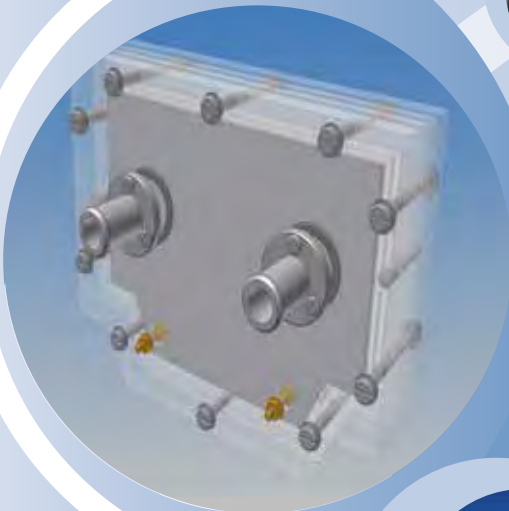
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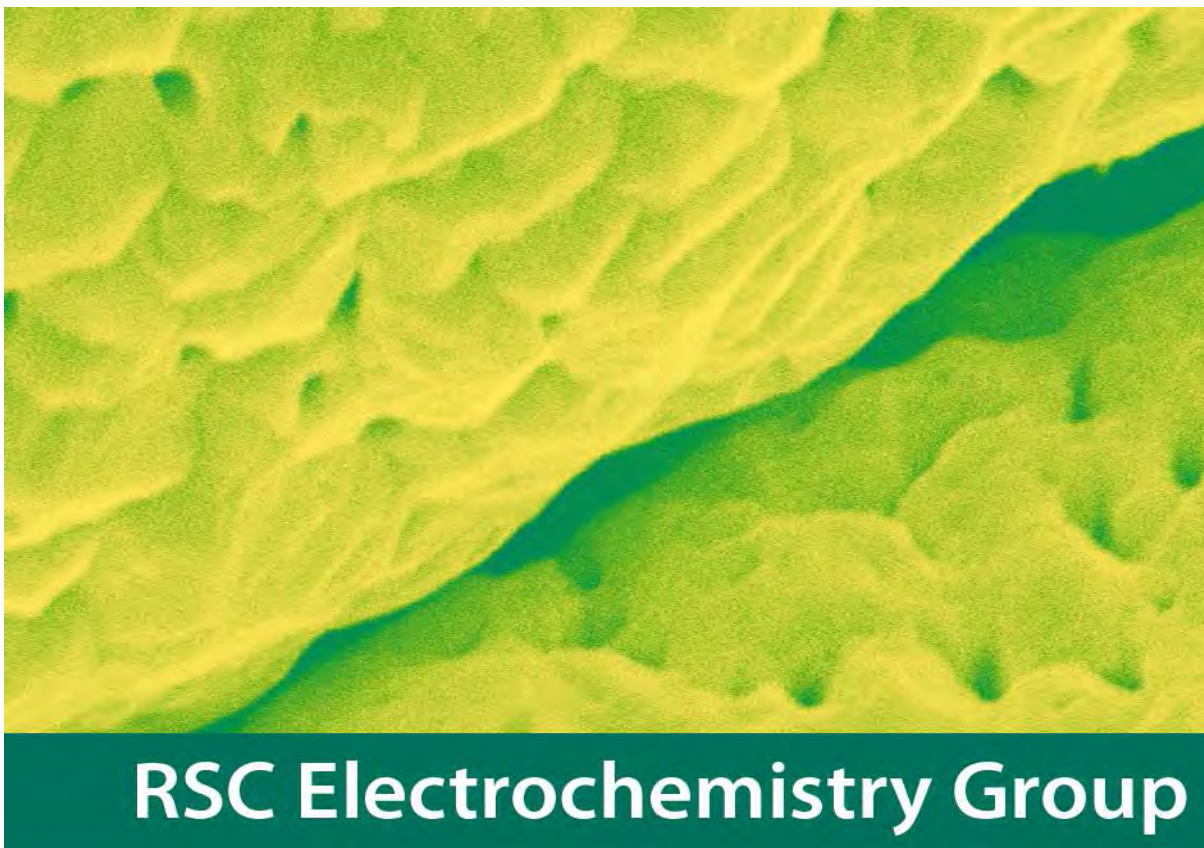
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