two 2011

NEWSLETTER

Electrochem2011: Electrochemical Horizons

Special Issue

September 5-6, 2011
The University of Bath, United Kingdom

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

RSC | Advancing the Chemical Sciences

SCI Where science meets business
an environment to advance knowledge exchange

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Editorial

This very special edition of *The Electrochemistry Newsletter* features the programme and abstracts for the forthcoming **Electrochem2011: Electrochemical Horizons** which will be held at The University of Bath, Claverton Down, Bath, United Kingdom over September 5-6, 2011. Energetically organised by newly promoted ***Professor Frank Marken***, this meeting showcases Electrochemical Science and Technology within the United Kingdom and Ireland, with a diverse range of contributions from overseas participants. It is a vibrant and exciting scientific programme which incorporates input from ***The Institute for Corrosion***, ***The British Carbon Group***, and features a special symposium for the ***United Nations International Year of Chemistry*** dedicated to *Sensors for Africa*. The programme encompasses 149 talks and 49 posters in a programme involving fourteen symposia, and featuring **five plenary speakers**: ***Professor Héctor Abruña*** (Cornell) who is the RSC Electrochemistry Group Faraday Medallist, ***Professor Gerald Frankel*** (Ohio State) who is the recipient of the Institute for Corrosion Evans Medal, ***Professor Andrew Bocarsley*** (Princeton), ***Dr. Dan Brett*** (University College London) and ***Professor Marc Koper*** (Utrecht). A recorded video lecture will be shown of ***Professor Maria Skyllas-Kazacos*** (New South Wales), who received the Castner Medal awarded by the SCI Electrochemical Technology Group, discussing her work on the all-vanadium battery. The meeting will also include a **keynote** lecture to honour the work by the late Professor Richard P. Buck. Fittingly, this lecture (*q.v.* page 233) will be given by ***Dr. Tim Albrecht*** (Imperial), who is, in my view, the most brilliant UK-based electrochemist of my generation.

The social programme also looks entertaining – early arrivals will be treated to a Sunday evening hog-roast, with delegates treated to drinks and snacks during the poster session, followed by an evening reception at the Roman Baths in Bath (skinny dipping not essential!) where you will be welcomed by the Mayor of Bath, with ample time set for networking and catching-up. Watch out for the H_2 fuel cell cars developed by ***Dr. Bruno Pollet*** (Birmingham) – he may even allow you to testdrive them!

On behalf of Professor Marken and the various organising committees, I thank the meetings other supporting bodies: the ***RSC Electroanalaytical and Sensing Systems Group***, the ***SCI Electrochemical Technology Group***, and the ***RSC Electrochemistry Group***, and particularly thank all of those who have generously sponsored the meetings, in particular the ***International Society of Electrochemistry***, the ***Electrochemical Society***, **RSC Publishing** through ***Physical Chemistry Chemical Physics***, ***Johnson Matthey***, all the exhibitors listed on page 6, and all other sponsors. Very special thanks go to the ***Ellis Salsby*** team for managing much of the event logistics.

We, as a community, are very fortunate indeed to have such an enthusiastic, energetic and simply remarkable host for this event; on behalf of you all, I thank Professor Marken warmly for his generosity for this event and also in organising it for our benefit. I also thank the efforts of his local team of supporters, lead by ***John Watkins*** and ***Andrew Collins***, who, I am sure, will be help with any of your queries, and will endeavour to seek solutions to all problems, in their usual enthusiastically good humoured manner. I do hope you all enjoy the educative enhancements that you will experience at Electrochem2011 in Bath in a few weeks time; I am sure Professor Marken looks forward to welcoming you there.

Jay WADHAWAN
Editor-in-Chief

··· Electrochem 2011 ···

Electrochemical Horizons

University of Bath

5th - 6th September 2011

Electrochem 2011 is a Electrochemical Science and Technology Forum for the UK & Ireland electrochemistry community in industry and academia and for the upcoming generation of interdisciplinary researchers.

SYMPOSIA:

The 52nd Corrosion Science Symposium
Convenors: Dr. Nick Stevens & Dr. Gareth Hinds

Nano-Electro-Crystallization Symposium
Convenors: Prof W. Schwarzacher & Prof. S. Bending

Sensor Innovation and Electroanalytical Processes
Convenors: Prof J. Hart, Prof P. Fielden, Dr. R. Kataky

Nano-Electroanalysis Symposium
Convenors: Dr. Nathan Lawrence & Dr. Greg Wildgoose

International Year of Chemistry – Sensors for Africa
Convenors: Dr. K. Ozoemena & Dr. J. Limson

Nano-Carbon Technology Symposium
Convenors: Dr. Ian Kinloch & Dr. Katherine Holt

Microbial Electrochemistry Symposium
Convenors: Dr. Petra Cameron & Dr Ioannis Ieropoulos

Electrochemical CO_2 Conversion Symposium
Convenors: Dr. David Fermin & Dr. Frank Marken

Fundamental Electrochemistry Symposium
Convenors: Dr. Jay Wadhawan & Prof Robert Dryfe

Light Driven Electrochemistry Convenors: Andrew Collins & Dr. F. Marken

Electrochemical Processes in Exotic Media
Convenors: Dr. Darren Walsh & Dr. Daren Caruana

Inorganic & Molecular Electrochemistry
Convenors: Prof. Paul Low & Prof. Franti Hartl

Fuel Cells and Energy Systems
Convenors: Dr. Carlos Ponce-de-Leon & Dr. B. Pollet

Green Electrochemistry Convenors: Postgraduate Committee

Exhibitors

Exhibitions will be on display within Founders Hall throughout the conference.

- ***Alvatek***
- ***Ametek – AMT***
- ***Chemistry Central***
- ***EC-Lab, Ltd.***
- ***Gamry Instruments***
- ***Gensoric***
- ***Imperial College Press***
- ***Innovative Technology***
- ***Maney***
- ***Metrohm UK, Ltd.***
- ***Sherwood Scientific***
- ***SPECAC***
- ***Uniscan Instruments***

Annual General Meetings

RSC Electrochemistry Group	12H45 on Monday, September 5, 2011 in 3E3.5
SCI Electrochemical Technology Group	12H45 on Monday, September 5, 2011 in 3E3.8
RSC Electroanalytical & Sensing Systems	12H15 on Tuesday, September 6, 2011 in 3E2.1

Committee Meetings

CO_2-NMP Proposal Committee	16H00 on Monday, September 5, 2011 in University Hall
SCI/RSC Joint Executive Committee	17H00 on Monday, September 5, 2011 in 3E3.8
RSC Executive Committee	12H15 on Tuesday, September 6, 2011 in 3E3.5
SCI Executive Committee	12H15 on Tuesday, September 6, 2011 in 3E3.8

Electrochem 2011 Programme:

Sunday 4th September:

Registration open in Founders Hall from 18.00

FOUNDERS HALL:
"Hog-roast" and social gathering 19.00 – 21.00

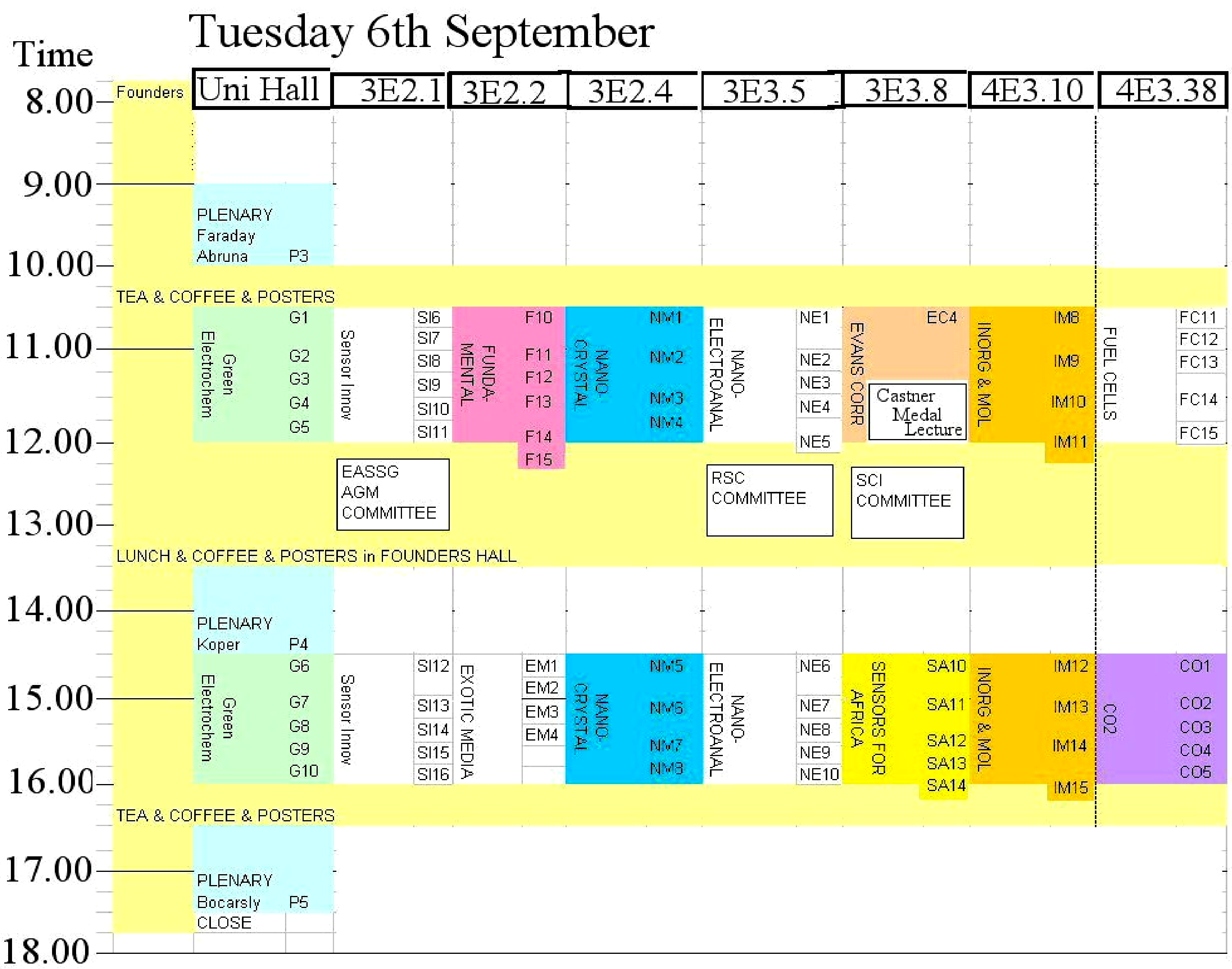
Exhibition, poster sessions, lunch, coffee, teas, etc. will happen in Founders Hall.

Monday 5th September

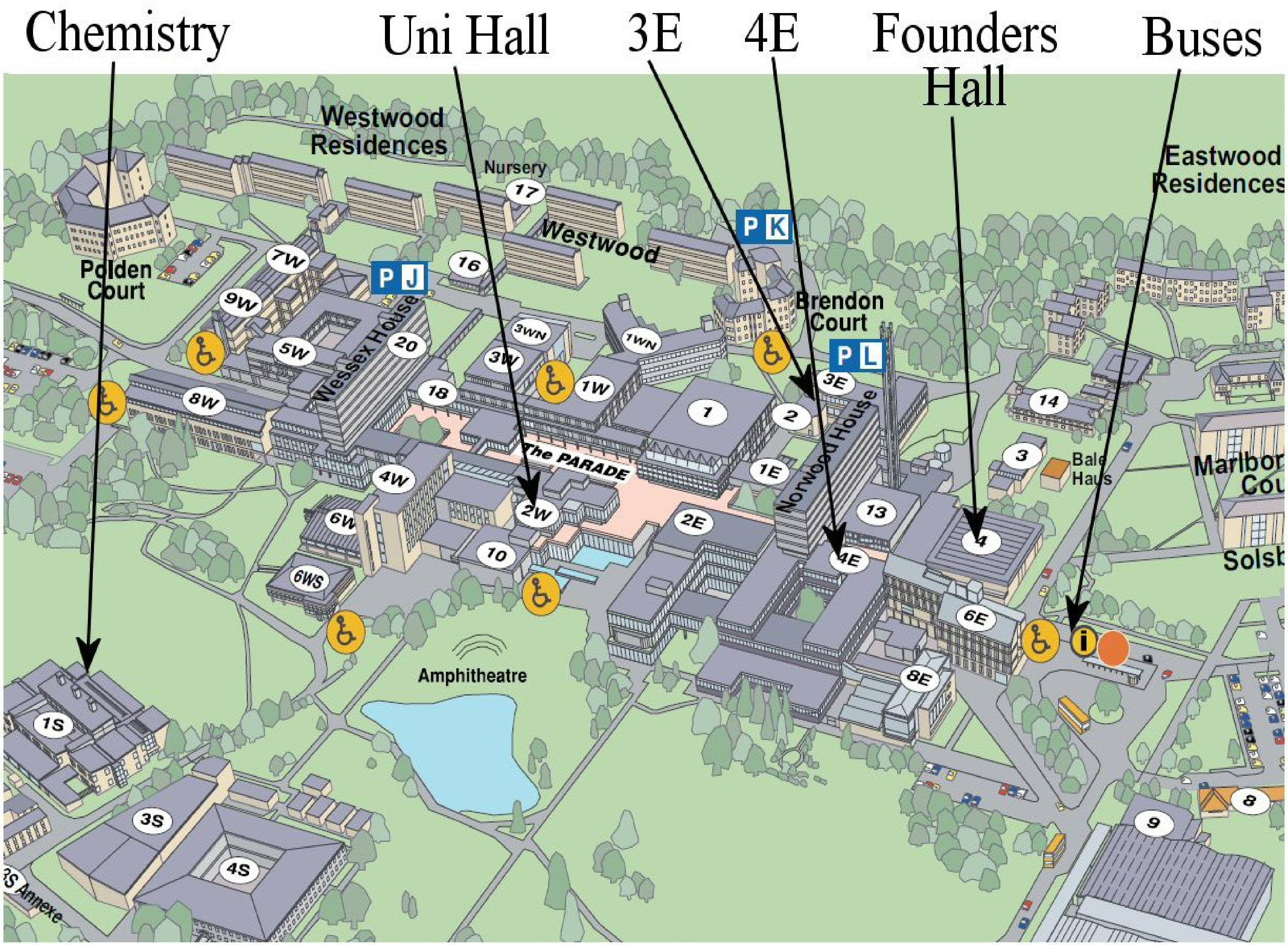
Time	Founders	Uni Hall	3E2.1	3E2.2	3E2.4	3E3.5	3E3.8	4E3.10	4E3.38
8.00	REGISTRATION								
9.00		PLENARY Dan Brett P1							
10.00	TEA & COFFEE & POSTERS								
11.00		FUEL CELLS FC1 FC2 FC3 FC4 FC5	SENSORS FOR AFRICA SA1 SA2 SA3 SA4	FUNDA-MENTAL F1 F2 F3 F4 F5	Microbial & Bio MB1 MB2 MB3 MB4	LIGHT DRIVEN LD1 LD2 LD3 LD4 LD5	Sensor Innov SI1 SI2 SI3 SI4 SI5	INORG & MOL IM1 IM2 IM3 IM4	NANOCARBON NC1 NC2 NC3 NC4
12.00						RSC AGM COMMITTEE	SCI AGM COMMITTEE		
13.00	LUNCH & COFFEE & POSTERS in FOUNDERS HALL	FUEL CELLS FC6 FC7 FC8 FC9 FC10	SENSORS FOR AFRICA SA5 SA6 SA7 SA8 SA9	FUNDA-MENTAL F6 F7 F8 F9	Microbial & Bio MB5 MB6 MB7 MB8 MB9	LIGHT DRIVEN LD6 LD7 LD8 LD9 LD10	EVANS CORR EC1 EC2 EC3	INORG & MOL IM5 IM6 IM7	NANOCARBON NC5 NC6 NC7 NC8
14.00									
15.00		PLENARY EVANS Frankel P2							
16.00		CO2 - NMP Proposal COMMITTEE							
17.00		POSTERS PIZZAZ WINE NIBBLES					SCI /RSC JOINT COMMITTEE		
18.00									

Transfer to Roman Baths
and Reception 19.00-21.00

Tuesday 6th September



Time		Uni Hall	3E2.1	3E2.2	3E2.4	3E3.5	3E3.8	4E3.10	4E3.38
8.00	Founders								
9.00		PLENARY Faraday Abruna P3							
10.00	TEA & COFFEE & POSTERS								
11.00		Green Electrochem G1 G2 G3 G4 G5	Sensor Innov SI6 SI7 SI8 SI9 SI10 SI11	FUNDA-MENTAL F10 F11 F12 F13 F14 F15	NANO-CRYSTAL NM1 NM2 NM3 NM4	NANO-ELECTROANAL NE1 NE2 NE3 NE4 NE5	EVANS CORR EC4 Castner Medal Lecture	INORG & MOL IM8 IM9 IM10 IM11	FUEL CELLS FC11 FC12 FC13 FC14 FC15
12.00			EASSG AGM COMMITTEE			RSC COMMITTEE	SCI COMMITTEE		
13.00	LUNCH & COFFEE & POSTERS in FOUNDERS HALL								
14.00		PLENARY Koper P4							
15.00		Green Electrochem G6 G7 G8 G9 G10	Sensor Innov SI12 SI13 SI14 SI15 SI16	EXOTIC MEDIA EM1 EM2 EM3 EM4	NANO-CRYSTAL NM5 NM6 NM7 NM8	NANO-ELECTROANAL NE6 NE7 NE8 NE9 NE10	SENSORS FOR AFRICA SA10 SA11 SA12 SA13 SA14	INORG & MOL IM12 IM13 IM14 IM15	CO2 CO1 CO2 CO3 CO4 CO5
16.00	TEA & COFFEE & POSTERS								
17.00		PLENARY Bocarsly P5 CLOSE							
18.00									


Chemistry
Uni Hall
3E
4E
Founders Hall
Buses
Westwood Residences
Eastwood Residences
Nursery
17
Westwood
P K
16
P J
7W
Polden Court
9W
5W
Wessex House
20
3WN
1WN
Brendon Court
P L
3E
8W
18
3W
1W
1
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Norwood House
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Bale Haus
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The PARADE
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i
Amphitheatre
8E
1S
3S
4S
8
9
3S Annexe

PLENARY SESSIONS

	Speaker	Title	Time	Location
P1	Dan J.L. Brett	Cost, durability and performance - Tackling the challenges facing fuel cell commercialization	**Mo 9.30-10.15**	UH
P2	Gerald Frankel	Evans Medal Award Lecture	**Mo 15.00-15.45**	UH
P3	Héctor D. Abruña	Electrochemistry at the Nanoscale: Building Blocks and Techniques	**Tue 9.00-9.45**	UH
P4	Marc Koper	Theory of multi-electron transfer reactions: implications for electrocatalysis	**Tue 13.30-14.15**	UH
P5	Andrew Bocarsly	The light-driven electrochemical reduction of CO_2 to organic products: single electron catalysis of a multi-electron process	**Tue 16.30-17.15**	UH

Fuel Cells and Energy Systems (chair: Pollet/Leon/Brett)

	Speaker	Title	Time	Location
FC1K	Ifan Stephens	Controlling the reactivity of Pt(111) by alloying at the sub-monolayer scale	**Mo 11.00-11.30**	UH
FC2	Oliver Curnick	Nafion-stabilised electrocatalysts for the PEMFC	**Mo 11.30-11.45**	UH
FC3	Georgios Nikiforidis	Substrates for the cathode reaction in the Zn/Ce redox flow battery	**Mo 11.45-12.00**	UH
FC4	Wen-Feng Lin	New insight into fuel cell electrocatalysis at atomic and molecular level: combined studies of in situ FTIR, ex situ electron diffraction and DFT atomistic modeling	**Mo 12.00-12.15**	UH
FC5	Jong-Won Lee	Strontium titanate-based interconnects for solid oxide fuel cells	**Mo 12.15-12.30**	UH
FC6K	Héctor D. Abruña	Materials discovery and in situ characterization for fuel cells	**Mo 13.30-14.00**	UH
FC7	Binyi Liu	Fundamental DFT studies on fuel cells	**Mo 14.00-14.15**	UH
FC8	Derek Egan	Progress in the development of aluminium-air batteries	**Mo 14.15-14.30**	UH
FC9	Christos Kalyvas	A new test system for the study of corrosion during the startup and shutdown of polymer electrolyte fuel cells	**Mo 14.30-14.45**	UH
FC10	Irene Merino Jimenez	Effect of the addition of surfactants in sodium borohydride solution on direct borohydride fuel cells	**Mo 14.45-15.00**	UH
FC11	Rizwan Raza	Sr^{3+}/Sm^{3+} Co-doped based nanocomposite electrolyte for SOFC	**Tue 10.30-10.45**	4E3.38

FC12	Martin Jönsson-Niedziolka	Enzymatic oxygen reduction at pyrene functionalized single walled carbon nanotubes	**Tue 10.45-11.00**	4E3.38
FC13	Dimitrios Presvytes	Towards a high temperature water electrolyser-electrocatalysis membranes	**Tue 11.00-11.15**	4E3.38
FC14K	Bruno Pollet	Hydrogen fuel cell battery electric vehicles (Hfcbev) vs. battery electric vehicles (Bev) 0 a Birmingham experience	**Tue11.15-11.45**	4E3.38
FC15	Maria Montes de Oca	CO and formic acid electro-oxidation at Au-Pd core-shell nanostructures	**Tue 11.45-12.00**	4E3.38

Sensors for Africa (chair: Ozoemena/Estrela/Limson)

	Speaker	Title	Time	Location
SA1K	Dave Newman	Developing the Cotton-Mouton effect as a replacement for antigen detecting RDT's in the diagnisis of Malaria	**Mo 11.00-11.30**	3E2.1
SA2K	Anthony Guiseppi-Elie	Microfabricated chemically sensitive impedimetric detectors for low cost quantitative lateral flow diagnostics	**Mo 11.30-12.00**	3E2.1
SA3	Thabile Ndlovu	The use of exfoliated graphite electrodes for detection of organic and inorganic pollutants	**Mo 12.00-12.15**	3E2.1
SA4	Justus Masa	Design of metalloporphyrin based micro sensors for technical applications and environmental monitoring	**Mo 12.15-12.30**	3E2.1
SA5K	Mark Baird	Sensor lighting in the dark cloud of TB diagnosis in Africa	**Mo 13.30-14.00**	3E2.1
SA6K	Francis Moussy	Diagnostics for the developing world	**Mo 14.00-14.30**	3E2.1
SA7	Peter Munyao Ndangili	Impedimetric response of a label-free genosensor prepared on a 3-mercaptopropionic acid capped gallium selenide nanocrystal modified gold electrode	**Mo 14.30-14.45**	3E2.1
SA8	Ronen Fogel	Challenges imposed on phenolics monitoring during amperometric biosensor application – a case study using laccase biosensors	**Mo 14.45-15.00**	3E2.1
SA9	Janice Limson	Panel Discussion: Reality, challenges and future opportunities for sensors in Africa	**Mo 15.00-15.15**	3E2.1
SA10K	Sandro Carrara	Key-note speech on Nanotechnologies, Biomaterials, and CMOS Systems for Low-Cost Medical Diagnostics in Developing Countries	**Tue 14.30-15.00**	3E3.8
SA11K	Louis de Smet	Biomolecular interactions sensed on multi-layer modified silicon	**Tue 15.00-15.30**	3E3.8
SA12	Kenneth	Redox-active and Redox-silent	**Tue 15.00-15.15**	3E3.8

	Ozoemena	Nanostructures in Electroanalysis		
SA13	Michael Niland	Accounting for Variability in Current Responses as a Factor of Electrode Surface Characteristics	**Tue 15.15-15.30**	3E3.8
SA14	Jesselan Pillay	Monolayer-Protected Gold Nanoparticles Self-Assembled Networks as Platforms for Probing the Electron Transfer Dynamics	**Tue 15.30-15.45**	3E3.8

Fundamental Electrochemistry (chair: Wadhawan/Fermin/Dryfe)

	Speaker	**Title**	**Time**	**Location**
F1K	Jochen Blumberger	What density functional based molecular dynamics can tell us about condensed phase electron transfer reactions	**Mo 11.00-11.30**	3E2.2
F2	Neil Rees	An experimental comparison of the Marcus-Hush and Butler-Volmer description of electrode kinetics	**Mo 11.30-11.45**	3E2.2
F3	Stephen Fletcher	The role of charge fluctuations in electron transfer	**Mo 11.45-12.00**	3E2.2
F4	David Fermin	Charge transfer mediated by two-dimensional assemblies of quantum dots	**Mo 12.00-12.15**	3E2.2
F5K	Alexei Kornyshev	Electrochemistry and nanophotonics	**Mo 12.15-12.45**	3E2.2
F6K	Emmanuel Maisonhaute	Electronic communication through small and large molecules	**Mo 13.30-14.00**	3E2.2
F7	Christopher Bell	Long-time chronoamperometry at an inlaid disc electrode	**Mo 14.00-14.15**	3E2.2
F8	Sarah Horswell	Electrochemical and spectroscopic studies of phospholipid bilayers supported on Au(111) surfaces	**Mo 14.15-14.30**	3E2.2
F9K	Richard Nichols	Single molecule electrical measurements	**Mo 14.30-15.00**	3E2.2
F10K	Patrick Unwin	Probing and imaging interfacial fluxes with electrochemistry	**Tue 10.30-11.00**	3E2.2
F11	Munetaka Oyama	Redox reactions of ferri/ferrocyanide on gold nanoparticle-modified electrodes prepared with paper supports	**Tue 11.00-11.15**	3E2.2
F12	Sara Dale	Salt matrix voltammetry	**Tue 11.15-11.30**	3E2.2
F13K	Andy Wain	Applications of scanning electrochemical microscopy in the characterization of catalyst and electrocatalyst activity	**Tue 11.30-12.00**	3E2.2
F14	Rui Campos	Rates of electron transfer in bilayer lipid membranes modified with bioactive molecules	**Tue 12.00-12.15**	3E2.2
F15	Richard Doyle	Enhanced oxygen evolution at hydrous iron oxide films in aqueous alkaline solution	**Tue 12.15-12.30**	3E2.2

Microbial and Bioelectrochemistry (chair: Cameron/Ieropoulos)

	Speaker	Title	Time	Location
MB1K	Frederic Barriere	Microbial fuel cell type biosensor for volatile fatty acid with acclimated bacterial community	**Mo 11.00-11.30**	3E2.4
MB2K	Ioannis Ieropoulos	Microbial fuel cell longevity	**Mo 11.30-12.00**	3E2.4
MB3	Iwona Gajda	Comparative study of multiple membranes for MFCs optimization of anode surface modification for improved microbial fuel cells	**Mo 12.00-12.15**	3E2.4
MB4	Rebecca Thorne	Electrochemistry as a tool for photo-microbial fuel cell study	**Mo 12.15-12.30**	3E2.4
MB5K	Danny O'Hare	Microelectrode arrays for the study of angiogenesis	**Mo 13.30-14.00**	3E2.4
MB6	Duncan McMillan	Electrochemical characterization of the tetraheme	**Mo 14.00-14.15**	3E2.4
MB7	Naing Tun Thet	An electrochemical impedance study of the effect of pathogenic bacterial toxins on tethered lipid bilayer membrane	**Mo 14.15-14.30**	3E2.4
MB8	Frankie Rawson	Interfacing cells with nanostructured electrochemical transducers for new insights in electron transfer from biological cells	**Mo 14.30-14.45**	3E2.4
MB9	Jason Riley	Bispecific antibodies – integration of molecular detection and signal components in a single agent	**Mo 14.45-15.00**	3E2.4

Light Driven Processes (chair: Collins/French)

	Speaker	Title	Time	Location
LD1	Robert French	Micro and nano-structuring for photoreactor intensification	**Mo 11.00-11.15**	3E3.5
LD2	P Kathir-ganamanthan	ZnO nanorods: dependence of method of electrodeposition	**Mo 11.15-11.30**	3E3.5
LD3	Senthilarasu Sundaram	An electrochemical route for improved flexible DSC	**Mo 11.30-11.45**	3E3.5
LD4	Bo Hou	$CdSe_xTe_{1-x}$ Alloyed Quantum Dots as Photoactive Components in Excitonic Solar Cells	**Mo 11.45-12.00**	3E3.5
LD5	Thomas Risbridger	Characterization of dye sensitized solar cells that utilize an aqueous electrolyte	**Mo 12.00-12.15**	3E3.5
LD6	Diego Colombara	$CuSbS_2$ and Cu_3BiS_3 thin films by electrodeposition/ sulfurization routes	**Mo 13.30-13.45**	3E3.5
LD7	Jay	Liquid nanotechnology for photo chemically-Induced Electron Transfer	**Mo 13.45-14.00**	3E3.5

	Wadhawan	Processes		
LD8	Andrew Collins	Liquid | liquid | electrode triple-phase boundary photovoltammetry of pentoxyresorufin in 4-(3-phenylpropyl)pyridine	**Mo 14.00-14.15**	3E3.5
LD9	P Kathir-ganamanthan	Highly efficient organic light emitting diodes based on Iridium(III) bis-(2-phenylpyridinato)-pyrazolonate	**Mo 14.15-14.30**	3E3.5
LD10	Charles Y. Cummings	Formation of Copper Indium Diselenide (CISe) Semiconductor Films	**Mo 14.30-14.35**	3E3.5

Sensor Innovation and Electroanalytical Processes

(chair: Fielden/Kataky/Hart)

	Speaker	**Title**	**Time**	**Location**
SI1K	Ronan Baron	Amperometric Gas Sensors: Mechanistic Studies and New Sensor Designs	**Mo 11.00-11.30**	3E3.8
SI2	Inderpreet Kaur	Self-Assembled Monolayers of S,-[4-[2-[4-(2-Phenylethynyl)phenyl]-ethynyl]phenyl]thioacetate Molecular Wires on Gold Surface	**Mo 11.30-11.45**	3E3.8
SI3	Adrian Crew	Development and comparison of anodic stripping voltammetric methods for the determination of Pb^{2+} in serum using microband screen-printed carbon electrodes	**Mo 11.45-12.00**	3E3.8
SI4	Charlotte Brady	Systematic Characterisation of Square Microelectrode Arrays	**Mo 12.00-12.15**	3E3.8
SI5	Laila Al-Shandoudi	Transient studies at microelectrodes: from model systems to O_2 reduction	**Mo 12.15-12.30**	3E3.8
SI6	Yann Bouret	New methods for pH predictions during electrochemical experiments	**Tue 10.30-10.45**	3E2.1
SI7	Mohammed Alshadokhi	Fabrication and characterisation of nanostructured palladium hydride pH microelectrodes	**Tue 10.45-11.00**	3E2.1
SI8	Jesus Iniesta	New Directions of Screen Printed Graphite Electrodes: Electrochemical Characterization of organic molecules in Room Temperature Ionic Liquids	**Tue 11.00-11.15**	3E2.1
SI9	Paula Lopez	Binding of chiral biomolecules at a micro liquid-liquid interface	**Tue 11.15-11.30**	3E2.1
SI10	Mark Platt	Detection of biomarkers using nanorods and coulter counters	**Tue 11.30-11.45**	3E2.1
SI11	Urszula Salaj-Kosta	Bioelectrochemistry of redox enzymes immobilized on mesoporous gold electrodes	**Tue 11.45-12.00**	3E2.1
SI12K	Sergey Gordeev	Amorphous carbon nanotools for cell surgery	**Tue 14.30-15.00**	3E2.1
SI13	Susan Warren	Electrochemical formation and characterization of a methylumbelliferone porous insulating film for	**Tue 15.00-15.15**	3E2.1

		catecholamine separation and quantitation		
SI14	Pedro Estrela	Label-Free Sub-Picomolar Protein Detection with Field-Effect Transistors	**Tue 15.15-15.30**	3E2.1
SI15	Jason Richard Butler	Bioaerosol Particle Detection by Flame Plasma Electrochemistry	**Tue 15.30-15.45**	3E2.1
SI16	Birgul Benli	Novel potential of nanoclay and nanoclay based electrodes	**Tue 15.45-16.00**	3E2.1

Evans Corrosion Symposium (chair: Stevens/Hinds)

	Speaker	**Title**	**Time**	**Location**
EC1K	Na Mi	Atmospheric corrosion of stainless steel studied with inkjet-printed salt deposits	**Mo 13.30-14.00**	3E3.8
EC2K	Majid Ghahari	Measurement and modeling of pitting corrosion of stainless steel for radioactive waste containers during storage	**Mo 14.00-14.30**	3E3.8
EC3K	Stefano Neodo	Benzotriazole corrosion inhibition on nickel-aluminium bronzes	**Mo 14.30-15.00**	3E3.8
EC4K	Siva Bohm	t.b.a.	**Tue 10.30-11.00**	3E3.8
Special lecture	Maria Skyllas-Kazacos	Castner Medal Lecture (Video)	**Tue 11.00-12.00**	3E3.8

Inorganic & Molecular Electrochemistry (chair: Hartl/Low)

	Speaker	**Title**	**Time**	**Location**
IM1K	Biprajit Sarkar	Donor-acceptor systems and electron transfer-induced reactivity	**Mo 11.00-11.30**	4E3.10
IM2K	Joe Crayston	Attachment of redox-active Ru complexes to gold surfaces	**Mo 11.30-12.00**	4E3.10
IM3K	Mike Ward	Polynuclear ruthenium(II) complexes displaying electrochromism and solvatochromism: redox and spectroscopic behaviour	**Mo 12.00-12.30**	4E3.10
IM4	Joanne Tory	Electrocatalytic CO_2 Reduction with Manganese and Osmium Carbonyl Complexes	**Mo 12.30-12.45**	4E3.10
IM5K	Nicholas J. Long	Ferrocenyl-Functionalised Catalysts for Redox Control and Switching	**Mo 13.30-14.00**	4E3.10
IM6K	Frederic Barriere	Applications of weakly coordinating electrolytes in organometallic electrochemistry	**Mo 14.00-14.30**	4E3.10
IM7K	Mark Whiteley	Redox Chemistry and Electronic Structure of Molybdenum Alkynyl Complexes	**Mo 14.30-15.00**	4E3.10
IM8K	Bas de Bruin	Ligand Redox Non-innocence in Open-	**Tue 10.30-11.00**	4E3.10

		Shell Transition Metal Catalysis		
IM9K	Lesley Yellowlees	How spectroelectrochemical techniques can help you	**Tue 11.00-11.30**	4E3.10
IM10K	Marc Robert	Proton-coupled Electron Transfers. Concerted processes in chemistry and biology: a joint electrochemical and photochemical approach	**Tue 11.30-12.00**	4E3.10
IM11	Paul Low	Guilty as Charged: The case for redox non-innocence in bimetallic ruthenium complexes	**Tue 12.00-12.15**	4E3.10
IM12K	Heinrich Lang	Ferrocenyl-based transition metal complexes: synthesis, structure, bonding and spectro-electrochemistry	**Tue 14.30-15.00**	4E3.10
IM13K	John Henry	Density Functional Theory: A Tool for the Prediction of Redox Properties for Heteroaromatics	**Tue 15.00-15.30**	4E3.10
IM14K	Frantisek Hartl	π-Dimerization of Pleiadiene Radical Cations	**Tue 15.30-16.00**	4E3.10
IM15	Wing Man	Redox Non-innocence in Ruthenium Vinyl complexes	**Tue 16.00-16.15**	4E3.10

Nanocarbon Technology Symposium (chair: Holt/Kinloch)

	Speaker	**Title**	**Time**	**Location**
NC1K	Karl Coleman	Nanocarbons: an overview	**Mo 11.00-11.30**	4E3.38
NC2K	Robert Dryfe	Carbon nanotube electrochemistry: fundamentals and applications	**Mo 11.30-12.00**	4E3.38
NC3K	Michael Lyons	Transport and kinetics at carbon nanotube - redox enzyme composite modified electrode biosensors : modelling redox enzymes dispersed in nanotube mesh films of finite thickness	**Mo 12.00-12.30**	4E3.38
NC4	Anna Valota	Electrochemical behaviour of exfoliated single and multi layer graphene microelectrodes	**Mo 12.30-12.45**	4E3.38
NC5K	Julie Macpherson	How to get the most out of boron doped diamond in electroanalysis	**Mo13.30-14.00**	4E3.38
NC6K	Rabah Boukherroub	Electrochemical and sensing properties of reduced graphene oxide	**Mo 14.00-14.30**	4E3.38
NC7	Katherine Holt	Redox reactions at nanodiamond surfaces revealed by attenuated total reflectance infrared spectroscopy	**Mo 14.30-14.45**	4E3.38
NC8	Katherine Lawrence	Carbon nanoparticle surface modification for sensor development	**Mo 14.45-15.00**	4E3.38

Green Electrochemistry (chair: Watkins/Wadhawan)

	Speaker	Title	Time	Location
G1K	Derek Pletcher	The Development and Application of Microflow Electrolytic Reactors for Synthesis	**Tue 10.30-11.00**	UH
G2	Henry Burch	Hydrogen from sunlight at textured zinc ferrite electrodes	**Tue 11.00-11.15**	UH
G3	Jennifer Hartley	Ionometallurgy – Properties and Applications of Metal Ions in Ionic Liquids	**Tue 11.15-11.30**	UH
G4	Samina Akbar	Tuning of channels in 3D inverse bicontinuous cubic Fd3m-type nanostructured platinum films	**Tue 11.30-11.45**	UH
G5	Emma Smith	Electrochemical Characterisation of Mixed Poly(pyrrole-thiophene) Films Immersed in Choline Chloride Based Ionic Liquids	**Tue 11.45-12.00**	UH
G6K	James Utley	Electrochemistry and biomass – backwards to the future?	**Tue 14.30-15.00**	UH
G7	John Watkins	Electrosynthetic Processes at the Carbon Membrane Stabilised Triple Phase Boundary Interface	**Tue 15.00-15.15**	UH
G8	Lavinia Astratine	Formation of Electrochromic PTFA Films Utilizing Room Temperature Ionic Liquids	**Tue 15.15-15.30**	UH
G9	Harun Chakrabarti	Effect of anode materials on wastewater denitrification and TOC removal in an upflow electrochemical reactor	**Tue 15.30-15.45**	UH
G10	Anne Vuorema	Carbonized Layer-by-Layer Cellulose-PDDA-TiO2 Composite Thin Films: Carbon enhanced surface conductivity	**Tue 15.45-16.00**	UH

Electrochemical Processes in Exotic Media (chair: Caruana/Walsh)

	Speaker	Title	Time	Location
EM1K	Alexei Kornyshev	Electrical double layer in ionic liquids: from fundamentals to applications	**Tue 14.30-15.10**	3E2.2
EM2K	Steve Bramwell	The “electrochemistry” of magnetic monopoles	**Tue 15.15-15.45**	3E2.2
EM3	Darren Walsh	Mass transport in room temperature ionic liquids	**Tue 15.45-16.00**	3E2.2
EM4	Daren Caruana	Plasma electrochemistry: electron transfer at the solid/gas interface	**Tue 16.00-16.15**	3E2.2

Nano-Electrocrystallization (chair: Schwarzacher/Bending)

	Speaker	Title	Time	Location
NM1K	Olaf Magnussen	The dynamic copper electrode: growth and additive interactions on the atomic scale	**Tue 10.30-11.00**	3E2.4
NM2K	Benjamin Horrocks	DNA-templated conductive nanowires	**Tue 11.00-11.30**	3E2.4
NM3	Jeerapat Nutariya	Growth of Pt films on Au(111) via surface limited redox replacement (SLRR)	**Tue 11.30-11.45**	3E2.4
NM4	Nawal Al Abass	Electrodeposition of platinum from lyotropic liquid crystal mixtures	**Tue 11.45-12.00**	3E2.4
NM5K	Karl Ryder	Electrocrystallisation of Silver in Deep Eutectic Solvents; an Electrochemical Kinetic Study Using Real Time in-situ Holographic Imaging	**Tue 14.30-15.00**	3E2.4
NM6K	Yvonne Grunder	Nucleation of gold nanoparticles at the water|1,2-dichloroethane interface	**Tue 15.00-15.30**	3E2.4
NM7	David Parker	Ultra Thin Layer Deposition of Low Band Gap semiconductors onto ZnO Nanowires for Photovoltaic Applications.	**Tue 15.30-15.45**	3E2.4
NM8	Sara E.C. Dale	Electrodeposition of Core-Shell Superconducting-Ferromagnetic Mesocrystals	**Tue 15.45-16.00**	3E2.4

Nano-Electroanalysis (chair: Albrecht/Marken)

	Speaker	Title	Time	Location
NE1K	Izzet Kocak	Covalent Chemical and Electrochemical Modification of Carbon Nanotubes by Redox Probes for Biosensor Applications	**Tue 10.30-11.00**	3E3.5
NE2	Sara Shariki	Trace metal electroanalysis in cotton films	**Tue 11.00-11.15**	3E3.5
NE3	Evelyn Caldwell	Development of Au nanorods arrays in alumina for SERS substrates	**Tue 11.15-11.30**	3E3.5
NE4	Kelly Leonhardt	Modelling the amperometry of AFM-SECM systems	**Tue 11.30-11.45**	3E3.5
NE5K	Stanley Lai	Quantitative Visualization of Electrocatalysis at Individual Metal Nanoparticles	**Tue 11.45-12.15**	3E3.5
NE6K	Tim Albrecht	Electrochemistry in nanopore/ electrode structures - from pore fabrication to DNA sequencing-by-tunneling	**Tue 14.30-15.00**	3E3.5
NE7	Yige Zhou	The electrochemistry of single silver nanoparticles via nanoparticle-electrode	**Tue 15.00-15.15**	3E3.5

		collision processes		
NE8	Gareth Keeley	Simultaneous determination of paracetamol and dopamine using thin film pyrolytic carbon electrodes	**Tue 15.15-15.30**	3E3.5
NE9	Petr Dudin	Single Walled Carbon Nanotubes (SWNTs) as a Template for the Controlled Deposition of Functional Gold Nanostructures	**Tue 15.30-15.45**	3E3.5
NE10	Md. Abdul Aziz	Facile preparation of nanogold in solution or on solid surfaces for electrochemical applications	**Tue 15.45-16.00**	3E3.5

Electrochemical CO_2 Conversion (chair: Fermin)

	Speaker	**Title**	**Time**	**Location**
CO1K	Guido Mul	Solar driven fuel synthesis: Opportunities and Challenges	**Tue 14.30-15.00**	4E3.38
CO2	Zarko Jovanov	The Importance of Surface Morphology in Controlling the Activity of Polycrystalline Copper towards CO_2 Electroreduction	**Tue 15.00-15.15**	4E3.38
CO3	Josie Googall	Bio-inspired Metal Sulphide Electrocatalysts for CO_2 Reduction	**Tue 15.15-15.30**	4E3.38
CO4	Briony Setterfield-Price	Electrocatalytic Carbon Dioxide Reduction	**Tue 15.30-15.45**	4E3.38
CO5	Daniela Plana	Cu and Au Electrocatalysts for CO_2 Reduction	**Tue 15.45-16.00**	4E3.38


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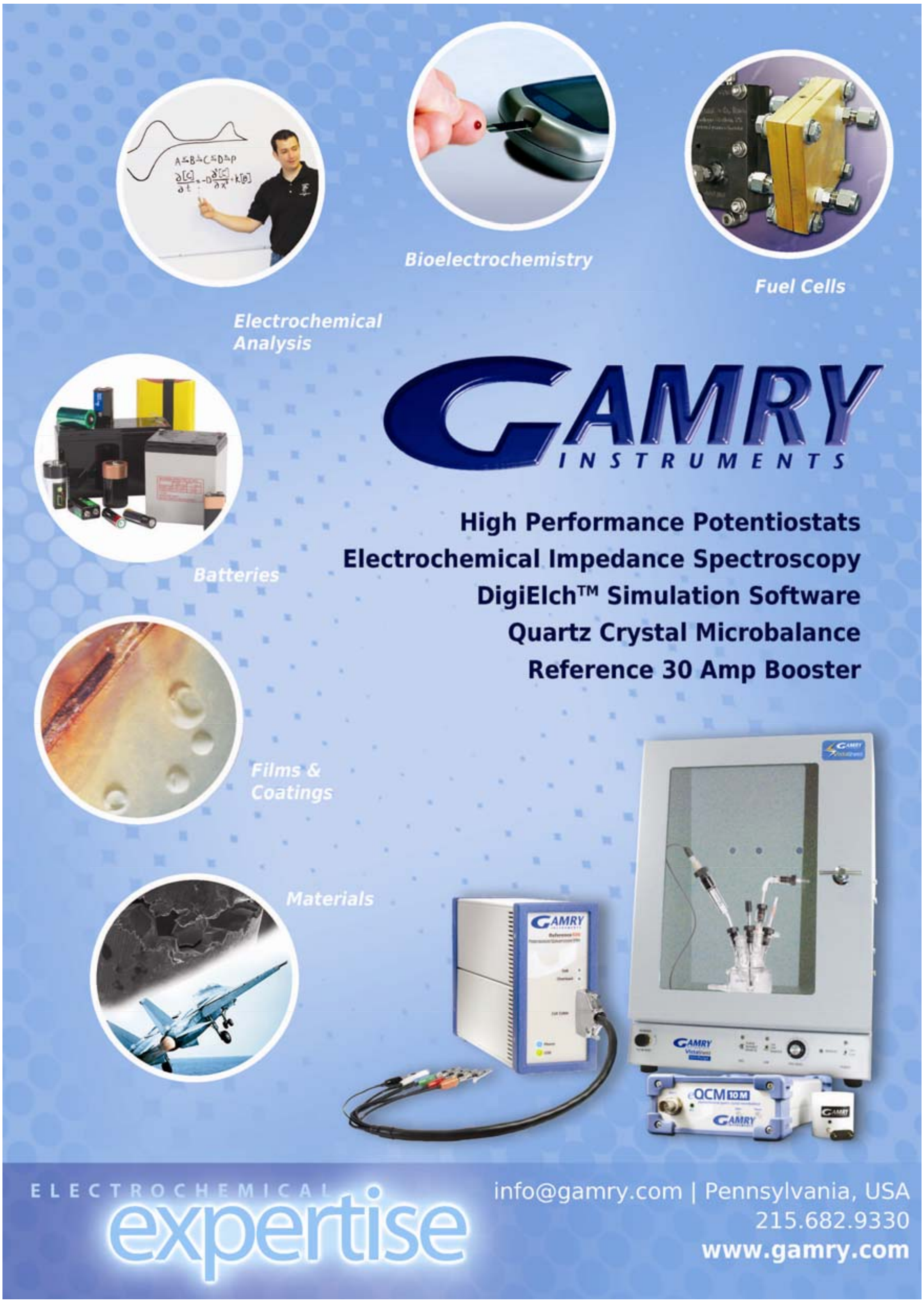


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Plenary Speakers

P1

Dan Brett

Dr. Dan Brett received his first degree in Chemistry from King's College London and obtained his Ph.D. in Physical Chemistry from Imperial College London on the Electrochemistry of Self-Assembled Monolayers. Dan then worked as a Research Associate and Research Fellow as at Imperial College looking at various aspects of fuel cell science and engineering. He joined the Department of Chemical Engineering at UCL as Lecturer in 2007, where he is currently a Senior Lecturer.
Dan is the Director of the UCL Electrochemical Innovation Lab and Co-Director of the Centre for CO_2 Technology. He was awarded the DeNora Prize from the International Society of Electrochemistry for his outstanding contribution to fuel cell research and the Baker Medal from the Institute of Civil Engineers for his work on microgeneration.

Abstract

Cost, durability and performance - Tackling the challenges facing fuel cell commercialization

D. J. L Brett,
E. Ali, S. Ang., F. Daniels, C. Gibbs, R. Jervis, N. Mansor, T. Mason, J. Millichamp.

Centre for CO_2 Technology
Department of Chemical Engineering
University College London, UK
d.brett@ucl.ac.uk

Fuel cells are a highly promising energy conversion technology, with applications ranging from small portable electronic items, through micro-combined heat and power units for the home and vehicle prime-movers, to large scale distributed energy generation.

However, there are still major technical issues to be overcome in order for fuel cells to reach their full market potential. This presentation describes research taking place at the UCL Electrochemical Innovation Lab to tackle the key objectives of *cost*: new fuel cell designs and non-Pt catalysts; *durability*: coke formation at SOFC anodes and advanced metallic bipolar plates, and *performance*: controlled compression fuel cell operation and system efficiency improvement via multi-objective optimization.

P2

Gerald Frankel

Sc.D., Massachusetts Institute of Technology, 1985
OSU Distinguished Scholar award, 2010
Fellow, NACE International, ASM International, and The Electrochemical Society
Humboldt Research Award for Senior US Scientists, 2003
Former Chairman, Research Committee of NACE International

ECS Corrosion Division H.H. Uhlig Award, 2010
OSU College of Engineering Harrison Faculty Award, 2000
Former Chairman, Corrosion Division of the Electrochemical Society

Dr. Frankel's primary interests are in the fields of corrosion and electrochemistry. He has focussed on localized corrosion, passivation, coatings, and inhibition.

The current activities in Dr. Frankel's group include the study of Al alloy inhibition by chromate-free inhibitors. He is investigating the effects of surface pretreatments on corrosion protection. His group is using new approaches to measure quantitatively the adhesion energy of coatings and the degradation of that adhesion during exposure to aggressive environments. One focus is on the connection between accelerated tests for atmospheric corrosion and the behaviour in the field to improve lifetime prediction. The effects of UV light and ozone on atmospheric corrosion are studied. Other projects include atmospheric pitting corrosion (under thin water layers), cracking of steel in ethanol, corrosion fatigue testing in thiosulfate solutions as a safe alternative to H_2S solutions, and the degradation of Sn catalysts used in electrochemical reduction of CO_2.

P3

Héctor D. Abruña

Professor Abruña, Emile M.Chamot Professor of Chemistry is Director of the Energy Materials Center at Cornell (emc^2) and the Center for Molecular Interfacing (cmi). He completed his graduate studies with Royce W. Murray and Thomas J. Meyer at the University of North Carolina at Chapel Hill in 1980 and was a postdoctoral research associate with Allen J. Bard at the University of Texas at Austin. After a brief stay at the University of Puerto Rico, he came to Cornell in 1983. He was Chair of the Department of Chemistry and Chemical Biology from 2004-2008.

Prof. Abruña has been the recipient of numerous awards including a Presidential Young Investigator Award, Sloan Fellowship, J. S. Guggenheim Fellowship and J. W. Fulbright Senior Fellow. He is the recipient of the Electrochemistry Award for the American Chemical Society (2008), and the C.N. Reilley Award in Electrochemistry for 2007. He was elected Fellow of the American Association for the Advancement of Science in 2007, member of the American Academy of Arts and Sciences in 2007 and Fellow of the International Society of Electrochemistry in 2008. He received the D. C. Grahame Award from the Electrochemical Society for 2009 and most recently, the Faraday Medal of the Royal Society for 2011. Prof. Abruña is the co-author of over 350 publications and has given over 450 invited lectures world-wide. Out of the 36 students that, to date, have obtained a Ph.D. under his direction, 12 have gone on to faculty positions.

Abstract

Electrochemistry at the Nanoscale: Building Blocks and Techniques

Héctor D. Abruña Dept. of Chemistry & Chem. Bio. and Center for Molecular Interfacing Baker Lab. Cornell University Ithaca, New York 14853-1301

This presentation will focus on the synthesis and characterization via electrochemical, spectroscopic, computational and transport measurements of molecular assemblies, of deliberate design, for application in molecular devices. We have prepared and characterized single-molecule devices incorporating transition metal complexes and other molecular assemblies designed so that electron transport occurs through well-defined charge states of a single molecule. We have also employed more complex molecular architectures whose transport can be modulated by optical and electrochemical stimuli. Preliminary results with novel optical techniques and new device geometries, including mechanical break junctions, will also be discussed. Recent work on graphene and carbon nanotubes will also be discussed.

P4

Marc Koper

Marc T.M. Koper is a Professor of Surface Chemistry and Catalysis at Leiden University, The Netherlands. He received his PhD degree (1991) from Utrecht University (The Netherlands) with Prof. Dr. J.H. Sluyters on the topic of electrochemical instabilities and oscillations. He was an EU Marie Curie postdoctoral fellow at the University of Ulm (Germany) with Prof. W. Schmickler, and a Fellow of Royal Netherlands Academy of Arts and Sciences (KNAW) at Eindhoven University of Technology, before moving to Leiden in 2005. He was also a visiting professor at the Catalysis Research Center of Hokkaido University (Sapporo, Japan) in 2010. His research interests encompass fundamental studies of electrochemical and electrocatalytic processes through a combination of experimental and theoretical investigations.

Abstract

Theory of multi-electron transfer reactions: implications for electrocatalysis

Marc T.M. Koper
Leiden Institute of Chemistry
Leiden University, 2300 RA Leiden, The Netherlands

Practically all relevant electrocatalytic reactions require the transfer of at least two electrons, and often more than two. A full theory of such reactions does not only require knowledge of the activation energy associated with the event of a single electron, i.e. Marcus theory and its various extensions, but also insight into the relative energies of the intermediate states, i.e. the thermodynamics of all intermediates and the associated elementary steps in which they are formed. Based on this idea, I will show that are fundamental differences in the catalysis of reactions involving 1, 2 or more than 2 electrons, or, partly equivalently, reactions involving 0, 1, or 2 or more catalytic intermediates. For the latter two classes, knowing the thermodynamics of the full reaction is more important than the ability to predict the activation energy of a single step, and in fact the optimal catalyst is first and foremost that material that is able to generate a "thermodynamic landscape" that does not have a sink or mountain. In essence, this is a multidimensional Sabatier principle for the optimal catalyst. The principle will be illustrated on a few examples of important electrocatalytic reactions, such as hydrogen evolution, oxygen reduction/evolution and carbon dioxide reduction.

M.T.M. Koper, J.Electroanal.Chem. (2011), doi:10.1016/j.jelechem.2010.10.004

P5

Andrew Bocarsly

Andrew Bocarsly received his Bachelor of Science degree jointly in chemistry and physics from UCLA in 1976, and his Ph.D. in chemistry from M.I.T. in 1980. He has been a member of the Princeton University, Chemistry Department faculty for thirty-one years. He is affiliated with Princeton's Materials Institute and Princeton's Environmental Institute. Professor Bocarsly has published over 180 papers in peer reviewed journals and co-authored nine patents. Research in his laboratory is focused on the materials chemistry associated with visible light photoelectrochemistry for the conversion of carbon dioxide to alcohols; elevated temperature proton exchange membrane fuel cells; cyanogel sol-gel processing; and molecule-based multielectron photoinduced charge transfer processes.

Professor Bocarsly serves as a consultant and contractor to various fuel cell and alternate energy companies. He is a founder and President of the Science Advisory Board for Liquid Light Inc., a company formed to commercialize the formation of organic commodity chemicals from carbon dioxide using alternate energy sources. Professor Bocarsly has received an Alfred P. Sloan Fellowship, the Sigma Xi (Princeton Section) Science Educator Award, the American Chemical Society-Exxon Solid State Chemistry award, and has served as the electrochemistry editor for *Methods in Materials Research: A Current Protocols Publication*. Presently, he is serving as a volume editor for *Structure and Bonding* in the area of fuel cells and batteries.

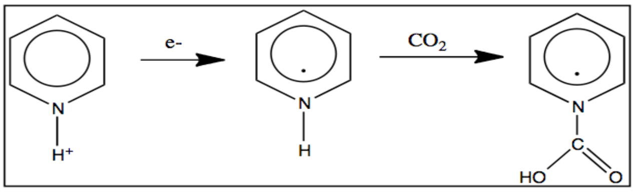
Abstract

The Light Driven Electrochemical Reduction of CO_2 to Organic Products: Single Electron Catalysis of a Multielectron Process

Andrew B. Bocarsly, Kate A. Keets, Elizabeth L. Zeitler, Amanda J. Morris, Emily E. Barton-Cole, Yuan He, Kuo Liao, and Zachary M. Detweiler *Department of Chemistry, Princeton University Princeton, New Jersey 08544, USA bocarsly@princeton.edu*

The visible light driven photoelectrochemical production of energy rich liquids from carbon dioxide is appealing both in terms of climate change issues and new sustainable energy resources. To this end, we have proposed the electrosynthesis of alcohols from CO2 as an energy conversion and storage approach, which recycles carbon that would otherwise end up as an atmospheric greenhouse gas. The thermodynamically uphill nature of this reaction coupled with the large activation energy associated with this multielectron, multiproton reduction makes conversion of CO2 problematic. Alternative energy schemes for this conversion only become possible if the typically observed system activation overpotentials (≥1V) can be significantly reduced. Thus, key to a successful process is the development of a stable catalytic system.

We have previously reported the pyridinium catalyzed electrochemical reduction of CO2 to methanol at illuminated p-GaP photocathodes, where we find that faradaic efficiencies are >95%, when run at several hundred millivolts of underpotential. [1] The observed reduction involves a mediated charge transfer process, which is initiated by the one electron reduction of pyridinium leading to the formation of formic acid through the reduction of a carbamate intermediate (Scheme I).



Scheme I: Initial pyridinium reduction to form a radical carbamate.

Reaction with two more equivalents of reduced pyridyl radical generates formaldehyde with close to 100% faradaic efficiency. A final two equivalents of reduced pyridyl radical produces methanol at this interface.

The processes outlined here can be modified to introduce the formation of carbon- carbon bonds by substitution of the pyridine ring, introduction of other aromatic amines or variation of the electrode material. The appropriate mating of substituted aromatic amines with semiconductor surfaces can produce high energy products such as oxalate, isopropanol, or butanol.

[1] (a) Barton, E.E., D.M. Rampulla, and A.B. Bocarsly. *Journal of the American Chemical Society*, 130 (2008) 6342. (b) Cole, E.B., P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev, and A.B. Bocarsly, *ibid*, **132 (**2010) 11539.

Fuel Cells & Energy Systems Symposium

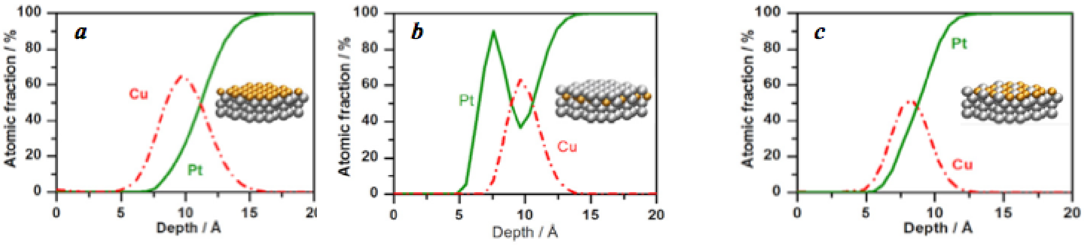
FC1K

Controlling the reactivity of Pt(111) by alloying at the submonolayer scale

Ifan E.L. Stephens, [1] Alexander, S. Bondarenko,[1] Francisco J. Perez-Alonso,[1] Federico Calle-Vallejo,[2]
Mohammedreza Karamad, [2] Lone Bech,[1] Tobias P. Johansson, [1] Jan Rossmeisl,[2] Ib Chorkendorff.[1]

1: CINF, 2: CAMD
Technical University of Denmark (DTU) ifan@fysik.dtu.dk, ibchork@fysik.dtu.dk

Pt is the most active monometallic catalyst for the reactions occurring at fuel cell electrodes, including the oxygen reduction reaction, the hydrogen oxidation reaction and the methanol oxidation reaction. However, the high cost and scarcity of Pt present a significant barrier towards the widespread uptake of low temperature fuel cells. To overcome this limitation, the catalytic activity of Pt can be improved by alloying it with other metals. Herein, we investigate the effect of alloying at the submonolayer scale on the reactivity of Pt(111). We achieve this by introducing up to a monolayer of Cu into the surface or near-surface region of a Pt single crystal, as shown in the figure below. Our investigations incorporate electrochemical measurements in 0.1 M $HClO_4$, ultra high vacuum experiments and density functional theory calculations. We find that the surface reactivity is highly sensitive to the *exact* location of the Cu component. In a Cu/Pt(111) surface alloy,[1] where Cu is located in the first atomic layer of Pt(111), the surface binds adsorbates such as OH* and H* more strongly than Pt. On the contrary, in a Cu/Pt(111) near-surface alloy, where Cu is located in the second atomic layer, the surface binds H* and OH* more weakly than Pt. [2] We use these phenomena to tune the surfaces for two electrocatalytic reactions, O_2 reduction and CO adlayer oxidation.



Non-destructive depth profiles from angle resolved X-ray photoelectron spectroscopy measurements of Cu/Pt(111) structures, for (a) overlayer (b) near- surface alloy and (c) surface alloy. The insets show schematic illustrations.

[1] K.J. Andersson, F. Calle-Vallejo, J. Rossmeisl, I. Chorkendorff, J. Am. Chem. Soc.131 (2009) 2404-2407. [2] I.E.L. Stephens, A.S. Bondarenko, F.J. Pérez-Alonso, F. Calle-Vallejo, L. Bech, T.P. Johansson, A.K. Jepsen, R. Frydendal, B.P. Knudsen, J. Rossmeisl, I. Chorkendorff, J. Am. Chem. Soc. (2011) DOI: 10.1021/ja111690gDOI: 10.1021/ja111690g.

FC2

Nafion-stabilised electrocatalysts for the PEMFC

Oliver Curnick and Bruno G Pollet
School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham
B15 2TT, UK

Abstract

FC3

Substrates for the cathode reaction in the Zn/Ce redox flow battery

G. Nikiforidis, L.E.A. Berlouis, D. Hall * and D. Hodgson *
WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL.
**Plurion Limited, Glenrothes, Fife KY6 2TF.*

Redox flow batteries (RFB's) are energy storage devices in which the electrochemical reactions involved at the anode and cathode in the cell utilize soluble redox species. The active material is stored externally to the battery system itself and thus the energy of the redox battery can be determined independently of the battery power because it is related to the electrolyte volume and concentration whereas the power is related to the electrode size and electrode reactions. The zinc-cerium hybrid RFB has one of the largest open circuit values (~2.3 V) of any current RFB system[1]. The key to maintaining this and so, the energy efficiency, as high as possible during charge and discharge is to minimize the overpotential losses by careful choice of electrode employed and additives to the solution to inhibit gas evolution reactions at both anode and cathode. In this study, the cathode reaction, *i.e.*, $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$ was examined on a variety of electrode substrates consisting of Pt, Pt/Ir and Ti/Ta as well as commercial DSA's in order to assess the electron transfer kinetics and so allow benchmarking for future material developments to take place. The experiments were performed over the temperature range 24ºC to 60ºC in methane sulfonic acid (MSA) as the base electrolyte with the cerium concentration set at 0.8 M. The techniques of cyclic voltammetry, Tafel extrapolation, polarisation resistance, electrochemical impedance spectroscopy (EIS) as well as rotating disk (RDE) techniques were employed in order to assess the performance of the different electrocatalytic coatings for the Ce^{3+}/Ce^{4+} reaction.

Fig.1 Linear Polarisation analysis on Pt-Ti mesh electrode at 298 K. Scan rate: 0.1667 mV s^{-1}

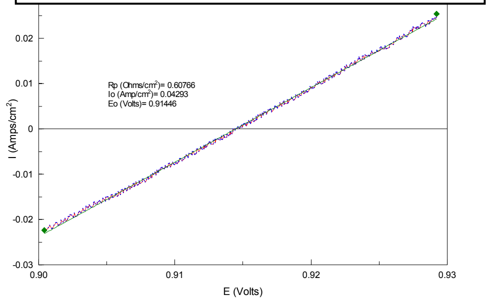
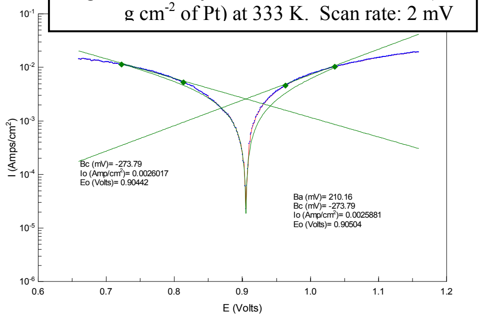


Fig.2 Tafel analysis on Pt- based electrode (3 g cm^{-2} of Pt) at 333 K. Scan rate: 2 mV



Charge-discharge cycles on the Pt disk and Pt/Ti mesh electrodes revealed as expected 100 % coulombic efficiencies in solutions consisting of 0.2-0.5 M Ce^{4+} in 6.9 M MSA at current densities < 100 mA cm^{-2}. However, at higher values, the sharp increase in potentials suggest that oxygen (during charging) and hydrogen (during discharge) evolution reactions are occurring with resulting loss in current efficiency at these electrodes.

FC4

New Insight into the Fuel Cell Electrocatalysis at Atomic and Molecular Level: Combined Studies of in-situ FTIR, ex-situ Electron Diffraction and DFT Atomistic Modeling

W. F. Lin, J. M. Jin, B. Liu, P. Hamer, M. Brandon, C. Hardacre, P. Hu

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

The increasing demand for clean and sustainable energy sources in today's world has become a strong driving force in continuing economic development, and improvement of human health and living conditions. Fuel cells, as an emerging new clean energy technology for transportation, stationary power generation and portable power, have drawn global attention and competition in recent years thanks to their high energy efficiency and zero/low emissions. In the last two decades, great progress has been made in both hydrogen fuel cells (PEMFCs) and direct (methanol) fuel cells [D(M)FCs], in terms of power density increases and cost reduction. Nonetheless, two major technical gaps hindering commercialization have been identified: high cost and low durability. Fuel cell catalysts, such as Pt-based catalysts, are the major factors in these challenges. 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.

In this work, the surface structure and reactivity of the well-defined Pt, Ru and various PtRu electrodes towards the adsorption and electro-oxidation of a range of small organic fuel molecules in various electrolyte solutions have been studied by combined *ex-situ* electron diffraction, *in-situ* electrochemical FTIR spectroscopy and Density Functional Theory calculations, and the new insight into the surface electrocatalysis has been obtained at atomic and molecular level. The electro-deposition of Ru on Pt(111) 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 RuPt(111) surfaces toward CO 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 obsreved 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(H) layer was also present. The (2x2)-O(H) phase was inactive towards CO_{ads} oxidation. The oxidation of CO_{ads} took place *via* reaction with the active (1 x 1)-O(H) phase formed at higher potentials. Furthermore, it is shown that RuO_2(100) phase is formed at even higher potentials and it is highly active. Build upon these fundamental studies, optimum PtRu and other nanocatalysts have been developed.

FC5

Strontium Titanate-Based Interconnects for Solid Oxide Fuel Cells

Jong-Won Lee, Beom-Kyeong Park, Seung-Bok Lee, Tak-Hyoung Lim,
Seok-Joo Park, Rak-Hyun Song, Dong-Ryul Shin
Fuel Cell Research Center, Korea Institute of Energy Research
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A strontium titanate ($SrTiO_3$)-based material with a perovskite structure is considered to be one of the promising alternatives to $LaCrO_3$-based interconnect materials, since $SrTiO_3$ shows high chemical stability under both oxidizing and reducing atmospheres at high temperatures. $SrTiO_3$ materials exhibit an *n*-type semiconducting behavior when they are donor-doped and/or exposed to a reducing atmosphere [1]. In this work, La-doped $SrTiO_3$ materials with 'stoichiometric' and 'Sr-deficient' compositions were synthesized by the modified Pechini method. The synthesis parameters such as the chelating agent-to-metal ratio and the post-heat-treatment temperatures were controlled to prepare nano-sized, single-phase particles. Electrical, thermal and mechanical properties were determined on the 'stoichiometric' and 'Sr-deficient' materials sintered in an oxidizing atmosphere. Furthermore, a thin layer interconnect was coated on the porous Ni-YSZ anode support by using a screen printing process. The process parameters were optimized to obtain a dense interconnect and to form adherent interfaces between the interconnect and the anode support.

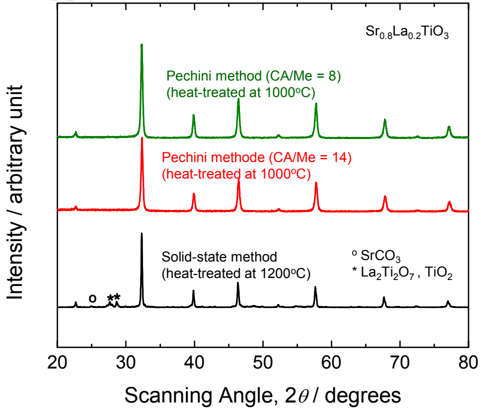

Figure 1. XRD patterns of $Sr_{0.8}La_{0.2}TiO_3$ powders synthesized by the solid-state method and the modified Pechini process.

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FC6K

Cornell University

emc²

ENERGY MATERIALS CENTER at CORNELL

"Materials Discovery and In-situ Characterization for Fuel Cells"

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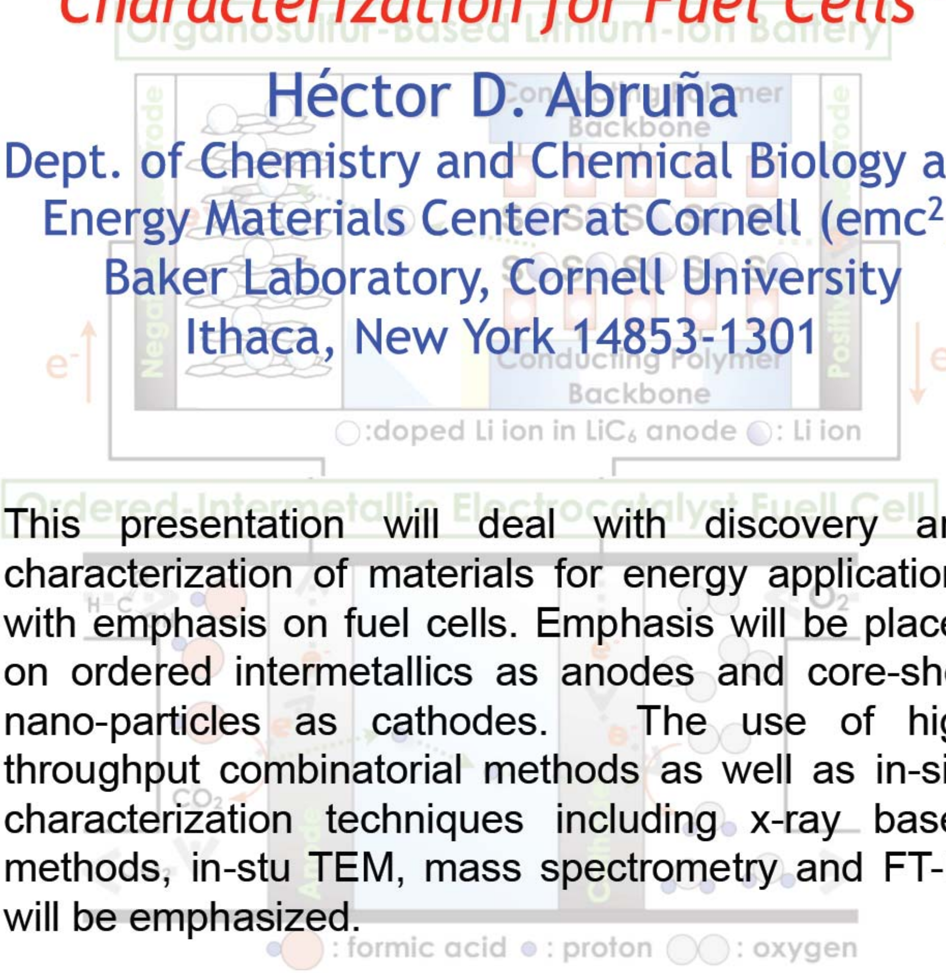

This presentation will deal with discovery and characterization of materials for energy applications with emphasis on fuel cells. Emphasis will be placed on ordered intermetallics as anodes and core-shell nano-particles as cathodes. The use of high throughput combinatorial methods as well as in-situ characterization techniques including x-ray based methods, in-stu TEM, mass spectrometry and FT-IR will be emphasized.

FC7

Fundamental DFT Studies on Direct Methanol Fuel Cells:
An Understanding of Methanol Dehydrogenation and Oxidation on the Pt(211) Surface

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A periodic self-consistent density functional theory (DFT) study of methanol dehydrogenation to CO and subsequently oxidation to CO_2 on the Pt(211) surface has been carried out. Two main pathways[1, 2] in the CH_3OH dehydrogenation to CO, which are the O-H bond scission of CH_3OH to form methoxy (CH_3O) intermediate followed by sequential dehydrogenation and the C-H bond scission of CH_3OH to form hydroxymethyl (CH_2OH), have been examined. The oxidation product of CO_2 is formed with the presence of oxidants of O/OH. The possible intermediates involved are fully invested with respect to the specific geometric structures, adsorption energies and reaction barriers for all elementary steps. It has been shown that the O-H pathway is energetically more favorable than the C-H pathway; furthermore, the step of H cleavage from CHO to CO in the O-H pathway is considered to be the rate-determining step. In addition, the effect of water/solvent towards the rate-determining step has been explored and discussed.

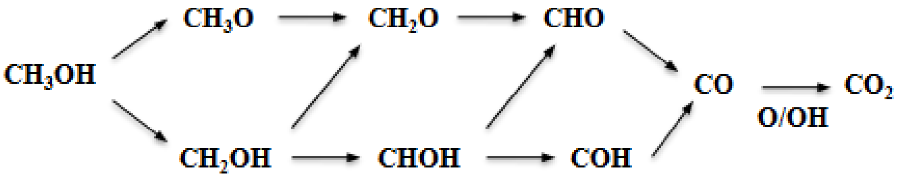

Figure 1. Scheme showing the methanol dehydrogenation comprising two main pathways.

Table 1, Reaction barriers (eV) of all elementary steps involved in the two main pathways, the data in bracket include the water effect.

O-H pathway			C-H pathway	
$CH_3OH \rightarrow CH_3O$	0.74		$CH_3OH \rightarrow CH_2OH$	0.63
$CH_3O \rightarrow CH_2O$	0.51		$CH_2OH \rightarrow CHOH$	0.97
$CH_2O \rightarrow CHO$	0.13		$CHOH \rightarrow COH$	0.19
$CHO \rightarrow CO$	0.84 (0.54)		$COH \rightarrow CO$	0.87
$CH_2OH \rightarrow CH_2O$	1.11		$CHOH \rightarrow CHO$	0.03
$CO+O \rightarrow CO_2$	1.11		$CO+OH \rightarrow OCOH$	0.82
			$OCOH \rightarrow CO_2+H$	0.64

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FC8

Progress in the development of aluminium-air batteries

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The corrosion and dissolution of super-pure aluminium in NaOH and KOH electrolytes was investigated as an electrode for an aluminium-air battery. The goal is to design a light-weight aluminium-air battery, with a weight of 50 g and with energy and power densities of 400 W h kg^{-1} and 400 W kg^{-1} respectively [1]. The alloy contained 0.5 % Mg and 0.07 % Sn with a 99.999 % Al base. This alloy has been identified as a suitable alloy for an aluminium-air battery because it yields discharge efficiencies greater than 90 % at current densities greater than 17 mA cm^{-2} [2]. The aim was to quantify the corrosion currents of this alloy in NaOH and KOH at open-circuit and under discharge, and to compare them with that of 99.999 % aluminium. Galvanostatic tests were carried out for 1 hour over the current density range, 0 to 100 mA cm^{-2} in a three electrode glass cell, and the electrode potential and the volume of evolved hydrogen were measured as a function of time. Corrosion currents were calculated from the hydrogen volume data using Faraday's Law. Inhibition efficiencies were calculated as a function of current density, where inhibition efficiency is the percentage by which the Mg and Sn alloying elements reduced the corrosion of 99.999 % Al. The effect of electrolyte concentration on the corrosion and dissolution of the alloy was investigated. SEM images were taken of the corroded surface and tin inclusions were identified on the surface, confirming the metal dissolution-deposition process as the activating mechanism [2-4]. A lightweight prototype aluminium-air cell was developed using the aluminium alloy as anode and air-cathode supplied by Yardney Technical Products. The first prototype Al-air cell delivered an energy and power density of 67 W h kg^{-1} and 63 W kg^{-1} respectively.

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FC9

A new test system for the study of corrosion during the startup and shutdown of polymer electrolyte fuel cells

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Degradation of proton exchange membrane fuel cells (PEMFCs) is generally observed as slow, irreversible decay in the performance followed by sudden failure. The gradual performance loss is mainly linked to changes in the electrodes and membrane. The degradation of the electrodes is usually caused by catalyst degradation and carbon support corrosion. One of the distinct degradation modes is caused by the shutdown/startup cycling of the cell. During the startup or shutdown of fuel cells, when a change in gas on the anode side of the fuel cell often takes place, an air/fuel front can be formed. This causes the interfacial potential of the membrane to drop in the hydrogen starved region of the anode, resulting in high potentials (>1.4V) on the cathode side. Under such high potentials, carbon oxidation, water electrolysis or platinum dissolution can occur at the cathode, giving rise to a performance degradation [1-2].

A new fuel cell test system has been developed for the study of the carbon corrosion phenomena in PEMFCs. By using printed circuit board (PCB) technology, a PCB-fuel cell assembly is constructed. This contains a segmented PCB with a single flow channel routed on each segment. The anode electrode is segmented and bonded onto the PCB substrate with the membrane and the cathode hot pressed on it. A schematic of the test system is shown in Fig 1.

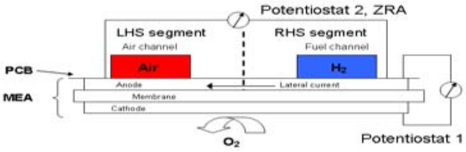

Figure1. Simplified schematic illustration of the experimental setup.

Potentiostat 1 measures the cell current while potentiostat 2 plays the role of a zero resistance ammeter (ZRA). The latter short circuits the two PCB segments and monitors the lateral (reverse) current flowing on the gas diffusion layer of the anode. This current is an indicator of the corrosion processes occurring. Various parameters of the experimental design are investigated in order to test the robustness of the method. Profiles of the lateral and total currents are presented demonstrating the capability of the technique to detect and measure them. The concentration of carbon dioxide produced by the carbon support oxidation is measured in the cathode exhaust. The carbon loss is quantified and the severity of the cathode catalyst layer corrosion is discussed.

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FC10

Effect of the addition of surfactants in sodium borohydride solution on direct borohydride fuel cells

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The direct borohydride fuel cell (DBFC) has been proposed as a promising alternative for power generation due to its high energy density (9.3 kW h kg^{-1}) and its capacity to release 8e$^-$ per molecule at a low electrode potential (-1.24V *vs*. NHE) [1]. However, there are drawbacks that still need to be resolved, such as the borohydride crossover and its hydrolysis reaction, which decrease the coulombic efficiency of the cell [2]. In order to minimize the hydrolysis of borohydride ions, several hydrolysis suppressors were tested in this work: (a) Triton X-100, (b) zonyl FSO, (c) Chemguard S-228M anionic fluorosurfactant and (d) sodium dodecyl sulphate (SDS). The electrolysis of 1 mol dm^{-3} $NaBH_4$ in 3 mol dm^{-3} NaOH in presence and absence of each additive at three different concentrations was carried out at a constant current (600 mA) while monitoring the amount of hydrogen gas generated and the anode potential. Two anodes of 3 cm^2 geometrical area were used: a gold flat plate and a carbon cloth covered with gold nanoparticles (0.5 mg cm^{-2}). The reference and counter electrodes were Hg/HgO and a Pt mesh, respectively. In the absence of surfactant, a hydrogen evolution rate of 1.95 cm^3 min^{-1} was obtained on the Au/C electrode, whereas with the surfactant (a), (b), (c) and (d) above at 0.001 wt. % concentration the rates were: 0.132, 1.134, 0.36 and 0.8 cm^3 min^{-1}, respectively. Using the flat plate electrode, 1.75 cm^3 min^{-1} rate of hydrogen was observed in the absence of surfactant and 3.04, 2.33, 1.68 and 1.1 cm^3 min^{-1} with 0.001 wt. % of surfactant (a), (b), (c) and (d) respectively; which means that the presence of surfactants in some cases, caused an increase in the hydrogen rate on this electrode. The effect on the borohydride oxidation was studied by cyclic voltammetry and rotating disk on a gold electrode in the presence of the two surfactants that best inhibit the hydrogen evolution: surfactants (c) and (d). The former produced a decrease in the borohydride oxidation peak when increasing the additive concentration. It is thought that due to its anionic nature, the additive competes with the borohydride ions for the occupation of the active sites on the catalyst. On the other hand, surfactant (c) did not affect the current of the oxidation peak and produced less hydrogen, thus improving the DBFC performance. The kinetic rate constant and the diffusion coefficient were calculated when surfactant (d) was added to the solution, showing that an increase in the concentration of surfactant caused a detriment in the reaction.

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FC11

Sr $^{3+}$/Sm^{3+} Co-Doped based Nanocomposite Electrolytes for SOFC

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Co-doped two phase nanocomposite electrolyte ($Ce_{0.8}Sm_{0.2-x}Sr_xO_{2-\delta}$) was synthesized by a co-precipitation method and added KCO_3/Na_2CO_3. The composite electrolyte homogenous morphology was found by SEM (Figure 1), TEM, and thermal analysis was determined with DSC. The particle size was calculated with ***Scherrer*** formula and compare with SEM/TEM results, 5-20 nm is in a good agreement with the SEM and XRD results. The fuel cell power density was 800-900 mW/cm^2 found at low temperature (500-550 °C) as shown in Figure 2. Ionic conductivities were measured with electrochemical impedance spectroscopy (EIS). The study explicitly shows that the observed remarkable temperature-dependent is primarily the result of softening/melting of the carbonate phase as the physical state of the carbonate phase transforms from solid, softened to molten. The stable conductivity and performance has been observed. The possible coexistence of various charge carriers was analyzed by FTIR.This co-doped approach with 2nd phase gives the good idea to realize challenges for solid oxide fuel cell (SOFC). The enhancement of conductivity at the interface between the two phase nanocomposites electrolyte is also studied with the percolation theory of interfaces.

Keywords: ceria-carbonate, co-doped, EIS, conductivity

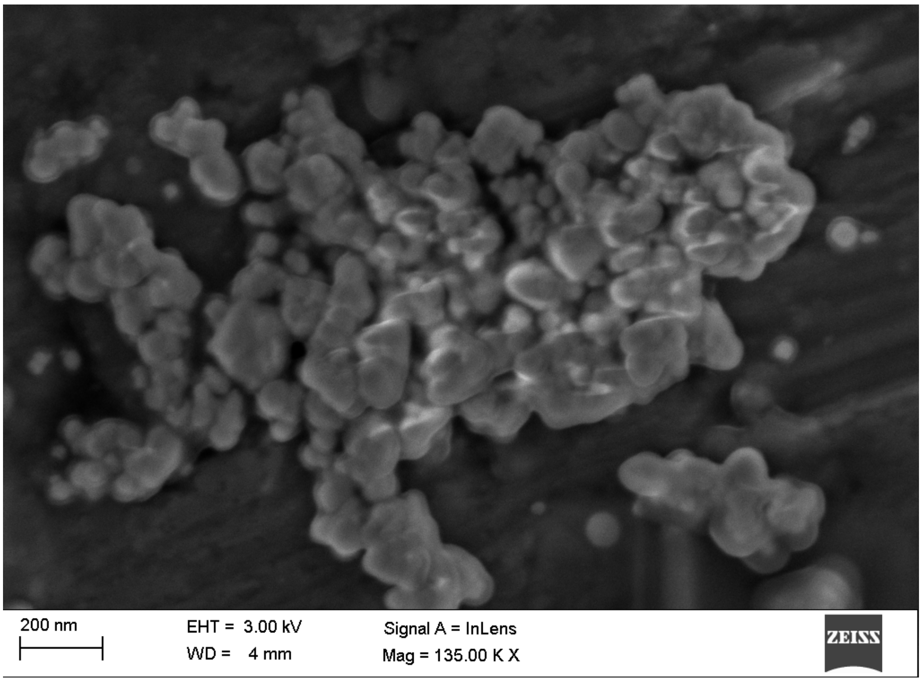

Figure 1. Microstructure of composite electrolyte

FC12

Enzymatic Oxygen Reduction at Pyrene Functionalised Single Walled Carbon Nanotubes

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Research into biofuel cells for possible implantable power sources has been an active area over the last years. We prepared electrodes modified with pyrene-functionalised carbon nanotubes and multicopper oxidases for the use as biocathodes for oxygen reduction. The nanotubes were immobilised in a silicate matrix on ITO and enzyme was either adsorbed from solution or co-immobilised with the nanotubes in the matrix. When the oxidase was adsorbed from solution the charge of the functionalised nanotubes was decisive for the efficiency of reduction of oxygen. In the case of co-immobilised enzyme the sign of the charge of the functional group has little effect on the catalytic efficiency. Rotating disk experiments show that the main limitation of the catalytic current is the supply of oxygen to the enzyme. [1]

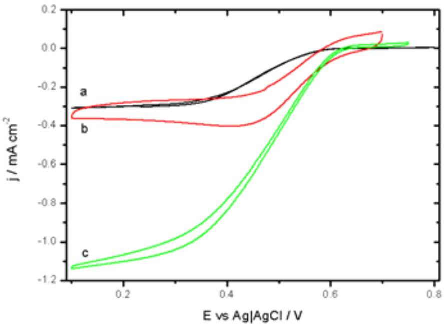

Figure 1 CVs of oxygen reduction at pyrene-modified a) SWCNT b) VACNT and c) air-breathing electrodes with enzyme.

To improve the access of oxygen to the enzyme electrodes were prepared using vertically aligned carbon nanotube forests glued to the ITO surface using a conductive epoxy as support for the enzyme. [2] The three-dimensional structure of the electrode provides a large active surface area for enzyme immobilisation, but also good oxygen flux resulting in a relatively high catalytic oxygen reduction current. We also present preliminary result using an air-breathing electrode to improve the cathode performance.

The modified electrodes were used as biocathodes in a zinc-oxygen battery, a hybrid device offering a higher operating voltage than a pure biofuel cell. [3]

However, the actual current measured from a particular electrode depends not only on the electrode itself, but also on the specific setup. We show that improved results can be achieved with minor changes to the cell geometry.

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[3] A. Heller, Anal. Bioanal. Chem. **385**, 469 (2006).

FC13

Towards a High Temperature Water Electrolyser - Electrocatalysis and Membranes

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Polymer electrolyte membrane (PEM) cells offer an attractive platform for water electrolysis as they combine high efficiency, high production rate and simpler design in comparison with Solid Oxide electrolysers. Current technology is limited by the use of Nafion proton conducting membrane that operates up to 80 ^{o}C. High temperature PEM fuel cells operate at 180 ^{o}C and utilize polybenzimidazole (PBI) membranes doped with phosphoric acid that induces proton conductivity in the membrane [1]. However solid acids like CsH_2PO_4 (cesium dihydrogen phosphate,DCP) are conductive above 200 ^{o}C [2]. Our goal is to increase the operating temperature of PEM based water electrolysers above 180 ^{o}C with the use of solid acids as proton conducting media. To achieve this we are currently determining the compatibility of state-of-the-art catalysts for oxygen evolution (i.e. IrO_2,RuO_2 and IrO_2-RuO_2 mixed oxide) with CsH_2PO_4 and also working to develop conducting membranes based on CsH_2PO_4.

Oxygen evolution catalysts are inhibited by the presence of H_3PO_4 in high concentration in PBI membranes. In the present study we compare the behavior of the catalysts in the presence of H_3PO_4 and CsH_2PO_4 solutions of 0.5M concentration. H_2SO_4 was also used as a reference electrolyte solution. Results for linear sweeps of IrO_2 catalyst in all three electrolyte solutions are depicted in Figure 1. It is obvious that the catalyst operates significantly better in the CDP solution, and achieves similar current densities at 70-100 mV lower overpotential in comparison to the other two solutions. A reason for that enhanced performance is possibly the low acidity of the CDP solution.

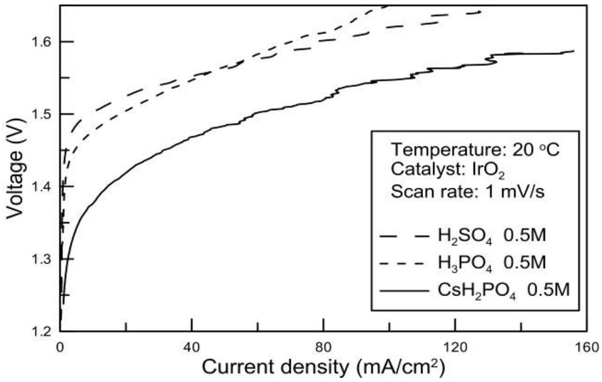

Figure 1. Linear sweep (1 mV/s) of IrO2 catalyst in various acid solutions of 0.5 M concentration in ambient temperature.

CDP powder was also pressed in pellets for use in a water electrolyser. 0.5 g of CDP pow-der were pressed in a 1.8 cm diameter disk pellet with a thickness of 0.76 mm. The pellet exhibited conductivity in the order of $1.6 \cdot 10^{-2}$ S/cm (in plane) at 250 ^{o}C which is promising in comparison to H_3PO_4 doped PBI membranes whose conductivity is about $3 \cdot 10^{-2}$ S/cm [1]. Our future plans will test oxygen evolution catalysts in higher temperatures and higher acid concentrations as well as the incorporation of CDP in membranes with conductivity and mechanical properties comparable to PBI or Nafion membranes.

This research was supported by the European Union through the ITN project SUSHGEN number 238678.

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FC14K

HYDROGEN FUEL CELL BATTERY ELECTRIC VEHICLES (HFCBEV) *vs.* BATTERY ELETRIC VEHICLES (BEV) – A BIRMINGHAM EXPERIENCE

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Keywords: hybrid vehicle; hydrogen PEM fuel cell; 350 bar hydrogen;
battery electric vehicle (BEV)

This abtstract describes the development, design, testing and commissioning of five HFCBEVs on the University of Birmingham campus (Figure 1). The HFCBEVs were tested to evaluate performance, range, efficiency and system cost and were compared to ‘pure’ lithium-ion BEVs (Mitsubishi iMiEV, 47 kW electric motor, 58 MJ of battery storage, 1100kg, £26,700 – Figure 2) and conventional internal combustion engine (ICE) diesel vehicles. The 11 kW electric motor in these HFCBEVs were powered directly by an inexpensive 1.5 kWh lead acid battery pack (£1,000) which was constantly charged up by a 1.2 kW Proton Exchange Membrane (PEM) fuel cell (Ballard Nexa, £4,000) running on a 350 bar hydrogen composite tank (Class III, Dynecell, Dynetek Industries, £4,000).

The electrolytic grade hydrogen (99.999%, Green Gases Ltd) was delivered by an Air Products refueller (Series 100) and refuelling 0.6kg of hydrogen took an average of 3-5 minutes. The hydrogen consumption of the HFCBEVs was 10.0 $g.km^{-1}$, giving an energy efficiency of 0.71 $km.MJ^{-1}$ (77 mpg of diesel equivalent) with up to 60 km range on full throttle with an acceleration of 1.5 $m.s^{-2}$ and a top-speed of 30 mph (note that 80 km range would require either 0.94 $km.MJ^{-1}$ or a 0.8 kg hydrogen tank). The weight of the HFCBEVs was 525 kg with a load capacity of 200 kg.

The BEVs showed better efficiency (2.22 $km.MJ^{-1}$) with higher range (up to 130 km) and speed (up to 80 mph) to that of the HFCBEVs. Overall, all hydrogen and pure BEVs offered better efficiency and performance than ICE diesel vehicles. Finally, we clearly demonstrated that hydrogen PEM Fuel Cell can be used as an ‘effective’ range extender when used with some batteries.

Figure 1: Hydrogen Fuel Cell Battery Electric Vehicles at The University of Birmingham (UK)

Figure 2: Battery Electric Vehicles (Mitsubishi iMieV) at The University of Birmingham campus (UK)

In our study, the HFCBEVs were designed with a fuel cell battery charger which topped up the lead acid accumulator when the vehicle was idle (Figure 3).

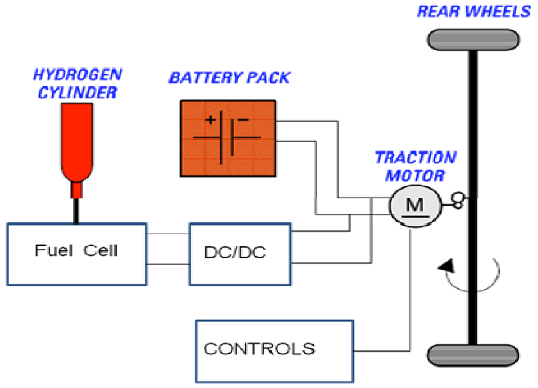
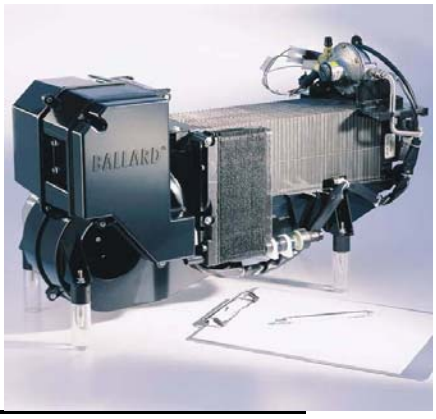


Figure 3: Mechanical drive system layout

The 1.2kW Ballard Nexa PEM fuel cell was used, as it was compact and relatively low cost, and provided the durability required for the demanding operating environment. The stack efficiency quoted by Ballard was 38% (LHV) at full power and 48% at half power inclusive of parasitic loads. This was consistent with measurements taken from the stacks installed into the vehicle fleet. Table 1 below shows the characteristics of the 1.2kW Ballard Nexa. The Nexa fuel cell system is designed for operation on pure gaseous hydrogen. No fuel humidification was required and hydrogen was supplied at pressures ranging from 0.7 to 17 bars (gauge).



Nominal power (at 0.55V per cell)	1200W
Heat dissipation	1600W (at rated net power)
Nominal operating point	26V (DC) x 46A (DC)
Efficiency (full load)[a]	32%
(50% load)	41%
Mass	13kg
Lifetime	2000 hours
Anode gas	99.999% H_2
Consumption (at full power)	17.5 SLPM
Pressure / Temperature / Humidity	7 to 17.2 bar/3-40^{o}C/0% -95%
Water emission	870ml/h (max)
Noise	72 dBA @ 1m

Table 1: Characteristics of the PEMFC stack

Overall, fuel cell reliability has been excellent to date, providing over 2,000 hours of operation across the fleet and 2,000 km travelled with no technical problems or observable degradation. Experimental *V-I* curves for the stacks in four of the vehicles are shown in Figure 4, and demonstrate that the PEM fuel cell performance is consistent between stacks and against manufacturer's specifications – despite incidences of fuel starvation, excessive current draw, rapid power cycling, ambient temperature extremes and vibration/shock received during operation.

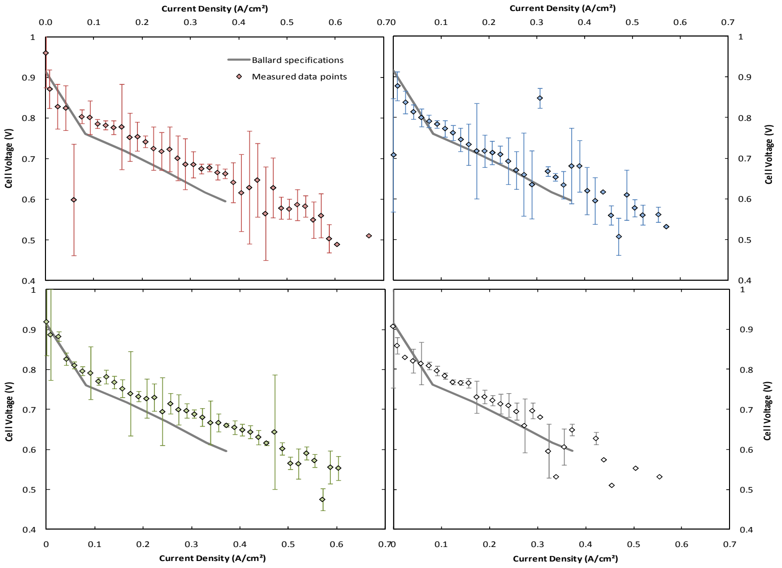


Figure 4: *V-I* curves taken from the Ballard Nexa stacks installed in each HFCBEV.

FC15

CO and formic acid electrooxidation at Au-Pd core-shell nanostructures

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Low temperature fuel cell technology is set to occupy a central role in powering society in the near future, particularly in the transport sector. Several challenges emerge in the preparation of active, robust and low-cost catalysts in order to improve the operation and commercialisation of fuel cells. Bi-metallic nanostructures are potential materials to use as catalysts in this application. The present contribution focuses on a study of the structure-reactivity relationship of Au-Pd core-shell (CS) nanostructures for CO and formic acid (HCOOH) oxidation in acid solutions as a function of Pd thickness.

Au-Pd CS nanostructures are obtained by the seeding growth method, where palladium chloride is reduced at 19 nm Au cores in the presence of ascorbic acid. Nanoparticles were characterised by high resolution transmission electron microscopy (as shown in figures A and B) and selected area electron diffraction (SADP). SADP patterns showed that Pd shells are epitaxially grown on Au seeds and their lattice strain decreases from 3.5 to 1% upon increasing the shell thickness from 1 (figure A) to 10 nm (figure B) [1]. The 3D assemblies of nanoparticles were generated by alternate electrostatic adsorption steps involving poly-L-lysine (PLL) and colloidal solutions. Electrochemical studies in H_2SO_4 containing electrolyte solutions show that the average CO stripping charge per particle and the current density for HCOOH oxidation decrease as Pd thickness decreases. The implications of these studies on the design of electrocatalysts for fuel cells, *e.g.* direct formic acid fuel cells (DFAFCs), will be discussed.

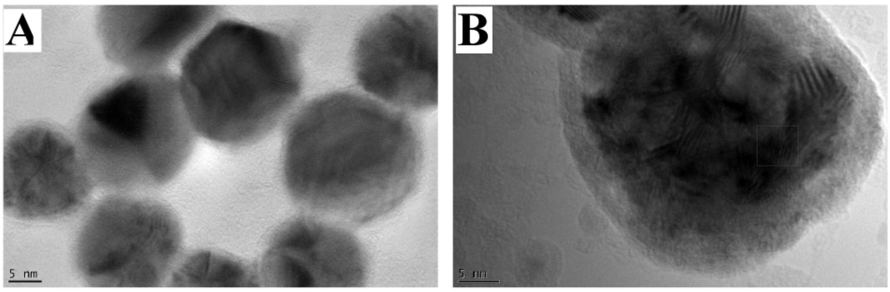

Figure 1. TEM images of 19 nm Au nanoparticles coated with epitaxial Pd films of 1 (A) and 10 nm (B) average thicknesses

Reference:

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FC16-Po

$La_{0.8}Ca_{0.2}CrO_3$ - Glass Composite Interconnects for Solid Oxide Fuel Cells

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Interconnects in solid oxide fuel cells (SOFCs) connect electrically the unit cells and separate the fuel from the oxidant in the adjoining cells. The key requirements of the interconnects are (i) high electronic conductivity, (ii) chemical stability in both oxidizing and reducing atmospheres, (iii) low gas permeability, and (iv) chemical/thermal compatibility with other cell components. Lanthanum chromites ($LaCrO_3$) with a perovskite structure have become the interconnect material of choice in most SOFC stack developments, since they satisfy the requirements mentioned above [1]. However, the chromites are quite difficult to sinter to high densities even at temperatures above 1600^{o}C in oxidizing atmospheres. Various strategies have been explored to enhance densification, including use of dopants, chromium deficiency, sintering aids and controlled atmospheres. This work reports the composite interconnects of LCC ($La_{0.8}Ca_{0.2}CrO_3$) and glass with improved densities. Phase stability, electrical and thermal properties of the composite interconnects were evaluated as a function of the glass content.

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FC17-Po

A stable bimetallic $Ru_xNb_{1-x}O_2$ catalyst for the anode side of Proton exchange membrane water electrolyzer (PEMWE).

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Noble metal based rutile type oxides such as IrO_2 and RuO_2 are found to be the best catalysts for the oxygen evolution reaction than any other metal oxides for polymer electrolyte membrane water electrolyzer. Since IrO_2 is expensive and RuO_2 has very low stability, most current research on PEMWE is focused on reducing the amount of noble metal in the catalyst and increasing the stability. Ruthenium was chosen as base metal and an efficient $Ru_xNb_{1-x}O_2$ bimetallic catalyst system has been developed and studied as potential oxygen evolution reaction (OER) catalyst. Niobium oxide is one of the stable transition metal oxides which are abundant in nature and less costly. A gradual replacement of Nb for Ru will increase the stability and reduce the noble metal content in the catalyst. Adams fusion method was used for the preparation of the catalyst. The structural and electrochemical studies of the catalysts have been examined using XRD, TEM, SEM, CV and EIS. Catalysts with various combination of niobium ranging from 0 to 100% have been studied. Electrochemical studies based on cyclic voltammetry and repetitive CV showed that electrochemically inactive Nb_2O_5 addition to RuO_2 increased the stability of the catalyst with slight compromise on the activity. Analysis using CV and charge calculation showed that $Ru_{0.8}Nb_{0.2}O_2$ have higher anodic charge and outer charge indicating a higher active surface area for this composition. The stability of the catalysts has been studied using repetitive cyclic voltammetry. Considering activity and stability, a 20% of Nb_2O_5 to RuO_2 ($Ru_{0.8}Nb_{0.2}O_2$) was found to be an optimum composition having good activity and better stability. The stability of this composition was found to be higher than RuO_2 catalyst prepared at same condition.

FC18-Po

High Temperature (HT) Polymer Electrolyte Membrane Fuel Cell (PEMFC) Stack Development for Automotive Vehicles

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Climate change is one of the most serious threats to our planet with an average planetary increase of 0.74 °C during the 20th Century according to the Intergovernmental Panel on Climate Change (IPCC) [1]. A big contributor to Green House Gas (GHG) emissions is the transport sector with ca. 800 million vehicles in use worldwide. This sector has a value chain in excess of 3 trillion USD per annum. One way of reducing emissions is through the use of hydrogen fuel cells (HFCs). HFCs are electrochemical devices that are able to produce electricity through the combination of hydrogen and oxygen, with the sole byproduct being water. HT-PEMFCs are high operating temperature (120°C – 200°C) PEM fuel cells that have recently received a lot of interest from car manufacturers for use in vehicles. There are several advantages to using a HT-PEMFC over its lower temperature variant including the fact that the overall cost of the fuel cell is reduced [2] as well as the increased resistance to impurities in the incoming fuel stream (Hydrogen) however there remain issues with increased degradation rates, durability and the long start up times (up to 1 hour).

The overall project aims to build and test a working HT-PEMFC stack for automotive applications (see Figure 2 [3]). This will involve the selection of low-cost/high-performing materials as well as the optimization of the stack design for use in a passenger vehicle, as well the as the optimization of the stack design for use in a passenger vehicle. This project will also involve the use of modeling packages, for example MATLAB, for the modeling of the fuel cell as well as the overall system (BOP). By the end of the project, a HT-PEMFC stack (up to 1kW) will be developed, constructed and commissioned which will be comparable or even better in durability, power output and size than commercially available HT-PEMFC stacks.

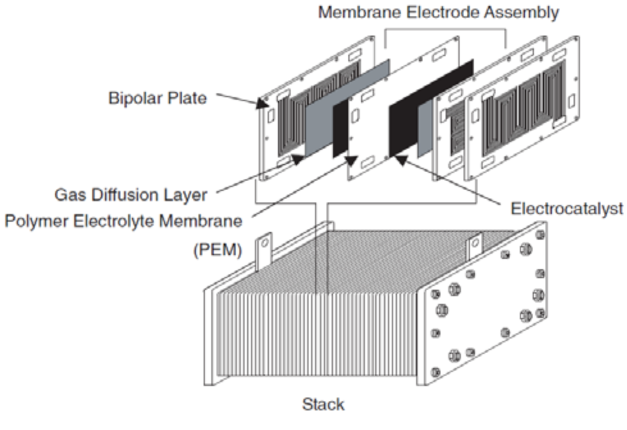

Figure 2: A PEMFC stack

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FC19-Po

Catalyst Development for the Alkaline Fuel Cell

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With the high cost and limited availability of platinum, much effort has gone into the reduction of catalyst loadings in fuel cell electrodes. Platinum is the most effective catalyst for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) in acidic polymer electrolyte fuel cells (PEM), but the vastly improved kinetics of the ORR in an alkaline medium opens up the possibility of utilizing cheaper catalysts for alkaline anion exchange membrane fuel cells (AAEM).

Rotating disk electrode (RDE) studies, along with *in situ* fuel cell testing, have shown a novel, high-efficiency low cost catalyst to have activation properties matching that of Pt, when used in alkaline conditions. The performance in an AAEM also matches that of Pt in the acidic PEM environment, suggesting a potential route for future reduction of cost and precious metal use in fuel cell electrodes.

FC20-Po
An optimized glucose oxidase (GOD) electrode exhibiting direct electron transfer

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The direct electron transfer (DET) of enzymes employed in bio–devices has gained recent worldwide attention [1]; most studies use carbon nanotubes, which have been shown to promote the DET of glucose oxidase (GOD) and thus improving the performance of the resulting bio–devices [2, 3]. The immobilization of the enzyme is essential for improved bio–electrode performances and stability. The use of natural (biocompatible) polymers such as cellulose [2] for enzyme immobilisation onto electrode surfaces offers cheap and simple electrode preparation.

A glucose oxidase (GOD) bio–electrode exhibiting highly responsive direct electron transfer (DET) has been prepared. Oxidised multi–walled carbon nanotubes (MWCNT) were applied directly to a glassy carbon electrode surface to facilitate GOD adsorption and DET, followed by the addition of a MWCNT–embedded cellulose matrix to improve the response and stability of the bio–electrode. A pair of clearly defined, high intensity redox peaks was observed **(Figure 1)** and the bio–electrode showed clear electrochemical response to both glucose and oxygen.

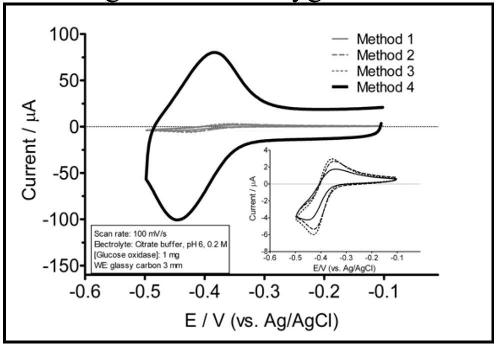

Figure 1. Cyclic-voltammograms of different glucose oxidase bio-electrodes

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FC21-Po

Novel Nanocatalysts, Electrodes and MEA Structures Employing Ti-meshes for Direct Alcohol Fuel Cell Applications

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The liquid feed direct methanol/ethanol fuel cell (DMFC/DEFC) is regarded as a potential power source for portable, stationary and transportation applications because of characteristics such as simple construction, easy operation, high efficiency and the existence of the extensive and effective network to deliver liquid fuels. However, obstacles still prevent their widespread commercial applications, e.g. low activity of methanol/ethanol electro- oxidation catalysts, fuels crossover from the anode to the cathode, carbon dioxide gas management, and water management. To date, the electrodes for DMFC/DEFC have been developed mostly on the basis of the gas diffusion electrodes employed in proton exchange membrane fuel cells. Typically, the structure of such electrodes comprises a catalyst layer and a diffusion layer, the latter being carbon cloth or carbon paper. However, unlike other fuel cells, the liquid feed DMFC/DEFC suffers from mass transport limitations predominantly at the anode due to the low diffusion coefficient of methanol/ethanol in water and the release of carbon dioxide gas bubble. A methanol concentration gradient exists within the thickness of the catalyst layer, which results in a poor utilization of the catalyst. In addition, a methanol diffusion limiting current is found in DMFC with the low concentration methanol solution, which prevents to get high power density. Therefore, the conventional anode structure based on the gas diffusion electrodes employed in proton exchange membrane fuel cells is not idea for the transport of the methanol and carbon dioxide. In addition, carbon paper is fragile and expensive and carbon cloth is soft compared with metal material, such materials are not as versatile as metals.

Here we report a novel nano-catalyst and anode structure prepared by thermal decomposition and electrochemical deposition of the corresponding metal chloride solutions on titanium mesh and tungsten carbide substrates for both DMFC and DEFC applications. In this structure, a fine Ti mesh, which is benefit of the methanol/ethanol transfer and carbon dioxide removal, is used as a substitute for the conventional gas diffusion layer in the anode. Optimal PtRu and PtSn nanostructure catalysts have been identified for the DMFC and DEFC anodes, respectively. The preparation procedures and the main characteristics of these anodes studied by SEM, EDX, *in-situ* FTIR spectroscopy, half cell and single cell tests will be reported, and the possible reaction mechanism discussed.

FC22-Po

Attachment of redox-active Ru complexes to gold surfaces

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We describe a method of attaching $[Cp^*RuCl_2]_2$ derivatives to gold surfaces using dithiocarbamate bridging ligands. The method lends itself to producing not only redox active monolayers but also additional multilayers on top. We also describe theoretical calculations on the interaction of Ru complexes with gold surfaces.[1]

[1] A. Gibson, B. Morton-Fernandez, J. A. Crayston, M. Buehl and J. D. Woollins, manuscript in preparation.

FC23-Po

Atomic Design of Nanoalloy Electrocatalysts

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Currently, hydrogen fuel cell technology based on Pt catalysts is considered as the most viable and promising route to green and efficient energy production in key areas such as transportation. However, its widespread commercial use is still hindered by limited performance, poor stability and the high cost of noble metal catalysts.

Bimetallic nanostructures represent a possible route to modifying the electronic and geometric properties of the catalyst, while lowering the noble metal content. A powerful method for achieving this growth control is known as the Surface Limited Redox Replacement Method (SLRR), also known as Galvanic Displacement [1]. The SLRR method has so far been successfully applied to the deposition of Pt overlayers on Au, using a Cu [1] or Pb [2] UPD layer as a sacrificial template.

In this work we will show the extension and optimization of this method to Au/Pt nanoalloy overlayers on Au. A schematic illustration of SLRR method is presented in Figure 1. Au – Pt has been shown to be a promising system for catalysing various reactions relevant to fuel cells [3, 4]. Here we will present the electrochemical, STM, EDX and X-ray diffraction characterisation of deposited alloys. We will discuss the observed trends in the catalytic reactivity dependent on Pt – Au composition.

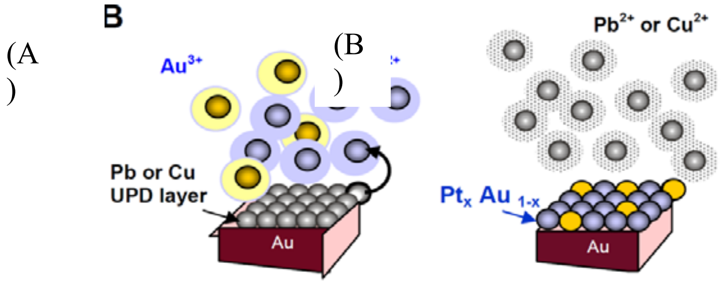

Figure 1. *Schematic drawing of the Surface Limited Redox Replacement (SLRR) process for Pt - Au alloy deposition. There are two well decoupled steps: (A) deposition of a sacrificial UPD layer under potential control followed by (B) galvanic replacement of the UPD layer by more noble metals.*

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FC24-Po

Electrocatalytic Activity of a Novel, Low-cost, High Efficiency Fuel Cell Catalyst

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A key factor inhibiting large scale fuel cell commercialisation is the high cost of the materials used. Electrocatalysts typically make use of very expensive metal particles; for example, platinum supported on high surface area substrate. In recent years, researchers have been focusing on developing catalysts with less noble material content and/or more efficient use of the existing metal catalyst content. However, lack of well-defined activity benchmarks and measurement methodologies for non-platinum catalysts lead to variation in the activities reported in literature, often by one order of magnitude[1].

We have developed novel, low cost and highly active catalysts for polymer electrolyte membrane fuel cells (PEMFCs) which have the potential to replace Pt. The catalysts were pre-screened prior to full lab-scale fuel cell testing. The screening criteria of interest are the electrochemical surface area (ECSA) and the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) kinetics. Using robust measurement methods, we have quantified the electrocatalytic property of *state-of-the-art* Pt/C catalysts and used this as a benchmark for our new catalyst materials.

[1] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, Applied *Catalysis B: Environmental*, **2005,** *56,* 9-35

FC25-Po

Electrochemical Characterization of Ruthenium modified Platinum surfaces

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Electrochemical and forced deposition methods were previously employed to decorate Pt surface to find better model surfaces for enhanced electrocatalytic activity. Here, we report the preparation of Ru quasi single surfaces on Pt electrode surfaces using a simple method developed by Attard and coworkers [1]. This method involves forced deposition of Ru under reductive condition on Pt surface followed by resistive heating in inert environment. Surface characterization of these surfaces were performed using copper under potential deposition [2]. However, fundamental studies related to surface structure properties are very rare [3]. To explore the surface structure properties, we have extended above mentioned process, initially designed for bead crystals to the large disk electrodes. The surface structure analysis of Ru quasi single crystal deposited on Pt(111) substrate was carried out using cyclic voltammetry and *in situ* scanning tunnelling microscopy (STM). An overlaid cyclic voltammogram for clean (red solid line) and Ru modified Pt(111) surface (black solid line) in 0.1 M H_2SO_4 is shown in figure 1. STM images for Ru modified Pt(111) surface will be presented.

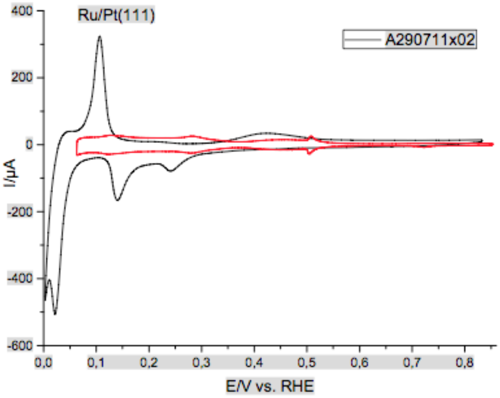

Figure 1: An overlaid cyclic voltammogram for a clean (red solid line) and a Ru deposited Pt(111) surface in 0.1M H_2SO_4, $\upsilon = 50$ mV/s

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International Year of Chemistry / Sensors for Africa Symposium

SA1K

Developing the Cotton-Mouton Effect as a Replacement for Antigen Detecting RDT's in the Diagnosis of Malaria

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Up to 50% of the world's population is estimated to be at risk of exposure to malaria but its rapid and accurate diagnosis in locations remote from clinical laboratory facilities remains problematic. Although increasingly relied on the performance of antigen detecting rapid diagnostic test (RDT) sticks under the non-ideal conditions and circumstances prevailing in remote locations is known to be unsatisfactory. Studies by the WHO found wide variability in the performance of these devices especially for parasite densities below about 200 parasites/μl [1]. Detection rates were dramatically reduced to less than 75% in more than half the types of device tested with some products returning values as low as 25%. Moreover, in the worst case scenarios only 60% of health workers conducted the test with sufficient rigor to obtain the correct result and even the briefest exposure to temperatures much higher than 30$_{o}$C, such as easily encountered during transport were found associated with significantly degraded performance. A less environmentally sensitive and more user friendly diagnostic test is urgently required for use in most circumstances where need is greatest. Over the past five years a reagent free test based on a magneto-optics has demonstrated the potential to meet this need [2]. Its diagnostic principle uses measurement of the Extraordinary Cotton-Mouton effect to perform a quantitative volumetric assay of the haemozoin produced by the malaria parasite as it metabolises haemoglobin. Under early blind clinical evaluation both in Kenya and the laboratory, prototype instrumentation operating on this principle attained performance levels for sensitivity and specificity of 78.5% and 72.6% respectively [3]. The newly developed handheld version of the technology shown has achieved a detection sensitivity ≈ 20 Plasmodium falciparum parasitized red blood cells per microlitre (PRBCs/μl) using samples created by the serial dilution of a malaria culture with fresh blood.

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SA2K

Microfabricated Chemically Sensitive Impedimetric Detectors for Low Cost Quantitative Lateral Flow Diagnostics

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Two issues plague successful development and deployment of Lateral Flow Devices (LFDs) as anything but non-quantitative, screening tests. LFDs suffer from poor coefficient of variation arising from poor reproducibility of the flow patterns of inexpensively available and abundant membrane materials that are widely used in their construction. LFDs also suffer from non quantitative detection modalities (colorimetry, reflectometry, etc.), that greatly limit their use in quantitative confirmatory bioassays. We address these two issues with the development and deployment of controlled geometry membranes with reproducible flow patterns and with the use of microfabricated chemically sensitive impedimetric detectors for enzyme and enzyme-immunoassays. Together these innovations have the potential to realize a quantifiable, low cost lateral flow platform suitable for deployment in resource poor regions.

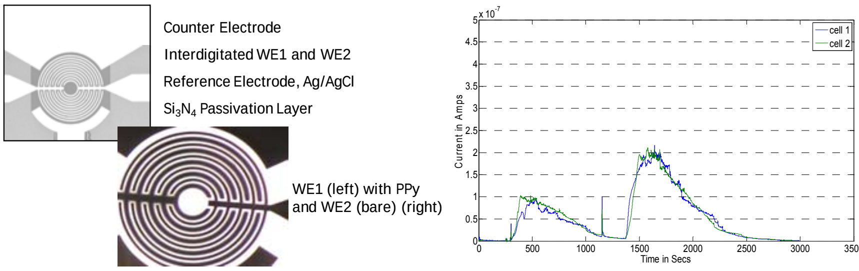

Figure 1. A) Optical micrographs (x50) showing one channel (cell 1) of the dual channel microfabricated electrochemical cell-on-a-chip interdigitated microsensor electrode (ECC IME) device. *Left*: The various electrodes of the individual cell, and *Right*: C1W1 with electropolymerized polypyrrole (PPy) with immobilized bioreceptor while C1W2 serves as an opposing driving electrode[1]. B) Electrochemical response of the dual channel detector to a redox challenge of 1 mM FcCOOH.

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SA3

The use of exfoliated graphite electrodes for detection of organic and inorganic pollutants

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One of the main challenges facing the analytical chemist is the development of methods that respond to the growing need to perform rapid analyses.[1] These methods must be sensitive ,accurate, and able to determine various substances with different properties in real-water samples.[2] Exfoliated graphite (EG) electrode is a promising carbon based electrode which is cheap and easy to fabricate. The electrode was characterized using $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ as a redox probe. The EG electrode has the right platform for modification with different nanomaterials. Poly(propyleneimine) dendrimer (PPI), CoO, Ag and Au nanoparticles have been used to successfully modify the EG electrode. This helps to increase the sensitivity of the electrode towards certain analytes. The anodic stripping of Pb, Cd and Cu were optimized and these heavy metal ions were found to behave differently in HNO_3 and KCl as electrolytes. Pb and Cu were best detected in HNO_3 while for Cd, KCl was the best electrolyte. Cd and Pb could be detected together when the two electrolytes were mixed (1:1, pH 5). The introduction of Cu suppressed the Pb and Cd response. The detection limits for Pb, Cd and Cu were 1 ppb, 8 ppb and 50 ppb respectively. The electrode also responded well to *o*-nitrophenol (*o*-NP), a model organic pollutant. Modification with PPI dendrimer gave higher response for the *o*-NP resulting in a lowered detection limit.

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SA4

Design of metalloporphyrin based micro sensors for technical applications and environmental monitoring

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Metalloporphyrins and other N_4-macrocyclic complexes akin to them are used as electrocatalysts for the oxidation and reduction of a wide range of molecules and compounds in electrochemistry. Examples of electrocatalytic reactions catalyzed by metalloporphyrins include electrooxidation of, nitric oxide, carbon monoxide, hydrazine, mercaptoethanol, oxalic acid among others, and the electroreduction of oxygen, carbon dioxide, nitrates ions, and cystine among others. Some of the molecules mentioned above are hazardous and their existence in the environment requires routine monitoring. However, wide commercialization of well known functional devices incorporating metalloporphyrins, such as sensors, still awaits the development and design of very active, robust and reliable devices. The mechanism of reactions eletrocatalyzed by metalloporphyrins involves an inner-sphere electron transfer step which precedes, succeeds or occurs simultaneously with an adsorption or desorption step of the electrocatalyzed substrate, its intermediates or the product(s). The strengths of the adsorption or desorption processes clearly influence the kinetics and mechanism of the overall reaction. However, the strengths of the adsorption or desorption processes depend on the nature of the central metal for a given N_4-macrocyclic ligand. Additionally, the strengths of the adsorption and desorption processes can also be varied by redesigning the ligand, for which a variety of strategies are feasible. In this presentation, the effect of variation of the central metal atom on the response of metalloporphyrin electrocatalyzed reactions will be discussed and demonstrated using the electrocatalytic reduction of oxygen, and the electrocatalytic oxidation of Nitric oxide. The dependency of the activity of these reactions on the central metal, for the first raw transition metals, will be graphically shown to yield a volcano shaped plot, whose description is in accordance with the Sabatier principle of heterogonous catalysis, which requires that, neither reactants, their intermediates nor the products should bind either too strongly or too weakly on a catalyst surface for optimal catalysis. This observation is satisfactorily explained using intermolecular hardness, based on the electrophilicity of the N_4-macrocyclic complex and corroborated by the frontier molecular orbital theory. Systematic criteria will be presented for the selection and design of microsensors for oxygen and nitric oxide as examples to illustrate the broad applicability of these principles.

SA5K

Mark Baird

SA6K

Diagnostics for the Developing World

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The UNICEF/UNDP/World Bank/WHO Special Programme for Research and Training in Tropical Diseases (TDR) is the leading UN- based organization dedicated to research on diseases of poverty. Infectious diseases continue to have a major impact on the developing world. One crucial factor is the lack of diagnostic tests that can be performed at low-infrastructure sites, which serve most of the global population. High-quality diagnostic tests are often unaffordable or inaccessible to patients in the developing world, while a lack of regulatory approval standards means that poor quality diagnostics are widely accessible and used. This leads to a high level of mortality and morbidity that could be prevented. The Diagnostics team within TDR has thus been focusing on (1) facilitating the development of diagnostics tools and methodologies for diseases such as Tuberculosis, Malaria, Dengue, Schistosomiasis, Leprosy and Visceral Leishmaniasis, (2) evaluating currently available diagnostics to assess if they meet the standards necessary for public health care; and (3) increasing access to appropriate diagnostics. The presentation will include a background on the need for diagnostics in the developing world, the currently available diagnostic tools and their limitations, the TDR diagnostics research activities, as well as discussion of other factors affecting the use of such tests, such as the lack of regulatory systems.

SA7

Impedimetric Response of a Label-Free Genosensor Prepared on a 3-Mercaptopropionic Acid Capped Gallium Selenide Nanocrystal Modified Gold Electrode

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Abstract

Biocompatible and water soluble 3-mercaptopropionic acid capped gallium selenide nanocrystals were synthesized from hydrated gallium (III) perchlorate and selenide ions. The nanocrystals were non-fluorescent but showed a sharp UV-vis absorption maximum at 260 nm. Transmission electron micrographs showed the formation of high quality non-aggregated particles with an average diameter of 65 nm. Gold electrode modified with the capped nanocrystals was used as a platform for impedimetric genosensing using NH2-5′-CCCACCGGTCCTTCATGTTC-3′ (probe) and 5′-GAACATGAAGGA CCGGTGGG-3′ (target) oligonucleotide sequences. The target oliginucleotide sequence is a component of 5-enolpyruvylshikimate-3-phosphate synthase, a common vector gene in glyphosate resistant transgenic plants. The impedimetric genosensor exhibited high sensitivity towards the target DNA (sensitivity = 11.61 Ω/nM) with a detection limit of 0.66 nM (3s, n = 8). The genosensor was able to discriminate between complementary, non-complementary and 3-base mismatched target sequences and maintained 87 % of its response towards the target DNA after one month.

Keywords: Gallium selenide, impedimetric genosensor, transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), 5-enolpyruvylshikimate-3-phosphate synthase (CP4 espsp).

SA8

Challenges imposed on phenolics monitoring during amperometric biosensor application - a case study using laccase biosensors

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Due to the variety of effects on both human and environmental health, the routine detection and monitoring of phenolic compounds *in situ* remains an elusive goal for several applications (pollution assessment [1], antioxidant assays in foodstuffs [2], etc).

Of the available detection technologies, electrochemical detection platforms are commonly cited as the most viable methods to address this need, often with the inclusion of biomolecules conjugated to the electrochemical transducer to enhance detection specificity (biosensors) [3]. For the purposes of phenolics monitoring, the most common biorecognition agents are the enzymes laccase and/or tyrosinase, which catalyse the oxidative formation of quinone species from dissolved phenolic compounds [4]. The cathodic reduction of these quinones drives the detection of phenolics under this paradigm [4].

However, despite the sustained and targeted research within this endeavor, no known commercially-available technologies using the aforementioned biosensors are available to date. This is due, in part, to two interrelated, analyte-dependent, problems limiting the application of the biosensor – signal variability between analytes [5], and the accumulation of phenolic/quinonic species at the transducer surface during biosensor application (fouling) [6].

Using current research surrounding the use of a laccase-based amperometric sensor configuration as a case study, these two sensor shortcomings will be discussed and a method relating these to biosensor performance via an electrochemical assessment prior to biosensor application will be proposed.

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SA9 - Discussion

Panel Discussion: Reality, challenges and future opportunities for sensors in Africa

Chair: Janice L Limson, Rhodes University, South Africa.

Panelists: Sandro Carrara, École Polytechnique Fédérale de Lausanne, Anthony Guiseppi-Elie, Clemson, USA, Francis Moussy, WHO, Switzerland, Kenneth Ozoemena, CSIR, South Africa

The clear need for sensors in several prospective markets globally continues to drive substantial research in the field of biosensors. The investment in pure research in biosensors has however not yet resulted in the large scale commercialization of such devices. In developing countries, with the largely decentralized nature of medical care, biosensors are predicted to play a substantial role in the health sector in areas such as infectious diseases.

Panel members in this discussion will consider the current reality of biosensors globally, the practical and technical challenges faced in the commercialization of biosensors, and finally the scope of biosensors for addressing Africa's sensing needs within the context of existing alternative analytical tools.

SA10-K
Nanotechnologies, Biomaterials, and CMOS Systems for Low-Cost Medical Diagnostics in Developing Countries

Sandro Carrara – EPFL Lausanne (CH)

The needs of such low-cost and multi-panel platforms in developing countries is also highlighted by the World Health Organization, which is highly interested to investigate new and very-cheap technologies to be used in countries, like India or Africa, by supporting research projects in this area of research. In these countries, low-cost technologies may enable patients for monitoring at the local hospital and/or doctors and, thus, avoiding trips of hundredth of kilometers to reach the closest larger cities for diagnostics.

Point-of-care and early diagnosis in patients with specific physiological conditions (e.g., virus infections, heart attack, cardiovascular diseases, and cancer diseases) or convalescents is a key factor to save Humans life in developing countries. Additionally, the development of new technologies in personalized therapy is required to increase the fraction of patients that can benefit from pharmacological treatments. For many of the major pathologies, the average rate of efficacy of drug therapies ranges from 20 to 60%. Moreover, approximately 7% of hospitalized patients experience serious adverse drug reactions. For this reason, a check on drug therapies is needed for personalization to the individual patient, while multi-panel technologies are definitely required to simultaneously address field screenings on pour populations that have not access to large hospitals and medical infrastructures.

So far, there are no available low-cost platform systems for multi-panel point-of-care monitoring of diagnostic markers and drugs in blood and/or saliva and/or urine. The only multi-target technologies present in the market of industrialized countries are costly, bulky, and high energy demanding. In developing countries, we need of very cheap, easily transportable and, some time, batteries driven devices.

Therefore, the main objective of this key-note speech is to present new developments toward low-cost and portable devices [1], with proper Nano-Bio interfaces [2,3], realized by using Proteins and Carbon Nanotubes [4], for applications in Multiple Drugs-&-Markers Detection. Some examples on Virus Detection [5,6], Human Metabolism control at molecular level [7], and Drugs Monitoring [8] in blood will be used as clear examples of the fields of application of such novel and low-cost Nano-Bio-CMOS technology.

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SA11K

Biomolecular Interactions Sensed on Multilayer-Modified Silicon

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Electrochemical Impedance Spectroscopy (EIS) has been used to study in great detail both (1) the adsorption of alternating polycations and polyanions in succession to form stable polyelectrolyte multilayers (PEM) and (2) the selective antibody-antigen interactions on a thin oxide layer of doped silicon semiconductors (Figure 1). The change of the system capacitance under depletion conditions, which is largely dominated by changes in the space charge region of the semiconductor, was found to be highly sensitive for the charge of the last added polyelectrolyte and for the number of deposited layers. Both n- and p-type doped silicon substrates have been investigated. It was observed that the change of capacitance was opposite between both type of dopants upon adsorption of polycations or polycations. This behavior can be readily understood in terms of changes in the number of majority charge carriers in the space charge region and the width of this region. Adsorption of single-stranded DNA molecules, which has a negatively charged back bone, shows similar behavior compared to the adsorption of a synthetic polyanion.

We have also shown that this method is very well applicable to detect antigen-antibody interactions, which occur near the silicon-silicon oxide interface, with a high selectivity and sensitivity of antigen concentrations in the picomolar concentration regime.

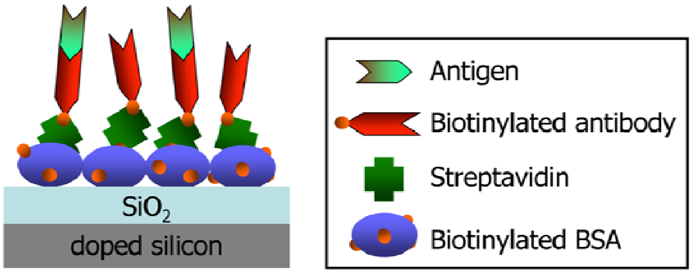

Figure 1. Schematic representation of selective antibody-antigen interactions on a thin silicon oxide layer.

SA12

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Research on chemically-modified electrodes (CMEs) has continued to dominateconstitute the main analytical devices in electroanalytical chemistry. The analytical performance of any CME is dependent amongst others, on the modification strategy and the redox-activity of the modifying species. One of the main research activities in my group has been the search for smart strategies of electrode-immobilisation protocols for redox-active and redox-silent nanostructures that could potentially be used in the sensitive and selective electroanalytical detection of various analytes that are important to health and the environment [1-5]. Some of the strategies that we adopt include the self-assemblying and drop-casting [1-4].

In this presentation, the physico-chemical properties of various CMEs will be discussed. The electrochemical properties (using various techniques including electrochemical impedance spectroscopy) of these CMEs for developing efficient electrochemical sensors will be presented.

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SA13

Accounting for Variability in Current Responses as a Factor of Electrode Surface Characteristics

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The generation of reproducibly stable electroanalytical responses is an obvious prerequisite for accuracy in electrochemical measurements. Attaining stability in voltammetric peak current responses (I_p) is however influenced by a number of interconnected factors and parameters. Variations in I_p, particularly for adsorptive analytes, as a result of variation in electrode surface condition across repeated analyses have been widely demonstrated. Within the confine of the electrode-analyte interface and assuming a uniform solution, stability in I_p is dependent on either chemically and geometrically uniform electrode surfaces, or the ability to account for minor variations in electrode surface condition, and thus the influences those variations have on resulting current responses. This trait is emphasized with the application of carbonaceous electrodes as their surface condition has been well documented as being spatially and compositionally non-homogenous.

The electric double layer is an interfacial region which forms between an electrode surface and the solution it is immersed in as a cumulative result of attractive and repulsive forces of charged molecules. The properties of the double layer are important as they have a significant effect on electrochemical measurements, and importantly arise as a factor of the electrode material, condition and state, the components and condition of the solvent or solution, the extent of adsorption of ions or molecules and the electrochemical parameters imparted on the system. In so doing, the extent of the double layer charging is variable according to the interaction of the electrode-analyte interface, and is the interaction which forms a focus of this research.

In this presentation we report on a means of accounting for variability in current responses as a result of variable carbonaceous electrode surface conditions, and provide a means of normalizing those responses such that they are analytically stable. We show this through the application of double layer capacitance (C_{dl}) as a global means of assessing the activity of an electrode, and through applying that to the resulting current response allow for the normalization of responses to analytically accurate levels. Importantly, the ability to account for variability in I_p through application of C_{dl} is shown from a voltammetric scan, allowing for this to be an extremely simple and effective technique. Furthermore we demonstrate that the applicability of using C_{dl} as a mediator across structurally and compositionally diverse electrode surfaces as well as structurally and compositionally distinct analytes.

SA14

Monolayer-Protected Gold Nanoparticles Self-Assembled Networks as Platforms for Probing the Electron Transfer Dynamics

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The rapid and vast progress of new nanomaterials are making it possible to develop electrochemical sensors with increased sensitivity that can be extensively applied to a wide variety of analytical problems including clinical, medicinal, drug discovery, food and environmental areas. These sensing devices are based on the electron transfer between the analyte and the modified electrode [1-3]. Monolayer-protected clusters of gold nanoparticles (MPCAuNPs) have emerged as excellent redox mediator species [4]. Most MPCAuNPs are insoluble in water; thus, for electro-bioanalytical applications, it is essential to develop MPCAuNP systems that are stable, water-soluble, and capable of molecular recognition in aqueous media [5]. In this work, novel MPCAuNPs were prepared by varying the ratio of their two different stabilizing ligands: (1-sulfanylundec-11-yl)poly(ethylene glycol)ic acid (PEG-COOH) and (1-sulfanylundec-11-yl)tetraethylene glycol (PEG-OH). The MPCAuNPs were self-assembled on a gold electrode to investigate their (i) electron transfer (ii) surface ionization properties, and (iii) electrocatalytic recognition properties towards the detection of epinephrine and ascorbic acid. The extent to which these mixtures of protecting ligands influence the electron transport and ionization of the surface-exposed functional groups of the protecting ligands is crucial for the potential applications of such platforms in areas, such as chemical and biological sensing. Atomic force microscopy, cyclic voltammetry and electrochemical impedance spectroscopy are electrode characterization techniques used to determine the surface morphology, stability and rate of electron transfer, respectively.

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SA15-Po
Solar UV Photooxidation as Pretreatment for Stripping Voltammetric Trace Metal Analysis in River Water

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We report on a new approach how to perform UV sample pretreatment of river water samples using solar UV-A radiation. Water samples were collected from River Warnow and acidified to pH 2 with ultrapure HNO_3. Hydrogen peroxide was added to the samples as a photochemical reaction initiator. The samples were transferred to PET bottles and irradiated with solar UV-A (3.6 mW/m^2) for at least 6 hours. The concentrations of Zn, Cd, Pb, and Cu were determined by differential pulse anodic stripping-voltammetry. The comparison of the values with the results obtained for the original untreated sample and the artificial UV treated one proved that solar UV radiation can be applied to the digestion of dissolved organic carbon in trace metal analysis in natural waters like river water, lake waters, well waters etc. [1].

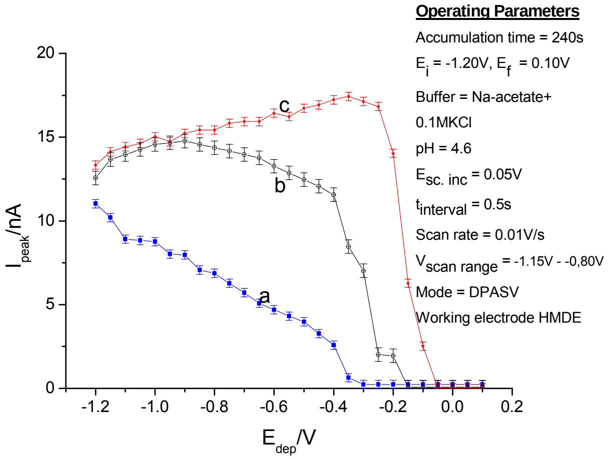

Figure 1. Pseudopolarograms of 10 ppb copper in a) *original Sample*, b) *solar-UV Sample* and c) *artificial-UV Sample.* [1].

An even larger effect of both UV treatment methods was observed in case of adsorptive stripping voltammetric determination of Ni, Co, and U. These analytes could not at all be measured without any UV treatment due to the surfactant components in the river water. Solar UV-A was as effective as artificial 254 nm UV from a 30 W lamp.

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Fundamental Electrochemistry Symposium

F1 K

What density functional based molecular dynamics can tell us about condensed phase electron transfer reactions

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With the advance of density functional based (or `ab-initio’) molecular dynamics (DFMD) simulation in the last decade, it has become possible to simulate condensed phase redox and electron transfer reactions at an unprecedented level of detail. The approach adopted differs from the standard solute + continuum model of the quantum chemist in the sense that both solute and solvent are treated at the same DFT level of theory. The advantages are obvious: there are no empirical and adjustable solute radii and dielectric constants any more, finite temperature fluctuations of the solute and the solvent are treated rigorously, and fast ligand exchange with the solvent can in principle be observed. But there remain certain challenges: GGA and hybrid density functionals are sometimes not accurate enough to describe adequately the ionic and electronic structure of open shell systems, redox properties are in general sensitive to the still small system sizes that we can treat for long enough times, and the periodic boundary conditions introduce additional complications when we are to compare to experimental redox properties.

In this talk I will briefly describe the theory underlying our computational approach to redox chemistry[11 and electron transfer [2], and discuss certain applications in more detail. In particular, I will report on the unique opportunity of DFMD in probing linear and non-linear solvent fluctuations in solutions of transition metal ions, and how nonlinear fluctuations can lead to a break-down of the Marcus picture of oxidation and electron transfer reactions[3]. I will also explain how DFMD simulation can be used to compute essential electron transfer parameter and interpret energy resolved photoemission spectra of redox active transition metal compounds[4]. Finally, leaving the aqueous milieu, I will present first results of a DFT-based scheme for the calculation of electron mobilities in organic solar cell materials [5].

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F2

An experimental comparison of the Marcus-Hush and Butler-Volmer descriptions of electrode kinetics. The one-electron oxidation of 9,10-diphenylanthracene and one-electron reduction of 2-nitropropane studied at high-speed channel microband electrodes

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We present an experimental comparative evaluation of the Marcus-Hush (MH) and Butler- Volmer (BV) kinetic formalisms. Numerical simulations using both kinetic models are used to fit experimental voltammetry of the one electron oxidation of 9,10-diphenylanthracene (DPA) and the one electron reduction of 2-nitropropane (NP) at a high speed channel microband electrode. For DPA the Butler-Volmer and Marcus-Hush formalisms yield indistinguishable fits, as expected for a system with fast electrode kinetics. For the BV formalism best fits were obtained using k_0 = 0.83 cm s^{-1} and α = 0.49, for MH the best fit parameters were k_0 = 0.85 cm s^{-1} and l = 0.58 eV. For NP neither Butler-Volmer nor Marcus-Hush models are able to obtain very accurate fits to experiment, although it was possible for the Butler-Volmer model to yield more accurate fits if the transfer coefficients, a and b , are not required to sum to unity, which is possibly justifiable due to the very large difference between oxidative and reductive peak potentials. The best fit obtained using MH kinetics used $k_0 = 7.0\times10^{-6}$ cm s^{-1} and λ = 1.0 eV, while BV kinetics was able to fit using $k_0 = 9.5\times10^{-4}$ cm s^{-1} and $\alpha = \beta = 0.24$.

F3
The Role of Charge Fluctuations in Electron Transfer.

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Electron transfer is the principal step in all electrochemical processes. It also plays a crucial role in many biochemical processes, such as photosynthesis, respiration, and nitrogen fixation. Indeed, more than 10% of the structurally-characterized proteins in the Protein Data Bank are redox proteins, i.e. proteins that participate in, or catalyze, electron transfer. In environmental science, electron transfer is fundamental to the chemistry of the world's oceans, and to the dispersal and remediation of toxic metals in soil and groundwater. Finally, electron transfer is central to the emerging new area of molecular electronics.

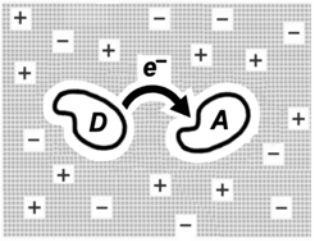

Figure 1. Electron transfer from a donor D to an acceptor A in an electrolyte solution.

In this talk, the presenter will summarize recent progress in the theory of electron transfer driven by charge fluctuations [1-4]. Similarities and differences with the Marcus theory of dielectric fluctuations will be noted. Finally, some possible directions for future work will be indicated.

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F4

Charge Transfer Mediated by Two-Dimensional Assemblies of Quantum Dots

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Interactions between nanostructures and electrode surfaces can lead to enhancement of charge transfer kinetics from the electrode to a redox species in solution. These processes can play an important role in the development of electrochemical solar cells and sensing devices. Recent works have shown that the well-established attenuation of electron transfer tunneling across insulating self-assembled molecular bridges [1] is significantly affected by the presence of metallic nanostructures [2-4] and carbon nanotubes [5]. In this contribution, we shall demonstrate that these phenomena are uniquely linked to changes in the density of states (DOS) at the redox Fermi energy introduced by the nanoparticle assembly. We contrast the behavior of 2D arrays of CdSe and CdTe quantum dots assembled at thiol modified Au electrodes.

Electrochemical and spectroscopic studies in the absence of redox species provide key information on the band edge positions as a function of size and surface termination of the nanostructures. In the case of II-VI quantum dots, the dependence of the electrochemical response on the average particle size is rationalized employing *Tight Binding* modeling [6]. The dynamics of charge transfer involving the ferricyanide/ferrocyanide redox couple across Au electrodes blocked by 11-mercaptoundecanoic acid were investigated as a function of the nanoparticle size, composition and surface termination. We provide clear evidence that the overlap between the DOS of the valence band of the nanostructures and the redox Fermi energy determines the average exchange current density of the assemblies. We shall also demonstrate that charge transfer can be mediated not only by band edges but also by *surface states* at the quantum dots. A semi-quantitative analysis of these experimental trends is presented on the basis of the *Gerischer formalism* for electron transfer [7,8].

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F5K

Electrochemistry and nanophotonics

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Once upon a time, physicists called electrochemistry a "surface science with a joy stick" (Ben Ocko). The stick is the potentiostat which allows to control voltage within a volt or sub-volt range, all localized in a nanometer thick double layer, thus causing high electric field there. For decades electrochemists were not only studing the effects of such fields on electrochemical reactions, but were also investigating the electric-field controlled self-assembly of various species on electrodes, from ions and molecules to macromolecules and colloid particles.

There was recently an increased interest in utilizing this capacity of electrochemical systems for building various electro-tuneable optical devices, in particular those based on manipulations of self-assembly of nanoparticles. Once recently launched area of this kind is electrovariable nanoplasmonics [1], where varying the electric field in the double layer can change a population of plasmon-active metallic nanoparticles at the solid-liquid or liquid-liquid electrochemical interfaces. Such manipulation could, in principle, allow to convert this interface from a mirror-like reflector of light to full transparency, opening a road for electro-tuneable, 1-Volt-controlled, smart windows. Another application is mirrors with variable shape, based on the electrowetting effect with the interface of two immiscible electrolytic solutions [2]. Electrovariable nanoplasmonics will also help to create SERS sensors or optical filters of various kinds. Manipulation with localization at electrochemical interfaces of nanoparticles of another kind, such as quantum dots [3] or magnetic nanoparticles, may also be of interest.

The main advantages of these systems are the (i) self-assembly and (ii) ability to control and fine-tune the structure of the nanoparticle layers, which is not available in solid state devices. But there is yet no blue sky in this challenging new research area: the road from the main principles to devices will not be easy. I will overview the main principles behind this new area, predictions of the theory, first experimental achievements, obstacles, and the ideas of the most perspective practical applications.

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F6K

Electronic communication through small and large molecules.

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Electronic communication inside molecular systems is very complex since nuclear motions affect electronic levels and thus the final efficiency of the device. In this field electrochemistry has proven to be relevant to estimate the rate of electron transfer from the redox center towards an electrode. For practical applications, there is a need for a fast signal transduction. However, this raises the difficulty of finding a method with an adapted temporal resolution. We rely on ultrafast voltammetry for this purpose, and several examples will be depicted. A first category will be molecular wires adsorbed onto electrodes. Here, a single electron is transferred per molecule. Larger systems such as dendrimers bear a multiplicity of redox centers, some of them beeing too far from the electrode to allow a direct communication. However a redox reaction can still occur by electron hopping between neighbouring entities.

Alternatively, communication through molecules may be evaluated by trapping a single molecule between the electrode and a STM tip. Here, a steady state current is measured so as to deduce a conductance. Onto identical systems, we performed both ultrafast CV and conductance measurements. Experiments revealed that surprisingly electronic coupling is slightly stronger in conductance measurements whereas electron transfer occurs over a distance approximately double, emphasizing the need for several approaches to evaluate electronic communication.

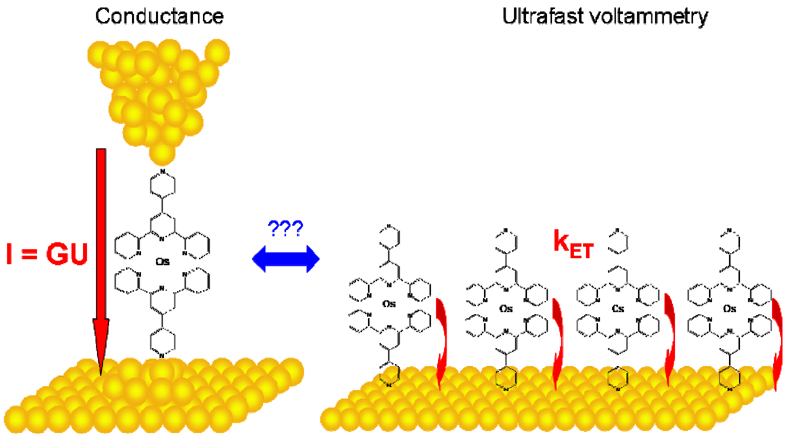

Figure 1. Conductance and ultrafast CV measurements onto an adsorbed osmium complex.

F7

Long-time chronoamperometry at an inlaid disc electrode

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Inlaid disc electrodes are widely used in voltammetry, in particular ultra- microelectrodes, [1], which have the ability to probe faster kinetics, along with the advantages of reduced double-layer capacitance and ohmic drop. Existing analytical expressions for the long-time chronoamperometric current response at an inlaid disc electrode are restricted to reversible/diffusion-limited reactions, [2, 3], with identical diffusion coefficients assumed for the redox couple. Here we derive a novel analytical expression for the long-time chronoamperometric current response produced by a quasi-reversible reaction at the electrode, which allows for non-identical diffusion coefficients. This extends the applicability of this technique to a much wider range of redox species and kinetic regimes. In Figure 1, we show that the analytical formula (dashed lines) agrees with numerical solutions (solid lines) calculated using the method in [4]. Differences in the diffusion coefficients of the redox couple can change the transient behavior, as also shown in Figure 1, and deductions from experiments must ensure that they account for these effects, cf. the recent work of Wang et al., [5], on the non-identical diffusion coefficients of the hexaammineruthenium III/II redox couple.

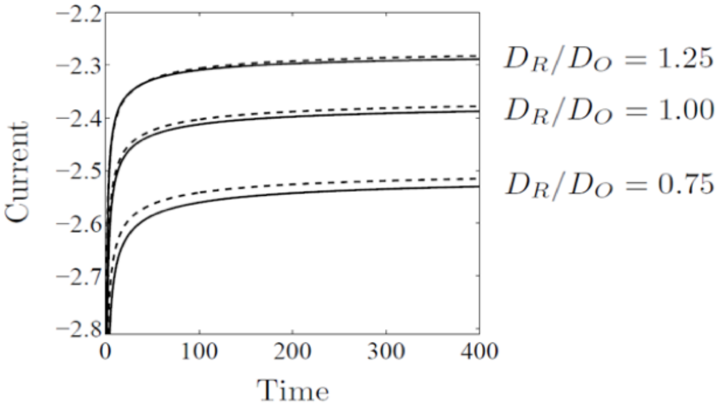

Figure 1. Long-time chronoamperometric current responses for a non-diffusion-limited quasi-reversible reaction at an inlaid disc electrode for different ratios of diff- usion coefficients, D_R/D_O. The axes are in non-dimensional units.

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F8

Electrochemical and Spectroscopic Studies of Phospholipid Bilayers Supported on Au(111) Surfaces

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The structure of phospholipid bilayers supported on surfaces is of widespread interest because they provide a natural environment for the immobilisation of proteins (such as membrane functional proteins, hormone and antibody receptors) on solid surfaces. This allows both the study of the function of proteins and the functionalisation of solids to produce sensing devices based on electrical or optical detection of ligand binding.[1] To investigate these fully, it is necessary first to study the supporting matrix; *i.e.*, the lipid bilayers.

Electrochemical studies of supported lipid bilayers provide a means to compare the degree of packing and solvent content of different compositions of lipid. More importantly, they also allow the application of an electric field across the lipid film comparable in magnitude to those found in naturally occurring biological cell membranes, typically ~10^7-10^8 V m^{-1}.[2] This is of particular importance because the field can be tuned in a continuous fashion, facilitating the study of the response of the membrane structure to a range of field strengths that could be experienced in a biological cell. By employing a Au electrode as a solid support for a lipid bilayer, it is possible to study the influence of the applied electric field on the structure and organisation of the lipid film at the molecular level using *in situ* spectroscopic and imaging techniques.[2]

We present a study of the effect of molecular structure on the ensemble properties of lipid bilayers on Au(111) electrodes. We compare three types of phospholipid with common acyl chains but different headgroups: dimyristoylphosphatidylserine (DMPS), dimyristoylphosphatidylethanolamine (DMPE) and dimyristoylphosphatidylcholine (DMPC). DMPE and DMPC are zwitterionic whereas DMPS is anionic. The supported bilayers have been studied with differential capacitance, chronocoulometry and *in situ* polarisation-modulated infrared reflection absorption spectroscopy. DMPE bilayers contain less solvent than DMPC and DMPS bilayers and are more tightly packed, with a hydrocarbon chain orientation less tilted from the surface normal than that of DMPC. Mixtures of these lipids display properties resembling those of the zwitterionic lipid when the DMPS concentration is below *ca.* 30%.

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F9K

Single Molecule Electrical Measurements

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Methods for forming stable molecular wires between a gold surface and a gold STM tip in both ambient conditions and under electrochemical control will be discussed and compared in this presentation. The resulting single molecule conductance (SMC) values for a variety of molecular wires, including more complex molecules with electrochemically active groups will be discussed. The versatility of the techniques is demonstrated on a variety of molecules including electrochemically active molecular wires.

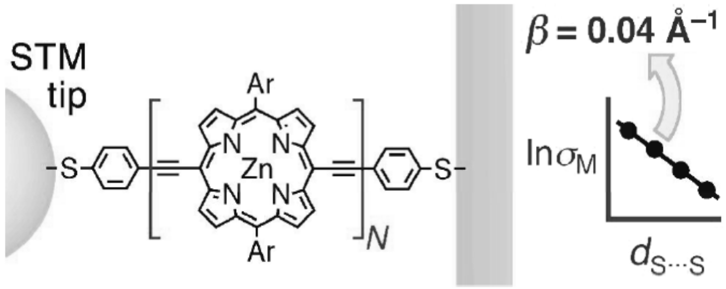

Figure 1. Highly transmissive porphyrin molecular wires.

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F10K

Probing and Imaging Interfacial Fluxes with Electrochemistry

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Interfacial physicochemical processes typically involve an exchange of material at phase boundaries, such that the boundaries are chemically ***in flux.*** Understanding and optimising processes involving interfacial fluxes underpins some of the most important current scientific and technological challenges, including, for example: energy conversion and utilisation, via improved surface catalysts; the development of new generations of molecular sensors, with improved sensitivity and selectivity; understanding cell function; and understanding the geophysical processes around us.

To achieve an understanding of interfacial processes, one needs to know the local flux; what controls it; and how the flux is related to the structure/properties of a surface or interface. While advances in high resolution microscopy and structural methods have provided detailed views of the structure/properties of a wide range of surfaces and interfaces, it has been difficult to obtain accurate (and high resolution) information of associated chemical fluxes.

Voltammetric-amperometric methods naturally provide a direct measure of electrode reaction rates (fluxes). This contribution will assess how electrochemical techniques and principles can be translated to other areas of science to provide new views of interfacial processes, mechanisms and kinetics. A range of approaches will be assessed, from hydrodynamic methods to high resolution electrochemical (1-4) and chemical (5) imaging, and the type of information that can be obtained will be illustrated with studies of crystal dissolution, membrane transport and biophysical processes.

We are grateful to the European Research Council, EU, EPSRC-MOAC Doctoral Training Centre, NPL, Syngenta, GSK and the Advantage West Midlands Science Cities programme for support.

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F11

Redox Reactions of Ferri/Ferrocyanide on Gold Nanoparticle-Modified Electrodes Prepared with Paper Supports

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In a previous paper [1], we reported a new trial to modify electrodes surfaces with gold nanoparticles (AuNPs) using paper support. By using Kimwipes as a paper material, AuNPs could be attached and grown using a seed-mediated growth method and modified in the vicinity of a base glassy carbon (GC) electrode. As the result, interesting promotion of the redox reaction of ferri/ferrocyanide could be observed with the AuNP-modified Kimwipe attached GC electrode [1]. However, as an unfavorable phenomenon, small strange redox peaks were observed overlapping the normal redox peaks of ferri/ferrocyanide in the electrochemical responses. Since we are now trying to make clear the reasons of the appearance of the strange peaks, some details of the redox reactions of ferri/ferrocyanide on the AuNP-modified Kimwipe attached electrodes will be presented.

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F12
Salt Matrix Voltammetry

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The triple phase interface between electrode | ammonium chloride salt crystal | gas is investigated. It is shown that through microscopic contacts between the salt crystals and the electrode it is possible to carry out voltammetry and electroanalysis. Humidity plays an important role in this process due to the existence of a thin layer of water on the salt crystals therefore allowing a current to pass. The negative portion of the potential window is controlled by the amount of oxygen present in the system. Removal of the oxygen by means of passing argon gas through the electrochemical cell increases the size of the potential window allowing the possibility for gas sensing applications. Electrodeposition of copper is also investigated and it is shown that copper deposits are only weakly bound to the electrode surface.

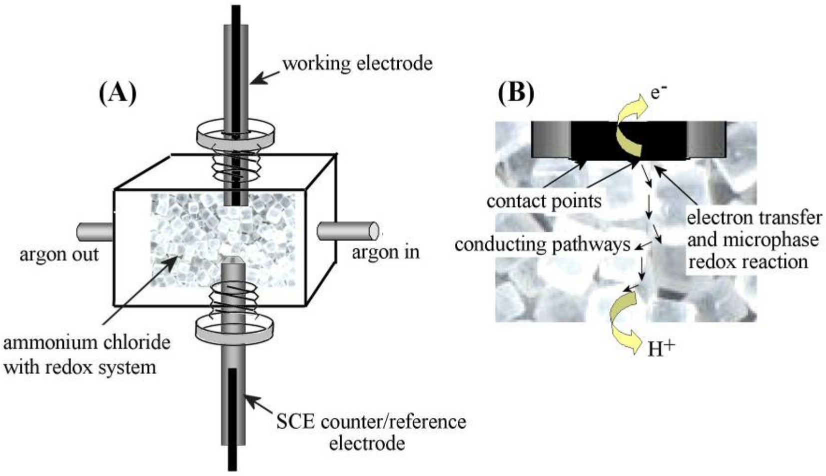

Figure 1. Schematic drawing of the electrochemical cell with an SCE counter/reference electrode and a gold disc working electrode. A redox system is immobilised onto the ammonium chloride crystals and gas such as argon is passed through the cell with defined relative humidity. (B) Schematic drawing of the redox process at the salt | electrode | gas triple phase boundary based on ion mobility across the salt crystal surface [1].

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F13K

Applications of Scanning Electrochemical Microscopy in the Characterisation of Catalyst and Electrocatalyst Activity

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Scanning electrochemical microscopy (SECM) offers a unique means with which to probe the chemical and electrochemical activity of solid-liquid interfaces with spatial resolution. Laterally scanning a microelectrode probe above the surface of a substrate allows one to monitor processes locally in solution and map corresponding surface reactivity. A variety of applications have been identified and in particular a great deal of attention has been given to the monitoring and screening of electrocatalyst performance.

We begin by presenting our research highlighting the use of amperometric SECM in the micron-scale characterization of model fuel cell catalyst films and commercial membrane electrode assemblies. We then explore the possible application of potentiometric approaches to measuring catalyst activity in-situ. Moving forward, the challenge is to use chemical mapping as a means to study structure-activity relationships in nanostructured catalysts using nanoscale SECM. One promising approach is the combination of SECM with atomic force microscopy (SECM-AFM), which allows sensitive topographical and electrochemical measurements to be made simultaneously. The key to achieving this is the fabrication of dual function SECM-AFM probes in which a nanoelectrode is integrated into the tip. A number of approaches have been demonstrated, each with different merits. We present our recent development of novel probes that are relatively simple to fabricate by modification of commercially available metallic needle probes. We demonstrate that imaging using the ‘lift-mode’ approach successfully enables surface electrochemical mapping with a resolution in the 100 nm range.

F14

Rates of electron transfer in bilayer lipid membranes modified with bioactive molecules

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Ubiquinone-10 is an integral component of the respiratory chain that mediates electron transfer in the inner mitochondrial membrane. α-tocopherol protects cell membranes from oxidation by reacting with lipid radicals produced in the lipid peroxidation chain reaction. The reduced form of ubiquinone can react with the oxidized α-tocopherol reactivating its capabilities.

A study of the charge transfer across tethered bilayer lipid membranes and across bilayer lipid membranes between two aqueous solutions was carried out using cyclic voltammetry and electrochemical impedance spectroscopy, using NADH as probe molecule. The bilayers were then modified with ubiquinone-10 (figure 1), α-tocopherol and a mixture of both. The electron transfer rate constant were determined and a comparison was made for the modified and unmodified bilayers.

When determining the theoretical rate of electron transfer one of the most important parameters is the potential independent electron tunneling coefficient (β). This value has been previously reported as being 0.72Å^{-1} [1] for BLMs made of L-α-Phosphatidylcholine (EggPC) and it yields a difference of several orders of magnitude when compared with the experimental rate of electron transfer (K^0_{app}). Mirkin and co-workers [2] showed, using SECM, that β can about one-half of what is usually reported. Using $\beta=0.38\text{Å}^{-1}$, both the theoretical and the experimental rates of electron transfer are in the same order of magnitude (10^{-8} cm s^{-1}).

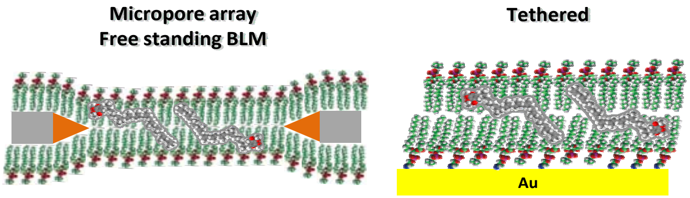

Figure 1 – Free standing and tethered bilayer lipid membranes modified with ubiquinone-10. The ubiquinone-10 is present in the hydrophobic part of the BLM.

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F15

Enhanced oxygen evolution at hydrous iron oxide films in aqueous alkaline solution

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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 the present work, we report on the redox properties and oxygen evolution electrocatalytic behaviour of polymeric iron oxyhydroxide electrodes. These films can be prepared simply *via* potential multi-cycling an iron electrode in alkaline solution (Figure 1).

Building on the earlier findings of Lyons et al. [7-8] the oxygen evolution performance of a multi-cycled iron electrode is shown to be significantly enhanced relative to an uncycled electrode. The kinetic behavior of a series of multi-cycled hydrous oxide coated iron electrodes with respect to active oxygen evolution is examined using a combination of steady state polarization and complex impedance studies. Tafel slopes and the reaction order with respect to OH^- ion activity is determined, especially as a function of hydrous oxide layer thickness .

In particular, a reduction in the Tafel slope from greater than 60 mV dec^{-1} to 40 mV dec^{-1} is observed for thick oxyhydroxide films (Figure 2a). These observations can be rationalized in terms of a duplex layer model (Figure 2b) in which the oxide/solution interface consists of a compact anhydrous inner layer and a micro- dispersed hydrous outer layer [9,10]. A general mechanism for the OER is developed which involves the generation of a physisorbed metal hydroperoxy intermediate in the outer hydrated oxide layer of the duplex film.

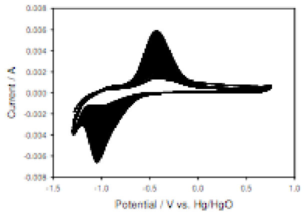

Figure 1. Cyclic voltammograms recorded during the growth of the polymeric iron oxyhydroxide film.

A plausible mechanism consistent with the available kinetic data and spectroscopic [11] experiments involving an Fe(VI) hydroperoxy intermediate is outlined below where p = 2m+n-6.

$$\begin{aligned}
&[Fe(VI)O_m(OH)_n]^{p-} + OH^- && \rightarrow [Fe(VI)O_{m+1}(OH)_{n-1}]^{p-} + H_2O + e^- \\
&[Fe(VI)O_{m+1}(OH)_{n-1}]^{p-} + OH^- && \rightarrow [Fe(VI)O_m\,\underline{OOH}(OH)_{n-1}]^{p-} + e^- \ \ldots RDS \\
&[Fe(VI)O_m\,\underline{OOH}(OH)_{n-1}]^{p-} + OH^- && \rightarrow [Fe(VI)O_m\,\underline{OO}(OH)_{n-1}]^{p-} + H_2O + e^- \\
&[Fe(VI)O_m\,\underline{OO}(OH)_{n-1}]^{p-} + OH^- && \rightarrow [Fe(VI)O_m(OH)_n]^{p-} + O_2 + e^-
\end{aligned}$$

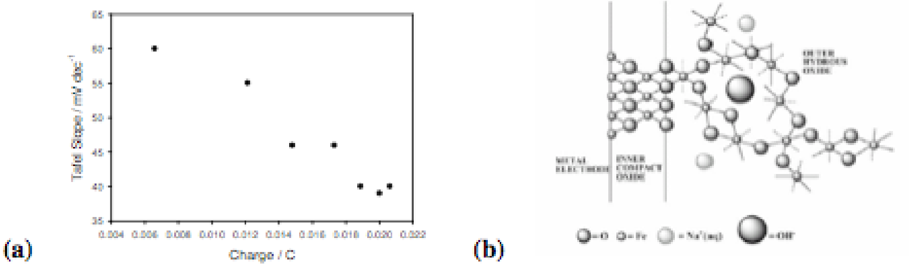

Figure 2. (a) Lower Tafel slope as a function of the charge under the hydrous oxide anodic peak, (b) Schematic representation of the electrolyte interface of the iron oxyhydroxide film.

Acknowledgements
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F16-Po

Cyclic Voltammetry of the Uranium Redox Couple

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This work is concerned with the redox behaviour of uranium in a potentially radioactive Geological Disposal Facility (GDF). The chemical properties of uranium, a redox-sensitive element, depend considerably on its oxidation states. Hence, it is important to elucidate the redox properties of uranium to predict its mobility in the environment. The aqueous solubility of uranium is strongly dependent on its redox state and also on the pH of the solution. The solubility of uranium has been shown to be very high at low pHs by several authors[1, 2] but much lower solubility of uranium at high pHs.

Of the four oxidation states of uranium (+3, +4, +5 and +6), the +6 and +4 oxidation states are most relevant to repository and environmental conditions. The most stable oxidation state of uranium in an oxic environment is +6. The standard potential of the UO_2^{2+}/U^{4+} redox couple, i.e. U (VI)/U (IV) couple, is an important thermodynamic quantity, as this value allows us to understand the chemistry of uranium in a potential nuclear repository better. There is no consensus value determined electrochemically at present, especially in the alkaline range. It is of great interest to understand the differences in the behaviour and chemical properties of uranium in the environment at both the +6 and +4 oxidation states, since U (VI) is generally mobile while U (IV) is generally less mobile.

The main aim of this work is therefore to investigate the effect of changing pH on the redox behaviour and the reversibility of the uranium couple using cyclic voltammetry. Experiments are performed using uranyl (VI) nitrate across the whole pH range from pH 1 to 14 and the effects on the kinetics; the mechanisms and the thermodynamics of the redox reactions are investigated. The redox potentials are observed to examine whether the redox potential changes significantly from acidic to neutral and subsequently to alkaline conditions. Experiments are carried out using both platinum and glassy carbon commercial working electrodes to determine which electrode would be suitable for further work.

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F17-Po

A Photo-Electrochemical and Mott-Schottky Study of Boron-Doped Diamond

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In this work, we examine the effect of electrochemical oxidation and reduction (hydrogenation) on the flatband potential and photoelectrochemistry of commercially- available,[1] heavily boron-doped ($> 10^{20}$ cm^{-3}) diamond electrodes interfaced with indifferent electrolyte.

The electrodes were found to exhibit a positive open-circuit photopotential upon illumination with a UV light source (200-600 nm); this is characteristic of a p-type semiconductor.[2] Further, by pulsing UV light during linear-sweep voltammetry, both cathodic and anodic photocurrents could be recorded, the former to be expected for a p-type semiconductor, the latter of more uncertain origin.[2,3] Flatband potentials were determined using a variant of the Mott-Schottky plot, replacing the usual capacitance by a constant-phase element. We examine the relationship between these flatband potentials and the observed photo-responses, plus the effect of the electrochemical pre- treatment of the electrode. Such information will be of value as the use of commercial boron-doped diamond electrodes becomes more widespread.

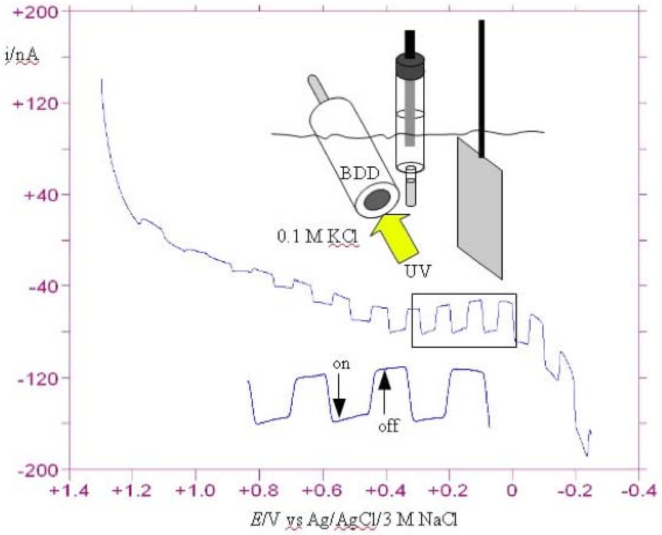

Figure 1. Photo-response of boron-doped diamond to UV illumination in 0.1 M KCl

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F18-Po

The Modification of Carbon Electrodes for Biosensor Applications

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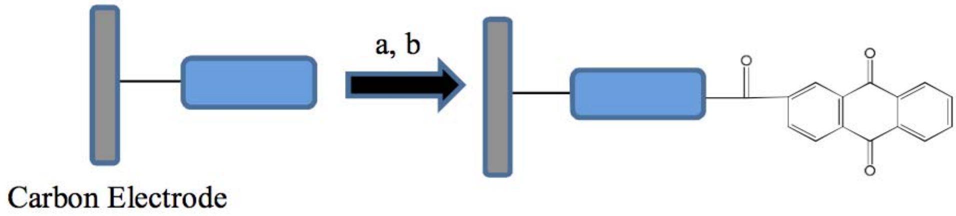
The covalent bonding of organic functionalities to conducting surfaces, carbon (Glassy carbon, carbon nanotube and HOPG), metal surfaces (nickel, gold) and semiconductors electrodes has drawn considerable interest for wide variety of applications in the field of electrochemistry such as sensors and bioelectronics [1]. In this study, the attachment of 4 different types of Boc-protected-diamines linkers to glassy carbon (GC) and edge and basal plane graphite electrodes was accomplished by electrochemical oxidation and reduction of corresponding diamines and diazonium salt, respectively. After removal of Boc group, coupling of anthraquinone (AQ)-2-carboxylic acid to those linker immobilized carbon electrode surfaces was carried out by solid-phase synthesis methodology [2]. For comparison, the direct attachment of AQ to relevant surfaces was carried out by electrochemical reduction of fast red al salt. The surface coverage, the effect of scan rate and pH and the kinetic parameters for the AQ-modified electrodes for each linker were investigated by cyclic voltammetry. O_2 reduction on modified electrodes by AQ was also studied by CV and rotating disk electrode technique (RDE). Depending on the pH, the number of the electron transferred during the O_2 reduction was evaluated by Koutecky Levich analysis.



Scheme 1. General procedure to obtain AQ-modified GC, edge and basal plane electrodes. a) 4.0 M HCl in dioxane, RT, 1 h. b) Anthraquinone-2-carboxylic acid, HBTU, DIEA, DMF, RT, 16 h.

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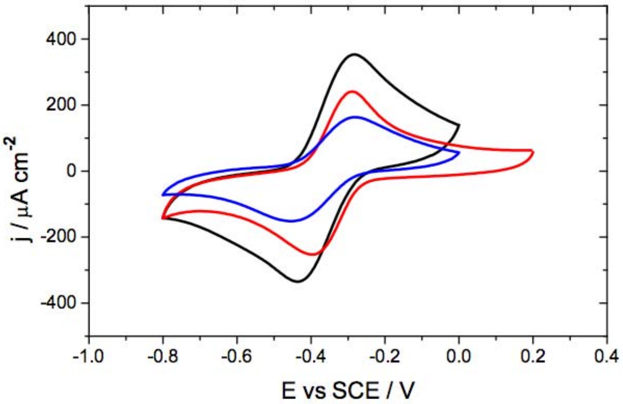

Figure 1. Cyclic voltammograms recorded at the scan rate of 50 mV s^{-1} in 0.1M of acetate buffer, pH 5, for GC, edge and basal plane electrodes modified with AQ through $NH(CH_2)_2NH_2$ various linker. Black, Red and Blue solid lines represent edge plane, GC and basal plane, respectively.

F19-Po

Enhanced oxygen evolution at hydrous nickel oxide films in aqueous alkaline solution

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Alkaline water electrolysis has been proposed as an environmentally inoffensive route to the production of the large volumes of hydrogen gas required by a possible hydrogen economy [1-5]. In practice, the efficiency of water electrolysis is limited by the large anodic overpotential of the oxygen evolution reaction (OER) [5]. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials, with the aim of achieving useful rates of active oxygen evolution at the lowest possible overpotential, in order to optimize the overall electrolysis process. 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 [6]. 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 [7]. For these reasons, the oxides of the first row transition metals offer a compromise solution. Although they are not as electrocatalytically active, their relatively low cost and long term corrosion resistance in alkaline solution makes them attractive OER anode materials [7-10].

In this work, we focus on the oxygen evolution electrocatalytic behaviour of polymeric nickel oxyhydroxide electrodes. These films can be prepared simply *via* potential multi-cycling a nickel electrode in alkaline solution (fig.1(a)). A characteristic feature of the voltammetric response of nickel electrodes in base is a well defined set of peaks corresponding to a Ni (II/III) redox transition located at potentials just prior to the onset of active oxygen evolution (fig.1(b)).

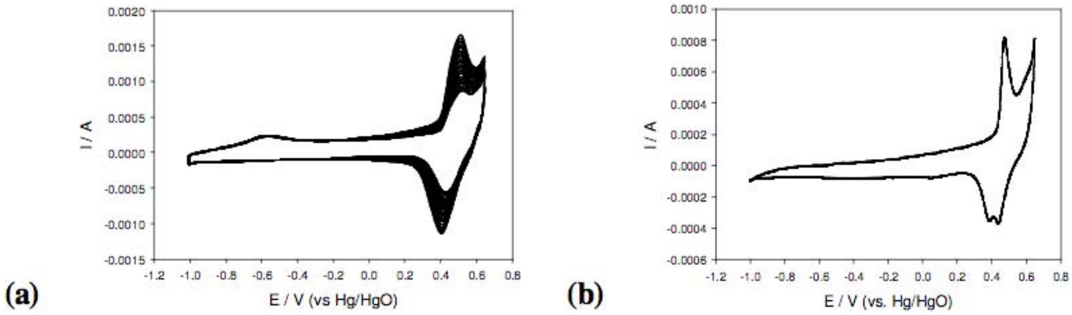

Figure 1. (a) Cyclic voltammograms recorded during the growth of the hydrous oxide layer (b) Cyclic voltammogram recorded after the growth of the hydrous oxide layer.

The oxygen evolution performance of a series of multi-cycled nickel electrodes was examined using steady state polarization techniques, and as illustrated in fig.2(a) the oxygen evolution current is enhanced when the Tafel plots for multicycled and uncycled Ni electrodes are compared 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 hydrous oxide layer thickness.

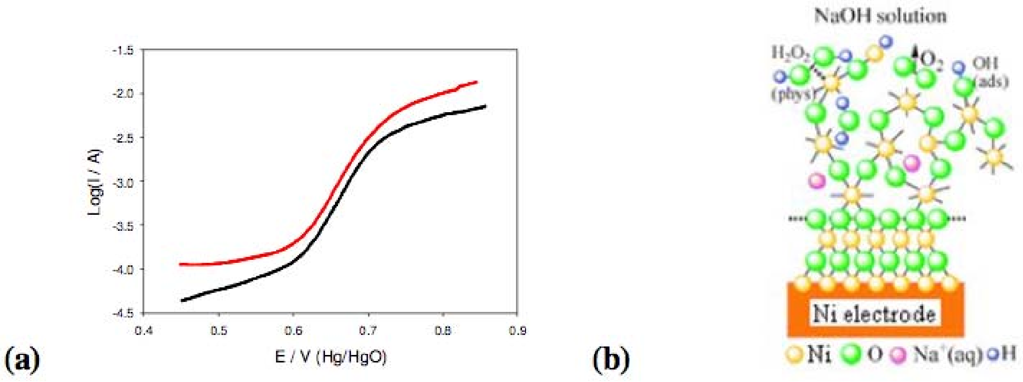

Figure 2. (a) Steady state Tafel plots recorded for an uncycled Ni electrode (growth cycles ( ). (b) Schematic representation of the mechanism of oxygen evolution at the Ni oxyhydroxide film.

We contend that a satisfactory oxygen evolution mechanism at oxidized nickel electrodes in aqueous base can be developed if attention is paid to the underlying surface chemistry of the hydrous oxide. Burke *et al.* have reported *negative super- nernstian* E-pH *shift* for the Ni(II/III) peaks associated with hydrous oxide redox switching [11]. Such shifts in peak potential with increasing pH, beyond the expected value of $dE/dpH = -2.303\times RT/F$ vs. a pH independent reference electrode, imply that the oxidised state has acquired a negative charge relative to the reduced state. This anionic oxide formation arises owing to the well known acidic properties of oxide surfaces in solutions of high pH,and can be equivalently regarded [11] in terms of, the adsorption of excess OH^- ions, proton loss from coordinated water molecules or the formation of hydroxyl surface complexes. We suggest [12] that the following may be considered a feasible pathway for the OER at oxidised Ni and hydrous nickel oxide thin films in base:

$$[Ni(III)O_m(OH)_n]^{p-} + OH^- \rightarrow [Ni(III)O_m(OH)_{n+1}]^{p-} + e^- \qquad (I)$$

$$[Ni(III)O_m(OH)_{n+1}]^{p-} \rightarrow [Ni(III)O_m(OH)_{n-1}]^{(p-1)-}\text{- -}H_2O_2 + e^- \ \ldots RDS \qquad (II)$$

$$[Ni(III)O_m(OH)_{n-1}]^{(p-1)-}\text{- -}H_2O_2 + 2OH^- \rightarrow [Ni(III)O_m(OH)_n]^{p-}\text{- -}HO_2 + H_2O + e^- \qquad (III)$$

$$[Ni(III)O_m(OH)_n]^{p-}\text{- -}HO_2 + OH^- \rightarrow [Ni(III)O_m(OH)_n]^{p-} + O_2 + H_2O + e^- \qquad (IV)$$

For a Ni(III) centred complex, $p = 2m+n-3$. The rate limiting second step is assumed to involve the formation of a physisorbed peroxide entity ($- -H_2O_2$), and the electron passed to the external circuit is supplied by a coordinated OH^- ion, bringing a decrease of one in the overall negative charge on the surface complex. Of course the concepts of anionic surface complexes and of hydroxide ions occupying lattice vacancies are essentially just different model approaches to the observed anionic character of hydrous oxides in base. However, the fact that the scheme outlined above dispenses with the need to admit the direct participation of lattice oxygen atoms in the OER, should make this representation more widely acceptable.

Acknowledgements

This publication has emanated in part from research conducted with the financial support of Science Foundation Ireland (SFI) under Grant Number SFI/10/IN.1/I2969.

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F20-Po

Gold film electrode prepared from oppositely charged gold nanoparticles for glucose oxidation

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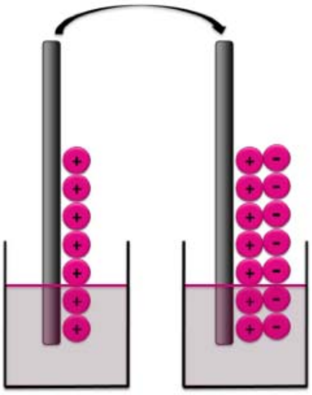
Gold nanoparticles are commonly used for electrode modification, of their catalytic properties, increase of electrochemically active surface, and relatively easy functionalisation [1,2]. There is a number of methods for gold nanoparticulate film preparation including electrodeposition [3], sputtering [4], electrophoresis [5] or layer-by-layer deposition of gold particles together with functionalized polymers [6,7].



Here we would like to present simple layer-by-layer method for thin gold film preparation without using polymer molecule as a linker. Recently we have used the same technique for carbon film preparation [8]. This method based on alternative immersion

and withdrawal steps of electrode substrate into the suspensions of gold nanoparticles with opposite charge. They were stabilized by 1-(11-mercaptoundecyl)-3-methyl- imidazolium or 11-mercapto-1-undecane sulfonate groups. Through strong electrostatic interactions stable gold nanoparticulate film is obtained.

We prepared electrodes by one, three, six and nine immersion and withdrawal steps. These electrodes were examined by cyclic voltammetry, UV-Vis spectrophotometry, SEM and AFM. The enlargement of electrochemicaly active surface was demonstrated by increase of capacitive current, characteristic gold “fingerprint” cyclic voltammetry and H_2O_2 reduction current. The gold nanoparticulate electrodes exhibit good electrocatalytic properties towards dioxygen reduction and glucose electrooxidation in alkaline medium. Acknowledgements The research was supported by the European Union within the European Regional Development Fund, through Grant Innovative Economy (POIG.01.01.02-00-008/08).

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F21-Po

Charge transfer at the electrochemical interface probed by resonant surface X-ray scattering

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An unsolved and crucial question in electrochemistry is the issue of charge transfer between the metal electrode and adsorbing species as this defines the nature of the bonding. Although there have been several theoretical studies of the charge transfer mechanism, there have been few experimental electrochemical studies due to the complexity of the electrochemical environment which makes the interface inaccessible to traditional electron-based probes of charge transfer. A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry. We have performed *in-situ* resonant surface x-ray scattering experiments on the Cu(001)-halide electrochemical system to investigate the suitability of this technique to probe the charge transfer and nature of the chemical bonding. Halide adsorption onto Cu(001) is an ideal system in which to attempt this measurement, as the halide anions, Br and Cl, both form simple ordered c(2x2) adlayers on the Cu(001) surface with adsorption uniquely into the 4-fold Cu hollow site. In the x-ray scattering experiment, the c(2x2) cell gives rise to rods of scattering (superstructure rods) that are separated from the Cu crystal truncation rods (CTR's) in reciprocal space. As a result of the symmetry of the surface the contribution to the superstructure scattering is only due to the halide anion and the second (subsurface) atomic layer of Cu atoms. It is therefore possible to probe both the surface Cu atoms, by performing resonant measurements at the Cu K-edge at an 'anti-Bragg' position of a Cu crystal truncation rod (CTR), and the sub-surface Cu atoms (second atomic layer) by performing resonant measurements at the Cu K-edge at the c(2x2) superstructure positions. A positive energy shift in the resonance at the Cu adsorption edge is indicative of a change in the charge state of the surface Cu atoms. The Cu-Br structure has the advantage that in addition to the Cu K-edge (8979 eV), also the Br K-edge (13474 eV) is accessible. This allows direct probing of the Br adatoms by performing measurements at the Br K-edge. A negative energy shift in the resonance at the Br edge is indicative of a negatively charged Br ion. The measurements show a strong dependence on the orientation of the surface with respect to the polarization of the incident x-ray beam. The results show that resonant surface x-ray scattering is a unique tool to investigate the charge transfer at an electrochemical interface.

F22-Po

Electrochemical Characterisation of Ion Exchange Processes in Mixed Pyrrole - Thiophene Polymers Immersed in Choline Chloride Based Deep Eutectic Solvents

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Electronically conducting polymers based on functionalised pyrroles and thiophenes have continued to stimulate academic interest as well as starting to be employed in practical applications and uses. [1] We have engaged in a study of the electronic properties of mixed pyrrole – thiophene polymer films (based on a custom synthesised mixed monomer precursor) in respect to energy storage applications including batteries and ion selective membranes. In such applications the movement of ion and solvent through the polymer film during oxidation and reduction cycles is critical to application and function, *e.g.* charging rate, metal ion permeability or adhesion stability.

Recently we have described the unexpected behaviour of polypyrrole in choline chloride based ionic liquids. [2] These liquids are especially attractive because of their unique solubility profiles, high stability, low volatility and low toxicity. Here we describe the electrochemical characterisation, DC capacitance behaviour and ion/solvent transport properties of mixed pyrrole – thiophene films (from the mixed monomer precursor) using a range of electrochemical methodologies in combination with acoustic impedance quartz crystal microbalance techniques. We contrast the behaviour of several mixed pyrrole – thiophene films in different electrolyte media; deep eutectic solvents, conventional organic solvents and aqueous media.

This research involves the development of a new class of rechargeable batteries based on a zinc-polymer system incorporating a novel, inexpensive, environmentally sustainable solvent. This work is necessitated by the problems associated with petrol and diesel powered vehicles and the limitations of batteries available for electric vehicles. PolyZion is an FP7 framework programme European-led consortium combining; world-class research organisations in ionic liquids, conducting polymers, zinc deposition, pulse charging and batteries, Several SME (small/medium enterprise) partners have expertise in technology development and specialised materials, and large industrial partners with industrial experience of battery manufacture and state-of-the-art testing facilities.

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F23-Po

Elucidation of mass transfer processes during redox cycling of poly (3, 4-ethylenedioxy) thiophene (PEDOT) in deep eutectic solvents using the acoustic impedance EQCM

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Deep eutectic solvents (DESs) are liquids that are formed when two solids, when mixed together, form adducts which have the effect of significantly suppressing the melting point. This work uses the DESs based around the room temperature liquids formed from mixtures of choline chloride (ChCl) with small hydrogen bond donating organic molecules (e.g. urea, glycerol, glycol and carboxylic acids).[1] One of their potential applications is as electrolytes in environmentally friendly batteries/capacitors as these liquids are known to display both low toxicity and good stability.

The performance of charge storage devices is strongly dependent on the electrolyte mass and charge transfer characteristics, as the speed of this process determines the charging/discharging rate (*i.e.* limiting current and internal resistance). [2] In this study we describe the electrochemical characterization of electrochemically generated PEDOT films, and how the unusual structure of DESs influences mass transfer of species into/out of PEDOT films during redox cycling in a range of DESs. We present data from dynamic, compositional and structural methods, including cyclic voltammetry, chronoamperometry and QCM as well as probe microscopy.

The complementary electrochemical and acoustic impedance QCM data provide valuable insight into the interaction of the polymer with the electrolyte as well as the identity of mobile species. We compare the electrochemical properties and stability of the films in a range of DESs with those in common molecular solvents, such as MeCN, during redox cycling. The hydrogen bond donor and molar ratio with ChCl has been shown to have a significant influence on the behavior of the PEDOT film.

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F24-Po

The influence of surface structure on interfacial processes

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It is well known that understanding the surface of electrocatalyst is the key to understanding its reactivity and stability. Improvements to catalytic properties are sought by modifying the surface structure, composition and controlling size of nanoparticles. While great improvements have been found for bimetallic and nanoalloy surfaces it is difficult to correlate the effect of individual features (steps and defects) of the surface structure with the changes in the surface properties of complex systems.

In order to systematically study the effect of morphology, step density and crystallographic orientation on interfacial processes our aim is to develop simple way to design and describe (model) surfaces with the varied structural parameters (steps, terraces, grain size).

In this work an electrochemical surface study of processes such as ion adsorption and metal deposition on Au single crystal and thin films has been carried out. Modifications to Au surface morphology were performed using both thermal and electrochemical annealing techniques while an oxidation-reduction process[1] has been explored as a possible method for controlling the step and defect density. Here we will present the STM and electrochemical study of Au oxidation/reduction i.e. nanostructuring of Au surfaces and the effect on underpotential deposition of different metals (Pd, Cu and Pb). The UPD systems have been examined on these Au surfaces because of their surface-sensitive nature[2-3] and for potential applications in methods for altering the surface composition.

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F25-Po

Fabrication and Potential Applications of Nanoelectrodes

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Fabrication and characterization of ultramicroelectrodes (UMEs), i.e. at least one dimension in the micron scale, is now well understood [1] and UMEs are used regularly as probes in electrochemical scanning probe microscopy techniques, such as scanning electrochemical microscopy (SECM). As the resolution of SECM is limited by the size of the electrode and the tip-substrate separation, in order to access faster kinetic processes and increase the spatial sensitivity it is necessary to be able to reliably produce electrodes with sub-micron to nanometer (nm) sized dimensions. In this poster we investigate procedures to fabricate platinum and pyrolytic carbon electrodes, with tip diameters of the order of a few hundred nm.

We describe the fabrication of these electrodes, and present cyclic voltammetry and SECM approach curve data for these tips. We will also discuss functionalization of the carbon tip surface e.g. with polyaniline in order to produce nanoscale biocompatible pH sensors [2].

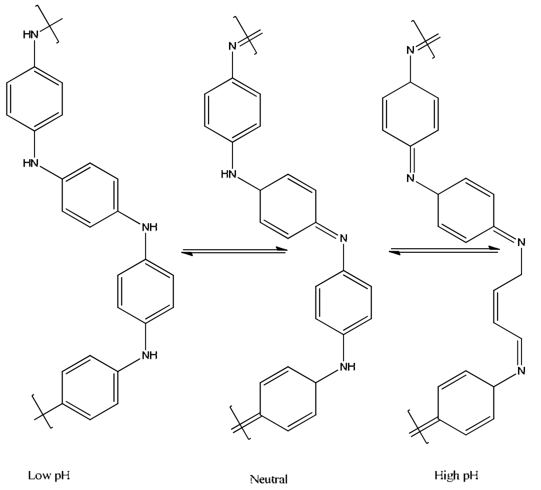

Figure 1. Schematic drawing of the structural changes of Polyaniline in varying pH.

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Microbial Electrochemistry Symposium

MB1-K

Optimization of Anode Surface Modification for Improved Microbial Fuel Cells

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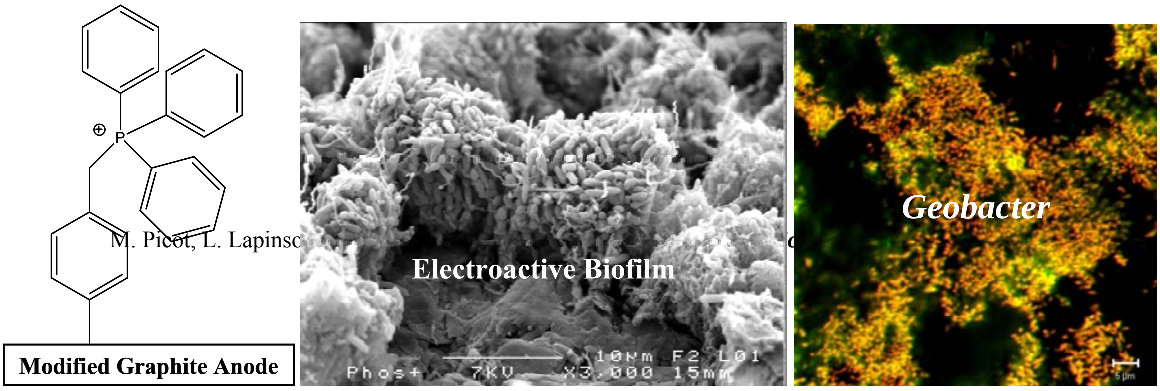
A carbon modification method (electrochemical reduction of aryl diazonium salts) has been used to introduce a large variety of chemical groups with different physico-chemical properties at a graphite electrode surface. These modified electrodes were implemented as anodes in microbial fuel cells whose performances were monitored. The extent of modification was found to be critical for the fuel cell performance. This has been studied in detail with the introduction of different amounts of a neutral group at the surface (aryl amine). An optimum of modifier grafted at the surface has been found that corresponds to the promotion of the development of an electroactive biofilm without compromising the rate of interfacial electron transfer. This has been evidenced with power density curves of microbial fuel cells, redox probes cyclic voltammetry at the modified electrodes and the study of the electrocatalytic oxidation of acetate at colonized anodes. The nature of the chemical group introduced at the electrode surface was also found to significantly affect the performance of the microbial fuel cells. Positively charged groups (phosphonium) were shown to be the most favourable for the establishment of an efficient electroactive biofilm at a modified anode as opposed to negatively charged groups (carboxylate). Scanning electron microscopy revealed that the microbial anode modified with positively charged groups was covered by a dense and homogeneous biofilm. Fluorescence in situ hybridization analyses also showed that this biofilm consisted to a large extent of bacteria from the known electroactive Geobacter genus. Importantly, the electrochemical technique used in this study to modify electrodes allows the fine tuning of the amount of modifier covalently grafted at the surface. This tuning is critical to optimize the beneficial effect of the modified electrode for implementation as an efficient anode in microbial fuel cells. The method used for modification is easy to control and can be optimized and implemented for many carbon materials currently used in microbial fuel cells and other bioelectrochemical systems.



MB2-K

Microbial Fuel Cell Longevity

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Introduction: Microbial Fuel Cells have been in existence for a century, but only recently has the technology developed to the point where it can be implemented in real world applications. For this implementation, longevity becomes critical especially when compared against existing proven technologies e.g. MCFC and SOFC, which have got lifetime requirements of 40,000 hours (4.5 years). This study has investigated the performance of small MFCs, under continuous flow conditions, fed with (a) domestic wastewater sludge (b) urine and (c) algal cells, in order to demonstrate dynamic steady-states and transitions over long periods of time.

Methods: Analytical type MFCs of 50mL total volume (25mL for each half-cell), consisting of 270cm$_2$ carbon veil electrodes folded to fit inside each half cell, were used in this investigation, with provision for continuous flow and recirculation. The MFCs were connected to 1kOhm resistors and the experiments were carried out under ambient temperature conditions. The anolyte was wastewater (700mL), fed from a 1L bottle and allowed to recirculate (at 240mL/h) through the anode compartment to reach steady state power outputs prior to experimentation. The catholyte was oxygenated water also recirculated through the cathodic chambers at a rate of 3600mL/h. Following the exhaustion of nutrients from the anolyte (i.e. cell starvation for at least 3 hours), sludge samples of specific volumes were injected into the input line of the MFCs, leading directly to the electrode and the responses were recorded using the PicoLog computer interface.

Results: The profile shown in Fig.1 illustrates the long-term performance of the MFC over 1½ years. The data points are expressed as weekly average values and transitions and steady-states shown depending on whether feeding was dosed or pulsed. All substrates were utilized and transformed into energy and adaptation periods were generally short (within minutes).

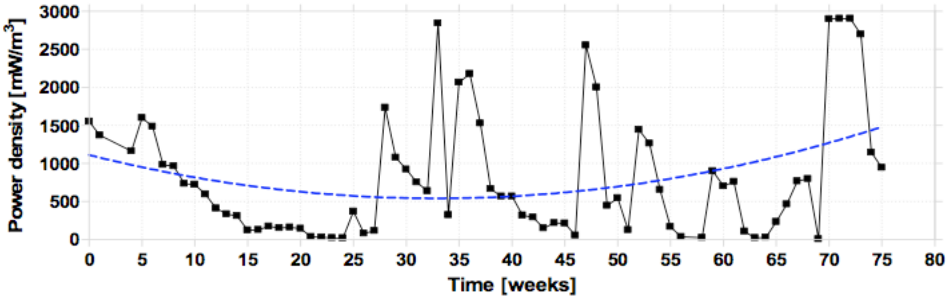

Figure 1. Time profile response of the MFC over a period of 18 months. Work has continued since and the MFCs are performing in the same manner. **Conclusions:** The MFCs used in the present study have been running for over 18 months with continuously improving performance illustrating that longevity of the responsiveness and adaptability, is one of the technology's main advantages, in addition to the flexibility of fuel stock. The chemical FC target lifetime is heavily dependent on the types of catalyst, which is not a problem for a living biofilm system.

MB3

Comparative study of multiple membranes for MFCs

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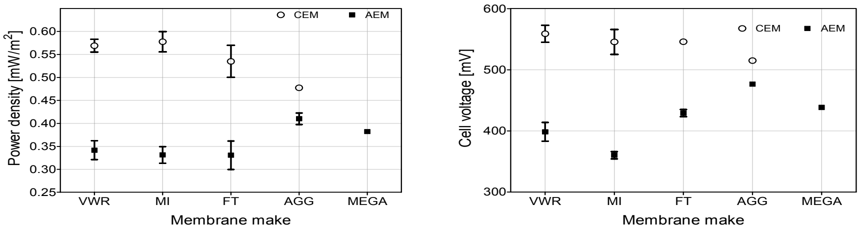
Introduction: Microbial Fuel Cells (MFCs) commonly employ proton or cation exchange membranes (CEM) to separate the anode and cathode chambers and keep the system electrochemically balanced. More recently, it has been shown however, that cation species other than protons transfer positive charge through the membrane [1]. This decreases the pH in the anode, thus impairing microbial activity, and increases the pH in the cathode reducing the cathode potential. Anion exchange membranes (AEM) have been reported to inhibit cation transfer and enhance power generation and our study was set out to test this hypothesis. The aim of this study was therefore to compare the performance of different membranes in air cathode MFCs.

Materials and methods: Five AEMs and four CEMs were tested in triplicate group MFCs assembled with open-to-air cathodes and 25mL anodes, which were inoculated with activated sludge. The anode and cathode half-cells contained carbon fibre veil electrodes with a total surface area of $270cm^2$. The experiments were carried out over a period of 34 days, with the cathodes being periodically hydrated on a daily basis. The MFC output was recorded in real time as millivolts (mV) using an ADC-24 A/D converter computer interface.

Results: Figure 1 shows the (a) mean power density and (b) Vo/c generated by the MFCs with the 9 different membranes. The best CEM was a CMI-700 that produced 0.58 mW/m^2, which was 30% higher than the best performing AEM (AGG; $0.41mW/m^2$). The open circuit voltage (Vo/c) for the AEMs ranged between 354mV-476mV, which was approx. 20-30% lower than that produced by the CEMs (505mV-578mV). No significant difference was observed between CEMs and AEMs in terms of anolyte pH change by the end of the fed-batch cycle.



Conclusions: In the present study, cation exchange membranes outperformed the anion exchange membranes both in terms of power output and open circuit voltage. These are essential parameters when building MFC stacks, since they dictate the quantity of units required for powering certain applications, and thus play an important role in the footprint of such an MFC stack.

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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.

MB4
Electrochemistry as a Tool for Photo-Microbial Fuel Cell Study

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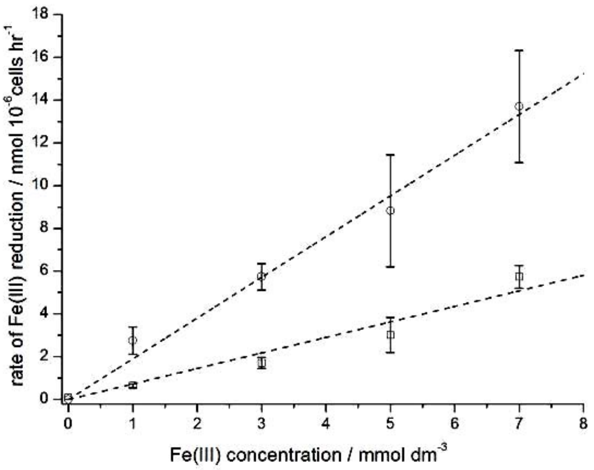
Photosynthetic-Microbial Fuel Cell (p-MFC) research aims to develop devices containing photosynthetic micro-organisms to produce electricity [1]. Micro-organisms within the device photosynthesise carbohydrates under illumination, and produce excess electrons from both carbohydrate production and the subsequent carbohydrate break down. Redox mediators are subsequently utilised to shuttle electrons between the organism and the electrode, by becoming reduced, and subsequently reoxidised at the electrode.

Electrochemical techniques have an essential role in understanding mechanisms (physiological, chemical and electron transport) involved in p-MFCs [2]. This work presents research into the reduction of redox mediators by the micro-organisms, including rates of reduction, and factors affecting the rate. Electrochemical techniques used include rotating disk electrochemistry and chronoamperometry. It is only through thorough characterization and understanding that p-MFCs can be optimized.



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MB5-K

Microelectrode arrays for the study of angiogenesis

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Angiogenesis is the growth of new blood vessels. It is of particular interest in cancer research where the limiting factor for tumour growth is frequently nutrient and oxygen supply. Consequently angiogenesis has been a major drug target. Current evaluation of anti-angiogenic drugs is based on time-consuming and expensive bioassays (the scratch assay) or *in vivo* models e.g. rabbit cornea.

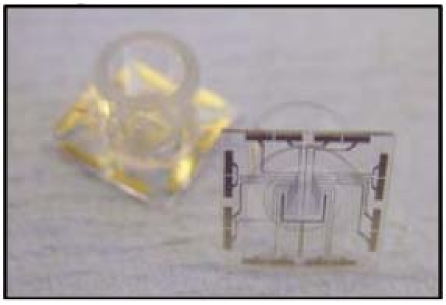

Figure 1: Microfabricated gold microsensor arrays

We have produced microfabricated sensor arrays[1], (Fig 1) comprising six or eight working electrodes which have been modified with various potentially biocompatible films. We have used cyclic voltammetry, steady state voltammetry and a.c. impedance spectroscopy to quantitatively characterize the effects of adsorption on the electrode reactions of interest[2,3], *viz.*O_2 reduction and NO oxidation. Furthermore, we have also examined the effects on cell growth and the effect of operating potential on the viability of endothelial cells using trypan blue staining. Fibronectin was the most satisfactory film from both the perspective of the cells and that of the sensors.

We have recently shown[4], 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[5] and given comparable data. The convenience of the electrochemical method enables inhibition of known intracellular processes including PI-3 kinase and ERK to elucidate the pathways of NOS activation in angiogenesis. We shall be presenting new data on angiogenin- induced NO production in a variety of cell types: porcine endothelial cells, HUVECs and endothelialised human stem cells[6]. We have recently extended the method to study oxygen consumption to identify the metabolic signatures of angiogenesis and hydrogen peroxide.

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MB6

Electrochemical characterisation of the Tetraheme Cytochrome CymA from *Shewanella oneidensis* reveals a bias towards reductive catalysis of Menaquinone.

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Enzymes which couple electrochemical potential with proton-motive force play central roles in respiration and photosynthesis across all phyla. The coupling of these vital biological processes is through the interconversion of lipophilic proton/electron carriers commonly referred to as the quinone pool. Despite the importance of these enzymes, this class of enzymes has rarely been studied in membranous environments or with their native lipophilic quinone substrates. In this study we focus on the tetraheme cytochrome CymA from *Shewanella oneidensis* MR-1. *S. onedenisis* is a facultative-aerobic gram-negative bacterium which is an important model organism for bioreactor and bioremediation studies, conferred in part by a multicomponent, branched electron transport chain. CymA has a central role in all of these electrochemical pathways.

Here we have interrogated the electrochemical properties of CymA using protein-film voltammetry after absorption on a modified atomically-flat gold electrode. CymA oxidation and reduction peaks were observed at -0.20 and -0.24 E/V respectively at pH 7.4 vs SHE. Variations in pH resulted in a modest peak shift of 0.02 mV per pH unit. We show that CymA is specific for menaquinone (MQ) conversion and is unable to catalyse oxidoreduction of ubiquinone or the soluble analogue of MQ, menadione. Moreover, substrate must be presented in a lipid phase, a point typified by the ability of CymA to catalyse MQ supplied in POPC vesicles, but not in DMSO. Despite a role *in vivo* of both menaquinone oxidation and reduction, in our system purified CymA is strongly biased towards MQ_7 reductive catalysis. This leads to the hypothesis that the electron accepting binding partner may have a role in the functional mode of this reversible enzyme.

MB7

An electrochemical impedance study of the effect of pathogenic bacterial toxins on tethered lipid bilayer membrane

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Pathogenic bacteria secrete various virulence factors that can directly interact with the outer lipid membrane of eukaryotic cells, including cell death by apoptosis or necrosis. Such virulence factors account for much of the toxic action associated with bacterial infection; therefore the detection of such proteins could provide a methodology for sensing/detection of pathogenic bacteria in, for example, food or human tissue. Detection and identification of pathogenic bacteria by conventional methods such as plating and counting in laboratory is expensive and time consuming. With growing concerns over emergence and re-emergence of pathogenic bacteria with high resistant to current antibiotics, there is a potential need for effective detection of pathogenic toxins in-vitro. This work presents the application of tethered bilayer lipid membrane (TBLM) [1] as a sensing platform for the detection of the clinically relevant pathogenic bacteria, Staphylococcus aureus MSSA 476 and Pseudomonas aeruginosa PAO1 via their secreted virulence factors, using electrochemical impedance spectroscopy (EIS) [2] and surface plasmon resonance (SPR). A non-pathogenic strain of bacteria, Escherichia coli DH5α was used as a control. A clear difference in the impedance of the TBLM for the pathogenic vs. non-pathogenic species was observed.

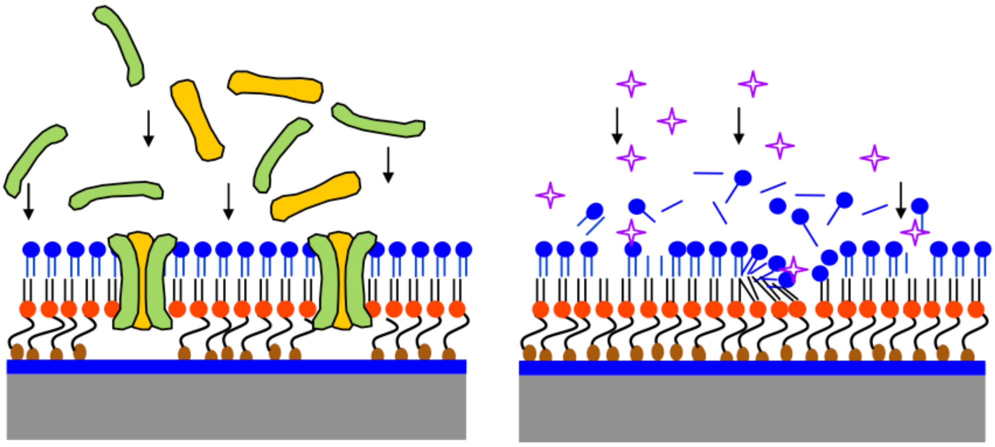

Figure 1. Schematic drawing of TBLM with (a) pore-forming toxins (PFTs) [3] – depicting the non-lipid loss interaction and (b) phospholipases [4] – showing lipid-loss interaction

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MB8

Interfacing cells with nanostructured-electrochemical transducers for new insights into electron transfer from biological cells

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Nano-electrochemical technology holds promise for new advances for cellular control and monitoring. With this insight in mind we have designed new technology based on carbon and ITO electrodes modified with nano films and structures. Exploratory studies were performed at interfacing these with biological cells. Electrochemical and physical characterisation of surfaces has been performed. We have detected current from the external surface of the cell wall of yeast by using an efficient redox mediator covalently bound to a carbon surface by a nano-tether layer. We have used AFM depth profiling to establish that the thickness of the carboxy-amine tether layer is 5.9 nm and with the osmium bipyridine mediator covalently attached a thickness of 8.3 nm was ascertained. The yeast cell wall is known to be approximately 100-200 nm thick, consequently any electrons detected must originate from the surface of the cell wall and not redox proteins located in the cell membrane. Electron transfer across the cell wall indicates a need to redefine the function of the yeast cell wall and may permit the engineering of cells for situations where elevated trans-wall electron transport is advantageous. In addition, we have used electrodes modified with carbon-nanostructures and developed new methods for their insertion in to the cells cytoplasm. Once here we have monitored the cells redox state of the cell. In summary we have developed nano-electrochemical technology that gives rise to new biological insight. These new devices also have possible applications within the medical, biosensor and biochemical industries and research.

MB9

Bispecific Antibodies – Integration of Molecular Detection and Signal Components in a Single Agent

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The biomedical problem of chronic wound healing and the continuing emergence of antibiotic-resistant species is addressed with the development of a detection system capable of the real-time assessment of bacterial load and diversity the ultimate panacea. The use of Bispecific Antibodies (*BsAb*) provides integration of molecular detection and signal response components of standard immunoassay methodologies resulting from steric hinderance mediated release of reporter molecules upon specific binding of target analytes to adjacent sites. The methodology is illustrated with respect to a novel fluorescence-based immunoassay enabling the qualitative detection of the *Staphylococcus Aureus Thermonuclease Enzyme (TNase)* that provides confirmation of the presence the *Staphylococcus Aureus* bacterium *in-vitro*. Rhodamine and Fluorescein labelled Haemocyanin from Megathura crenulata (KLH) were prepared as effective immunoconjugates containing a sensitive fluorescent reporter moiety. *BsAb* specific to this reporter conjugate and the *TNase* target antigen were produced using cell fusion techniques. Assays were performed to analyze properties attributable to steric hinderance mediated release of fluorescent reporter molecules upon adjacent *TNase* binding by monitoring the fluorescence emission intensity of the immunogenic reporter conjugate released into the aqueous environment at 578nm and 540nm respectively. Expansiom of the methodology to reporter molecules that can be detected using electroanalytical methods will be discussed.

MB10-Po

Microbial fuel cell type biosensor for volatile fatty acid with an acclimated bacterial community

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A microbial fuel cell (MFC) is a bioelectrochemical system that can be used to produce electrical power while simultaneously treating wastewater. With the increasing full scale application of MFC for treating waste water and biogas production there is a need to develop reliable methods for monitoring and control of the anaerobic digestion process. Since the current generated from a microbial fuel cell is predictably related to the energy content of wastewater used as the fuel, a MFC could be used to measure A biodegradable solute concentration in wastewaters (i.e. as a **biosensor** system). In this case, the biosensor is an analytical device for the detection of Volatile Fatty Acids (VFA) that combines with a biological component with a physicochemical detector.

Anaerobic digestion and hydrogen fermentation are complex process consisting of a series of microbial reactions catalyzed by consortia of different bacteria [1]. Under conditions of unstable operation, intermediates such as VFA and alcohols accumulate at different rates depending on the substrate and the type of perturbation causing instability [2]. Several parameters have been suggested as stress indicators such as gas production and composition, pH, solid content and VFA concentrations. It has long been recognized that the concentration of VFAs is one of the most important parameters for the accurate control of anaerobic digestion [3]. However in situ monitoring of VFA has not been studied extensively.

VFA sensors may be designed on the basis of isolated acclimatized microbial communities from MFCs and the community's appropriate immobilization on conductive matrices to detect the different concentrations of VFAs in the system. This in situ MFC based VFA sensor can replace the sophisticated and costly techniques for VFA analysis, therefore preventing system instability and failure, simultaneously maintaining high rates of productivity of bioenegy process.

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Light Driven Electrochemistry Symposium

LD1

Micro and Nano-Structuring for Photoreactor Intensification

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Introduction

Photocatalytic reactions are an attractive prospect within the chemical industry due to the many potential advantages, however industrial implementation remains a challenge due to two major scaling-up problems [1]:

- The first is that of mass transport. Many studies have investigated optimization of mass transport to the catalyst via spinning disc reactors, monolithic reactors and micro-reactors to great success.
- The second challenge is that of photon transfer with the main development coming from the use of optical fibers coated with a catalyst, with some developments into the microscale [2].

This project aims to push the idea of local illumination to the next logical stage by using nanoscale illumination where low-level luminescent nanostructures are in direct proximity to the catalyst increasing photon transfer by decreased light absorption by the bulk (Figure 1).

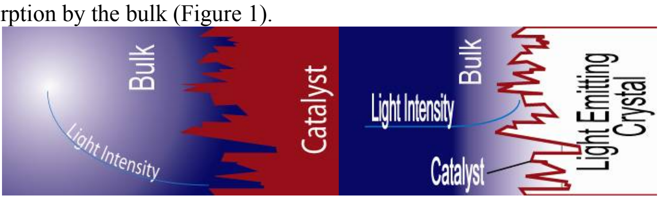

Figure 1. Graphical representation of a) Traditional photocatalytic approach, b) The local luminescent approach.

Experimental

Simple photolithographic exposure techniques are combined with hydrothermal deposition of zinc oxide nano-wires to form well structured luminescent nanostructures. Basic sputter and spin coating techniques are then used to form a photocatalytic reactive chip which is positioned inside a small reactor cell. Catalytic properties are tested using propane oxidation measured using a GC.

Results/Discussion

The control gained over the growth of the electroluminescent structure, by both substrate alignment, with substrates placed in solution vertically forming columns and those placed horizontally creating large crystal clusters, and the use of a seeding layer to promote growth only in the required areas allows for the optimized process conditions (mass and light transfer) in microreactors which will be evaluated and discussed in the presentation.

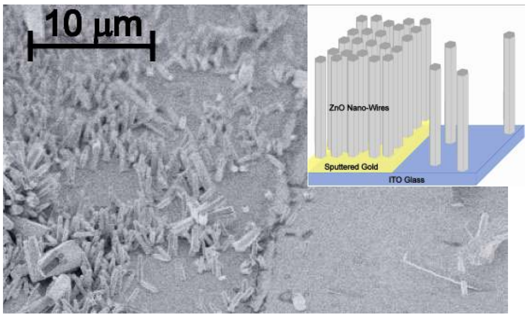

Figure 2. SEM images showing the control of crystal growth gained by using photolithographic techniques.

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LD2

ZnO Nanorods: Dependence of Method of Electrodeposition on the Physical Properties

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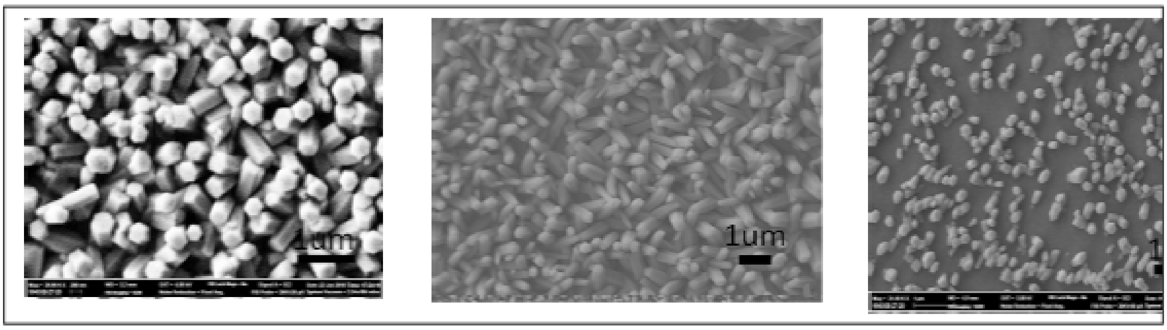
Nano-structures of zinc oxide have been a matter of considerable interest owing to their potential applications in transparent TFT's, photovoltaics and sensors. ZnO- nanorods have been produced by a number of techniques (example: CVD, MOCVD) in addition to electrochemical methods. Though, potentiostatic (PS), galvanostatic (GS)and potentiodynamic (PD,cyclic voltammetric) deposition methods have been attempted by several workers, they were performed under so disparate a condition that the properties of the resultant ZnO cannot easily be compared to ascertian which one of the three methods is best suited for the production of ZnO-nanorods with consistent quality. Here, we report the production of ZnO-nanorods by PS, GS and PD methods from an aqueous solution containing only zinc nitrate. The properties of the resultant ZnO have been examined in terms of their morphology (SEM), optical band gap and photoelectrochemical characteristics. Full analysis the results will be presented.

Sample	Method of Growth	Conditions (a)	Temperature /(^{0}C) (b)	Deposition time (s)	Band Gap/eV ©)
A	Potentiostatic (PS)	-1V	82± 2	600	3.12
B	Galvanostatic (GS)	300μA/cm^{2}	85± 2	600	2.98
C	Potentiodynamic (PD)	-1.1<V<0, 20 mV/s, 5 cycles	79± 2	550	2.93

(a): ITO working electrode, Pt counter electrode, SCE reference electrode. (b): Temperature of the electrochemical bath (c): Band Gap from the absorption edge.

Typical SEM of ZnO from potentiostatic (left), galvanostatic (middle) and potentiodynamic (right) deposition are shown below:



LD3

An Electrochemical Route for Improved Flexible DSC

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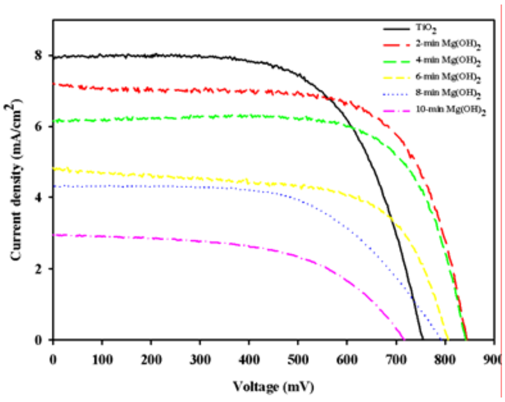
With the impending scarcity and raising cost of fossil fuels, efforts are underway to find/develop alternative energy sources. The most obvious energy source is the sun, origin of almost all the energy resources found on Earth. Photovoltaic (PV), is a form of solar energy conversion that harvest sunlight to generate electricity with no carbon or harmful gases emission with least industrial waste. Due to our complex life style today, the flexible and colored solar cells have received a significant attention. The demand for such devices is rising rapidly as a wide range of new applications are emerging. Flexible dye sensitized solar cell (DSC) is a 2nd generation PV cell and it is comprised of a semiconductor photoanode modified with a light harvester dye, a counter electrode (often a Pt coated electrode) and an electrolyte containing a redox shuttel.[1] Recently, DSCs developed on flexible substrates have received a significant interest due to their high compliance and ruggedness.[2] This work is focused on construction of flexible DSC and enhance their performance through an electrochemical technique.

Nanocrystalline TiO2 films were prepared on a conductive indium-tin oxide coated polyethylene naphthalate plastic substrate to fabricate flexible dye-sensitised photoanode. The surface of the photoanode was coated with a thin overlayer of Mg(OH)2 by Electro-deposition (ED). The effect of the ED time on the performance of flexible DSC was evaluated on the basis of their photoelectrochemical properties. The surface morphology of the photoanode was also related the PV performance. Flexible DSCs employing nanocrystalline TiO2 electrodes without the ED treatment yielded Voc of 0.744 V and short circuit current density (Jsc) of 7.94 mA cm-2 under 1 sun illumination, corresponding fill factor (ff) and the resulting overall conversion efficiency (η) were 0.64 and 3.76% respectively. When the TiO2 film was overcoated with Mg(OH)2 for 2 minutes, the Voc drastically increased to 0.847 V and hence improved the ff and η to 0.66 and 4.01% respectively3.



Current-voltage characteristics of flexible DSC (under 1 Sun) against the deposition time of $Mg(OH)_2$.

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LD4

$CdSe_xTe_{1-x}$ Alloyed Quantum Dots as Photoactive Components in Excitonic Solar Cells

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Quantum dots (QDs) are considered as a potential key component in the development of excitonic solar cells due to their highly controllable optical properties and simple wet-chemical preparation.[1] Some of the materials most widely investigated include CdS, CdSe, CdTe and PbS, which feature quantum confinement effects in particles of less than 10 nm diameter. In addition to altering the size of the crystalline domains, varying the elementary composition of alloyed QDs is a particularly attractive way of tuning the optical and electronic properties of the dots.[2, 3] The present contribution will focus on rationalizing the dependence of the optical band gap and the band edge energetic of CdSexTe1-x alloyed particles on the Se:Te ratio. Two highly reproducible QD synthesis methods, providing a range of alloyed particles with different sizes and compositions, are presented. The optical properties and structure of the alloyed dots were investigated by absorption/luminescence spectroscopy, high-resolution TEM and EDX. The position of the valence band edge as a function of the QD composition was examined by cyclic voltammetry at ultramicroelectrodes. Information extracted from these studies will be discussed in relation to the design of type II and tandem solar cells.

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LD5

Characterization of Dye Sensitized Solar Cells that utilize an aqueous electrolyte

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Since first being published in 1991[1], highly efficient Dye Sensitized Solar Cells (DSSCs) have seen an increasing level of research interest. With the possibility of relatively cheap manufacture and reasonable efficiency even in low light conditions, they are now beginning to be realized as a viable commercial solar device. In the early days of their development, water was a commonly used solvent for the electrolyte. However, it was found that changing to other solvents such as ethanol and acetonitrile led to major improvements in efficiency, and water began to be seen as detrimental to device efficiency. More recently, publications have suggested that this does not have to be the case[2], and that devices properly optimized to use an aqueous electrolyte can be effective. They also have the advantage of avoiding the problems caused by water leaching into the cell - which can adversely affect device efficiency - and are more environmentally friendly than cells that use organic solvents.

In this work we aim to understand the differences between water based cells and a more typical acetonitrile based cell. Water cells were produced with an active area of 1cm^2 and gave efficiencies up to 3.0% under AM1.5, 1 sun light. A number of electronic properties are examined, including the electron lifetime and changes in the number of electron traps under illumination. We see that there are no major changes in the electronic properties under open circuit conditions, however at short circuit there is considerable discrepancy between the cells. Results obtained using various techniques appear to suggest that diffusion limitations reduce the efficiency of the aqueous cell, which agrees with suggestions put forward in other work[2]. Cyclic Voltammetry has also been used to examine the interaction of the reduced form of the redox mediator with the oxidized dye in water and acetonitrile. We observed that I^- is able to effectively reduce oxidized Z907 in water.

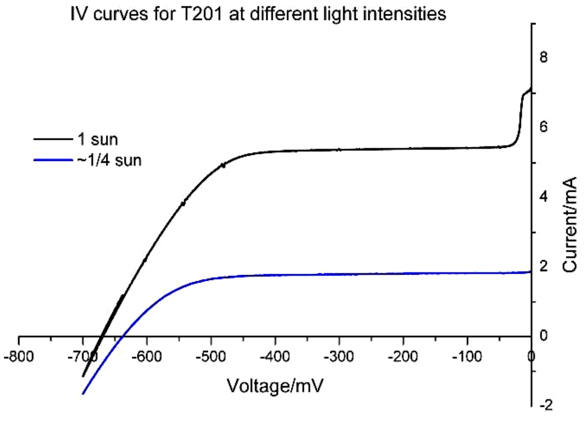

Fig. 1. Showing IV curve for water based cell. Note current peak a potential close to zero for higher light intensity measurement.

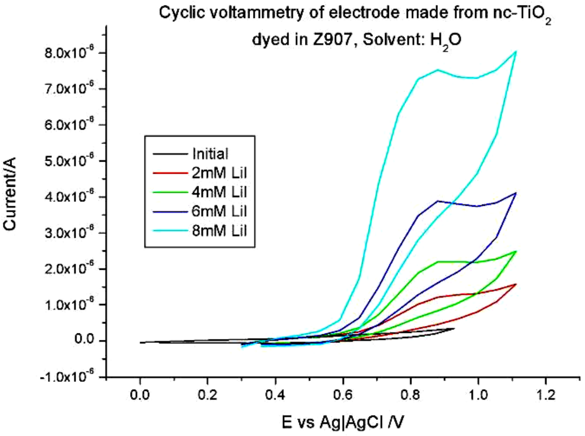

Fig. 2. Showing CV of Z907 dyed onto TiO_2 with increasing concentration of LiI. Note catalytic increase in current demonstrating effective reduction of the dye by I^-.

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LD6

$CuSbS_2$ and Cu_3BiS_3 thin films by electrodeposition/sulfurization routes

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Thin films of $CuSbS_2$ and Cu_3BiS_3 were produced by conversion of stacked and co-electroplated metal precursors in the presence of elemental sulfur vapour. The reaction sequences have been studied by ex-situ XRD analysis of the processed samples in order to optimise the sulfurisation parameters for achieving compact layers. For equal processing times, it was found that the minimum temperature required for $CuSbS_2$ to appear is substantially lower than for Cu_3BiS_3, suggesting that interdiffusion across the interfaces of the binary sulfides is a key step in the formation of the ternary compounds. The study placed particular emphasis on the structural, morphological and photoelectrochemical properties of the layers in the context of potential applications in thin film photovoltaics.

LD7

Liquid Nanotechnology for Photochemically-Induced Electron Transfer Processes

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Electron transfer chains play a fundamental rôle in biological systems for several processes including the photosynthetic solar energy conversion pathway. Such systems involve initially a form of activation of an electron donor, followed by electron transfer along the chain to an ultimate acceptor. Insofar as much work has been undertaken to try to mimic such processes, this has been undertaken primarily within a solution phase system, and so not really a realistic imitation of the confined and restricted space in which biological electron transfer chains exist. Moreover, the chemical synthesis of such intricate systems is challenging.

In this contribution, we examine the use of lyotropic liquid crystals as three-dimensional nanostructured media in which photochemically-induced electron transfer may occur. We will examine three systems. In a first, we are interested in developing a suitable mimic of the initial processes of Photosystem I, and demonstrate that a suitable candidate is the H_1 phase with chlorophyll a and vitamin K_1 populating the cylindrical micelles. In a second system, we are interested in the photoelectrolytic generation of hydrogen, and endeavour to realise this through the nematic state of a chromonic liquid crystal based on a food-dye. In a third system, we seek to unravel the interplay of subphase reactant partitioning and interphase electron transfer within a lamellar lyotropic system for photogalvanic cell application.

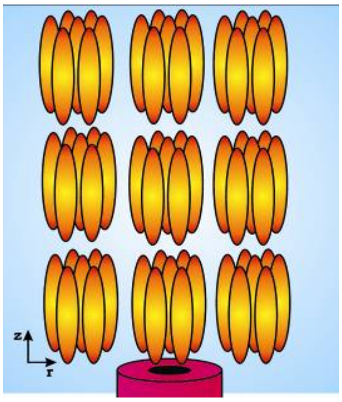

Figure 1. Schematic drawing of an electrode immersed within a liquid nanosystem [1].

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LD8

Liquid | Liquid | Electrode Triple-Phase Boundary Photovoltammetry of Pentoxyresorufin in 4-(3-Phenylpropyl)pyridine

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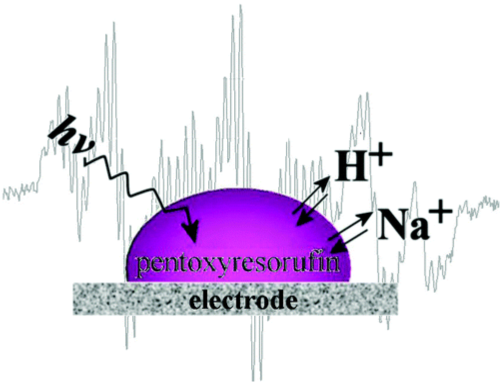
Voltammetric responses of pentoxyresorufin in 4-(3-phenylpropyl)-pyridine (PPP) microdroplets immersed in aqueous electrolyte are investigated in the absence and in the presence of light. The reduction of pentoxyresorufin to leuco-pentoxyresorufin in the dark is shown to occur in a two-electron, two-proton process sensitive to the aqueous pH and the PPP|aqueous electrolyte interfacial tension. No significant net photoelectrochemical current responses are observed, although transient responses indicative of distinct electron and hole charge carriers are seen in the presence of pentoxyresorufin. EPR evidence confirms the formation of radical intermediates upon illumination.

As a coreactant, duroquinone in the PPP microdroplet phase is investigated and also shown to undergo two-electron, two-proton reduction (to duroquinol) without significant photoelectrochemical activity. When investigated in combination, pentoxyresorufin acts as a photocatalyst for the oxidation of duroquinol to duroquinone. Wavelength-resolved photovoltammetry experiments clearly implicate pentoxyresorufin as the primary photoexcited intermediate. The photoelectrochemical mechanism is explained on the basis of the presence of a long-lived (possibly charge-separated) photoexcited intermediate in the PPP microphase. Implications for light-energy harvesting are discussed.



LD9

Highly Efficient Organic Light Emitting Diodes Based On Iridium(III) Bis (2-phenypyridinato) pyrazolonate

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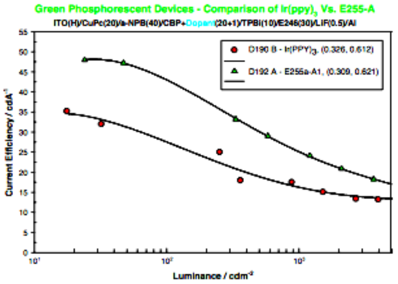
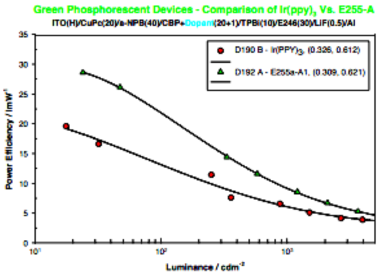
Phosphorescent organometallic complexes based on Ir, Pt, Os and Ru are subject to intense research because they enable the fabrication of high efficiency (100% internal quantum efficiency) OLEDs as both singlet and triplets participate in the electroluminescence. A red emitting Ir(III) complexe is already being employed commercial OLED devices such as mobile phones (Samsung Galaxy).

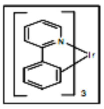
Both industry and academia use tris(2-phenypyridinato) Ir(III) (Ir(ppy)3) to benchmark the efficiencies of other green emitting complexes. We report here the synthesis, characterisation (electrical, optical, thermal and electrochemical) and its superior device performance of Bis(2-phenylpyridine-C2, N')(4-*tert*-butylacetyl-3-methyl-1-phenyl-pyrazol-5- onato) iridium (III) (E255a) over Ir(ppy)3. The superior performance is attributed to higher PL efficiency of the E255A and the better energy matching of E255a within the host, CBP. For simple device structure, ITO/CuPC(20 nm)/α-NPB (40 nm)/CBP + Dopant (20 nm , 5% Dopant)/TPBI (10 nm)/Zrq4 (30 nm)/LiF (0.5 nm)/Al, the device performance is summarised below:

Dopant	CIE colour co-ordinates (x,y)	Current Efficiency/cdA^{-1} (100 cdm^{-2})	Power Efficiency/lmW^{-1} (100 cdm^{-2})	Current Efficiency/cdA^{-1} (1000 cdm^{-2})	Power Efficiency/lmW^{-1} (100 cdm^{-2})
E255a	(0.309, 0.621)	35	18	22	9
E255a	(0.326, 0.612)	22	12	17	6

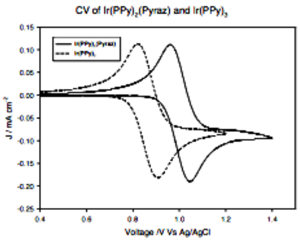
On changing the hole injector from CuPC to ZnTPTP, an efficiency of up to 80 cd/A and 50 lm/W at 100 cdm^{-2} and 50 cd/A and 25 lm/W at 1000 cdm^{-2} has been obtained respectively.

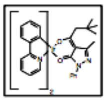






Ir(ppy)3





E255a

LD10

(CISe) Semiconductor Films

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The photovoltaic semiconductor copper indium diselenide ($CuInSe_2$) has attracted considerable interest for use as an absorber in solar cells due to its high absorption coefficient (10^5 cm^{-1}) and useful band gap 1.05 eV. On a laboratory scale solar cells based on $CuInSe_2$ have reached efficiencies of 19 % [1] with various companies commercialising this technology (eg: Sulfurcell, Würth Solar and Odersun). However, the high quality devices are prepared using expensive and technically challenging techniques. One practical method for depositing thin films of copper indium diselenide is electrodeposition. Electrodeposition is viewed as a safe, clean and efficient deposition method.

Technical problems exist when scaling up the electrodeposition of materials used for semiconductors. This is due to the strict requires of photovoltaic properties (stoichiometry, morphology and thickness) to be uniform over the entire sample. The substrate type and uniformity can affect the resultant film. By changing the underlying substrate for a more stable equivalent could lead to better uniformity. A study investigating the use of $Mo/MoSe_2$ substrates instead of the traditional Mo has been performed.

Irregularities occur due to a non-homogeneous environment at the electrode | electrolyte during the electrodeposition. The easiest way to minimise this effect is to induce mass transport to the surface of the electrode. There are various articles published which document the use of a rotating disc electrode [2,3] to control semiconductor uniformity. Here we demonstrate the use of the rocking disc electrode to induce mass transport to create uniform large area electrodeposits (12.1 cm^2). A model system of copper-indium alloy is electrodeposited and converted to the selenide. The resultant film is mapped (using photo-electrochemistry) to investigate the quality of the copper indium diselenide absorber.

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Sensor Innovation & Electroanalytical Processes Symposium

SI1K

Amperometric Gas Sensors: Mechanistic Studies and New Sensor Designs

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Amperometric electrochemical gas sensors are the most widely used type of gas sensors. They generally have a linear output, require negligible power and can be designed to be selective to specific gases. The sensing interface classically involves the use of nano-structured catalytic materials and it is generally assumed that the electrochemical reaction takes place at a three-phase interface and that it is governed by mass transport [1-2].

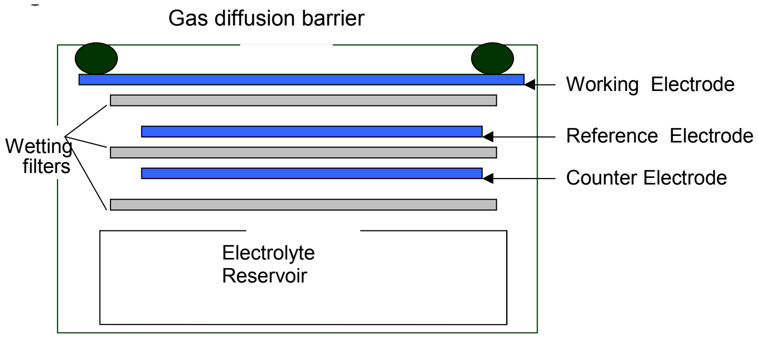

Figure 1. Schematic representation of an amperometric gas sensor.

Experimental work offers an insight into how the sensors work. More specifically, CO and H_2 oxidation were investigated. Specific studies do allow distinguishing between mass transport and kinetically limited electrochemical processes [3]. It is shown here that the diffusion model is not always applying to experimental data.

The second part of this presentation deals with new sensor designs. Specifically the results presented in the first part have practical implications for the design of better performance sensors. Diffusion barrier size, use of filters, use of a second working electrode, catalyst choice and loading will be parameters to look at for achieving better cross-sensitivity, lower background current and limit sensor output variability in diverse environmental conditions.

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SI2

Self-Assembled Monolayers of *S*,-[4-[2-[4-(2-Phenylethynyl)phenyl]ethynyl]phenyl]thioacetate Molecular Wires on Gold Surface

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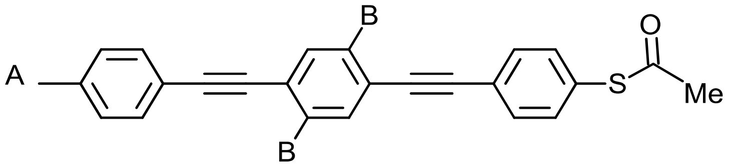
Four *S*,-[4-[2-[4-(2-Phenylethynyl)phenyl]ethynyl]phenyl]thioacetate derivatives **1, 2, 3** and **4** were investigated as molecular wires in self-assembled monolayers on gold electrodes for their electron transportation properties using electrochemical impedance spectroscopy and cyclic voltammetry. The anionic $Fe(CN)_6^{3-}$ was used as probe in CV experiments. These thioacetae molecular wires possess a high degree of conjugation and delocalization of electrons. It was found that the thioacetates **1** and **2** form well-behaved monolayers on gold electrode in comparison to thioacetes **3** and **4** which exhibit randomly distributed pinholes. The electron tunnelling resistance and fractional coverage have been examined using electron tunnelling theory. The analysis of results revealed that self-assembled monolayers of **3** shows microelectrode behaviour even in mixed monolayer with dodecanethiol (DDT). This is due to the influence of steric hindrance of methoxy side chains in patterning of molecular wire **3** in the monolayers on gold electrode surface. In the monolayer of dithioacetate **4,** lying down of molecules by binding from two ends to gold surface does not allowed the dense packing and led to the formation of monolayer with randomly distributed pinholes. Atomic force microscopy (AFM) was applied to examine the surface of the monolayers and height images gave root-mean-square (RMS) roughness. FT-IR was also used to support the characterization of self-assembled monolayers.



1. **A = H, B = H**
2. **A = NH_2, B = H**
3. **A = H, B = OMe**
4. **A = S-CO-CH_3, B = H**

Keywords: Self-assembled monolayers, Impedance, Cyclic voltammetry, Fractional coverage

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SI3

Development and comparison of anodic stripping voltammetric methods for the determination of Pb^{2+} in serum using microband screen-printed carbon electrodes

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Cyclic voltammetry was used to investigate the electrochemical behaviour of Pb^{2+} with a wide range of supporting electrolytes using a microband screen-printed carbon electrode (SPCE). The most suitable supporting electrolyte was selected on the basis of the most sensitive anodic signal produced on the reverse scan. The optimum instrumental conditions for the anodic stripping voltammetric (ASV) measurement of lead were deduced using square wave and differential pulse waveforms. Calibration studies were performed using these conditions and it was found that this analyte could be determined at concentrations in the ppt range. A simple method was developed for the determination of Pb^{2+} in serum which may be used to monitor subjects exposed to adverse levels of this toxic heavy metal. The potential interference from other metal ions was evaluated. This paper will describe the results of these studies.

SI4

Systematic Characterisation of Square Microelectrode Arrays

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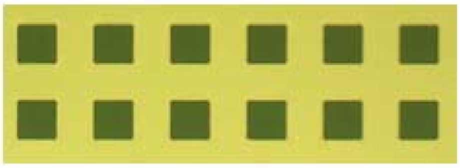
Microelectrodes are an invaluable tool for a variety of analytical studies. Their enhanced hemispherical diffusion mass transport leads to the rapid establishment of steady state currents without external convection. They also have reduced iR drop, increased Faradaic current densities and hence higher signal-to-noise ratios that vastly increase their detection sensitivity. However, to achieve reproducible enhancement, there is a need to employ fabrication techniques and develop processes that give microelectrodes of specific size and shape, with optimised response.. We have previously successfully used fabrication techniques based on microelectronic technology to produce individual square microelectrodes and have characterised their response[1]. A combination of simulation, theoretical analysis and measurement has established that although microelectrode characteristics similar to the previously characterized microdisc have been found, there is an enhanced current density for a microsquare electrode under mass transport limiting current conditions when compared to a microdisc of equivalent size, which can be attributed to the effects of enhanced diffusion at the microsquare corners.



Microelectrode arrays have the added advantage for sensing and electroanalysis that when the electrodes act independently (at high frequencies and/or short times), they possess the characteristics of multiple microelectrodes, giving microelectrode response whilst passing relatively large, easily measurable currents. Microdisc electrode arrays have been well characterized, however, microsquare arrays, with their different diffusional characteristics, have not. This presentation presents the microfabrication and characterization of arrays of microsquare electrodes of controlled size and spacing (see figure above). Simulated and measured (including cyclic voltammetry and electrical impedance spectroscopy) array responses show good agreement with each other and with single microsquare response. Systematic characterization of the array response regimes has been carried out as a function of electrode size and spacing, and this is related to the response of single microsquare and microdisc array electrodes. These measurements give insight into the fundamental response of microsquare arrays which is of real interest for sensing and electroanalytical applications.

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SI5

Transient studies at microelectrodes: from model systems to O_2 reduction

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Our group has previously reported the successful development of a steady state microelectrode sensor for the determination of dissolved oxygen concentrations in sea water [1, 2]. The work presented here underpins the development of a fast oxygen sensor for oceanographic applications; the overall aim is to determine the best conditions to measure dissolved oxygen concentrations with microdiscs on a time scale ranging from sub-milliseconds to seconds. Previous studies with rotating disc and microelectrodes [1, 3] have shown how the apparent number of electrons, n_{app}, varies between 4 and 2 as the steady mass transfer coefficient increases. The present study also aims to provide insight into the oxygen reduction reaction (ORR) and in particular to probe whether and how n_{app}, depends on the time scale of the reaction.

This presentation will describe the results of transient amperometric experiments recorded with microdisc electrodes. The experiments were carried out with different size Pt microdisc electrodes, using fast scan cyclic voltammetry, chronoamperometry and sampled current voltammetry. Model experiments were first conducted with ferrocene, $FeCp_2$, in acetonitrile to validate the experimental approach. Subsequent model experiments were conducted with hexaammineruthenium (III) chloride, $Ru(NH_3)_6Cl_3$, in aqueous chloride solutions. The ORR was also probed in aqueous chloride solutions. Experiments were also systematically conducted in absence of redox couple to investigate the role of background processes in determining the overall amperometric response over the different time scales considered. Where possible, fast scan voltammograms, chronoamperograms and sampled current voltammograms were compared to theoretical expressions or simulations. The presentation will also describesattempts to develop a potentiostatic conditioning waveform capable of pre-treating the microdisc electrode in order to produce reliable oxygen reduction chronoamperograms.

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SI6

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New methods for pH predictions during electrochemical experiments

SI7

Fabrication and characterisation of nanostructured palladium hydride pH microelectrodes

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The aim of the project is to create a nanostructured microelectrode pH sensor to measure the pH of brain fluids. The palladium hydride α + β transition is located between the α and β phases where H/Pd atomic ratios range between 0.02 and 0.6. This region was selected to fabricate the pH sensor because its potential (EPdHα+ β) is stable and independent of the hydrogen– palladium composition. In addition, EPdHα+ β follows a linear relationship with pH. A nanostructured Pd film was chosen to fabricate the pH sensor in order to obtain a large electroactive area because EPdHα+ β is not stable with microelectrode; a large area is needed to reach the equilibrium between palladium and hydrogen.

Also, neurobiological pH measurements require a small sensor as a result of the limited biological sample quantities available. The nanostructured pH sensor H1-e Pd was made by liquid crystal templating method (LCT). Scanning electron microscopy (SEM) and electrochemical characterisation were used to estimate the radius a and electroactive area of the nanostructured Pd film after the deposition process. The α + β transition was prepared by loading hydrogen electrochemically before the experiments were carried out. The nanostructured Pd hydride microelectrode was then used to estimate the pH in different solutions including artificial cerebral spinal fluid (aCSF) at human body temperature. The results obtained so far demonstrate the applicability of such electrodes to as pH sensors in brain fluid.

The presentation will describe the fabrication and characterization of the nanostructured Pd microelectrodes and their assessment for use as pH sensors [1].

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SI8

New Directions of Screen Printed Graphite Electrodes: Electrochemical Characterization of organic molecules in Room Temperature Ionic Liquids

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Screen printed graphite electrodes (SPGEs) have been characterized in a room temperature ionic liquid 1-alkyl-3-methylimidazolium hexafluorophosphate [C_nMIM][PF_6] in order to study the electrochemical parameters, diffusion coefficients and kinetics of a number of redox reactions. Ferrocene, 1,4-benzoquinone, 1,4-diphenyl-9,10-anthraquinone and tetraphenylcyclopentadienone (commonly called tetracyclone) were chosen as substrates for the characterization of SPGEs and for the identification of potential applications for electroanalytical measurements of SPGEs using room temperature ionic liquids.

Two types of fabricated in house SPGEs, edge plane and basal plane pyrolytic graphite, have been tested by cyclic voltammetry using different concentrations of the ferricinium/ferrocene redox couple. Diffusion coefficients and kinetics calculations together with Digisim simulations for comparison were performed for the optimum SPGE surface. Additionally, the reductive cyclovoltammograms of three organic carbonyl containing derivatives provided a valuable comparison of the electrochemical reduction of the C=O functional group in molecules of different size, solubility and aromaticity.

SI9

Binding of chiral biomolecules at a micro liquid-liquid interface

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The interaction of a drug with acute phase proteins in serum can influence their bioavailability and modify the function of biomolecules. Clinical effects of the plasma level of a drug are very important pharmacological parameters, traditionally determined by absorption, distribution and elimination [1-3]. Furthermore, the chiral purity of a drug plays an important role, since different isomers have distinctive clinical effects [4].

In this paper, ion amperometric measurements at a micro liquid-liquid interface is used to present proof of concept of binding of propranolol enantiomers to α_1-acid glycoprotein (AGP, orosomucoid), an acute phase plasma protein. Propranolol is a blocking drug for treating certain cardiovascular diseases via restraining sympathetic nerve and AGP is its main carrier.
The effect of pH and concentration in the binding of Propranolol to AGP were examined by CV and DPV. The results illustrate that the transfer of the analyte decreases in the presence of AGP, showing that both enantiomers of propranolol can bind to the plasma protein. Scatchard analysis was used to quantify differences in the association constant (K_a) for R-Propranolol (K_a=5.0x10^{4}M^{-1}) and S-Propranolol (K_a= 1.3x10^{4}M^{-1}) indicating that the binding of (+)- and (-)-Propranolol to the plasma protein is stereoselective.

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SI10

Detection of biomarkers using nanorods and coulter counters

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The move towards rapid and sensitive diagnostic platforms as close as possible to the patient which aid clinical decision making (point-of-care testing, POCT) has delivered a range of new assay formats. Omic technologies and the continuous monitoring or biomarkers offer the ability to provide a detailed readout of the patient that can be tailored for individual treatment. Significant research programmes are currently underway around the world to identify new markers with cancer and heart diseases being the most prominent in the literature. It's clear that as advances are made in this field new diagnostic devices that can simultaneously measure multiple biomarkers from complex biological media without complicated or time consuming sample preparation and equipment will be required.

When compared to rival technologies, superparamagnetic beads (SPMs) offer a simple, inexpensive and fast way of separating and purifying the target analytes prior to detection. Here we use template deposition through alumina oxide membranes to create particles with precise dimensions and magnetic properties. The multicomponent rods allow for control over the magnetic, optical and surface chemistries. The rods are functionalised with a protective polyethylene glycol, PEG, to prevent non specific adsorption of serum proteins and target analytes and functionalised with aptamers. The aptamers used here are short sequences of ssDNA that can bind to the targets with high specificity and selectivity, capturing the biomarkers from solution. A series of rods are created of differing lengths, with each one functionalised with a different aptamer sequence.

Upon binding to the analyte the nanorods undergo aggregation, the aggregates size and frequency is related to the concentration of the target. To detect the aggregation a new platform based upon the existing coulter counter technology is used. With the aid of a stretchable pore technology, analysis of the blockage current as the rods pass through this pore reveals the concentration of beads as well as their size and surface chemistry properties.

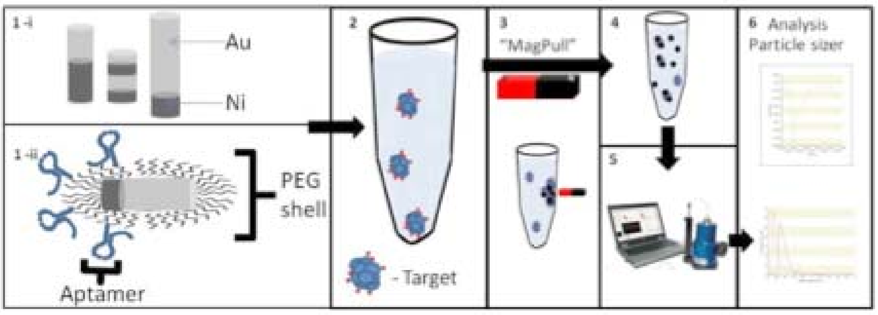

Figure 1. Schematic of the assay. 1i – Schematic of Rods created via template deposition, each rod contains a Ni segment and Au segment to make each rod contain a magnetic functionality and be visually unique . 1ii – Rods are coated with protective PEG layer and aptamer sequence. 2 - Rods are incubated with target. 3 i - Aggregation of the beads is aided via the use of an external magnetic field. 4 – During the "magpull" stage the beads may be washed. 5 – Beads are resuspended before analysis using a coulter counter technology.

SI11

BIOELECTROCHEMISTRY OF REDOX ENZYMES IMMOBILIZED ON MESOPOROUS GOLD ELECTRODES

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Nanoporous gold (NPG) is obtained by dealloying Ag-Au alloy in concentrated nitric acid for a certain period of time [1]. In the NPG layer the gold atoms assemble into a 3D-structure to form a large surface area material with tunable pore sizes ranging from a 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 and the NPG films have high electrical conductivity, indicating that NPG is a suitable material for the immobilization of redox enzymes for applications in biosensors and in biofuel cells. The creation of an efficient biofuel cell is dependent on 3 essential factors: choice of enzyme, choice of mediator, and choice of electrode material. The mesostructured electrodes allow 28 times higher enzyme loading compared to the polycrystalline gold electrode and can be utilised in the development of membraneless biofuel cells capable of generating high power densities. Currently the biofuel cells consisting of glucose oxidise as bioanode and bilirubin oxidise as biocathode are under developing.

[1] H. Qiu, C. Xu, X. Huang, Y. Ding, Y. Qu, P. Gao, *J. Phys. Chem. C* **2009**, 113, 2521.

SI12-K

Amorphous carbon nanotools for cell surgery

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Using a method of electron-beam induced deposition (EBID) of amorphous carbon, we have been able to fabricate free-standing nanostructures at the apex of Atomic Force Microscope (AFM) probes [1]. A variety of shapes has been obtained using this technique including 'nanoscalpels' and 'nanoneedles' (see Figure 1). We performed detailed mechanical tests of the fabricated nanotools and found that, for example, nanoscalpels are hard enough for a single cut to penetrate a 45 nm thick gold layer; and thus can be used for making narrow electrode gaps required for fabrication of nanoelectronic devices or as a nanosurgical tool in cell biology [2].

The EBID fabricated nanoneedles have cylindrical shape with hemispherical apex and diameters in the range of 18-100nm. We found that they are resistant to breaking and recover elastically even after large deformations (i.e. vertical deformations up to 60% of the needle length) [3]. To explore the capabilities of these nanotools, corneocytes isolated from human skin, were indented. We found that nanoneedle probes can penetrate to large depths within cells and can be used for "mechanical tomography" of cells, e.g. to measure profiles of the variation with depth in intracellular elasticity and viscosity.

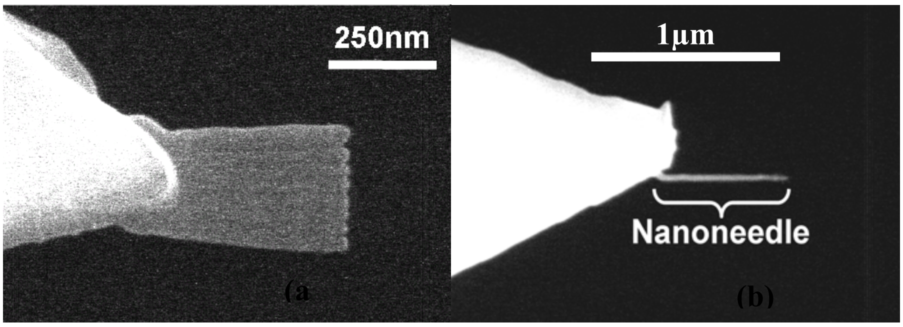

Figure 1. 'Nanoscalpel' (a) and 'nanoneedle' (b) fabricated on AFM probes.

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SI13

Electrochemical formation and characterization of a β – methylumbelliferone porous insulating film for catecholamine separation and quantitation

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The electro-oxidation of β-methylumbelliferone (βmU) at a graphite rod electrode produces a porous insulating 'layer', the pore size of which is dependent on the concentration of monomer solution and number of deposition cycles employed. The films were characterized and visualized using a combination of electrochemical and electron microscopy techniques (scanning electron microscopy and scanning electrochemical microscopy) with the aim to visualize and quantify the resulting "active sites" or / "pores" formed under specific electro-oxidation conditions (Figure 1). The size-selective properties of the optimized films were evaluated using square wave voltammetry for the separation of chosen mixtures of catecholamines, catechols and monoamines together with electroactive interferences. The potential for these films to be exploited as templates for nanoelectrode fabrication is also explored.

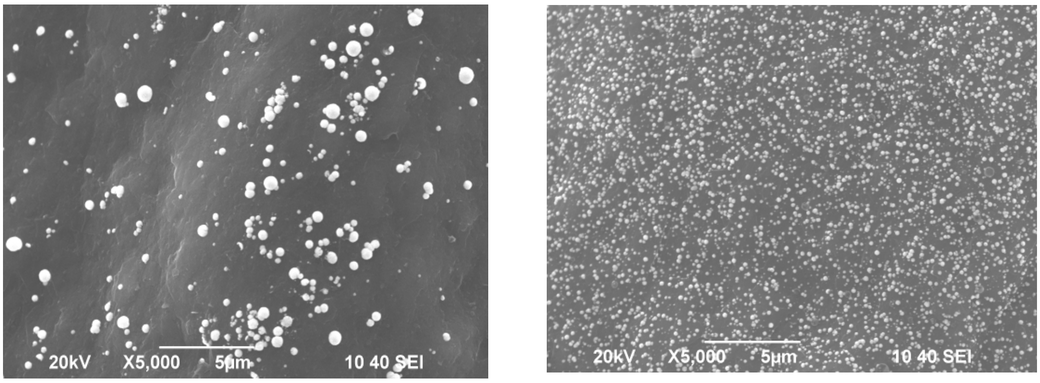

Figure 1. SEM images of platinum deposition on a) bare graphite rod and b) βmU coated graphite rod highlighting the "active areas" of the electrode surface

SI14

Label-Free Sub-Picomolar Protein Detection with Field-Effect Transistors

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A detailed understanding of complex biological systems requires information about the functional state of proteins, which perform the bulk of work in the cell. Proteomics currently plays a major role in many areas of biomedicine, such as the identification of cancer biomarkers. The ability to directly interrogate protein interactions is therefore of major importance. In particular, high throughput protein analysis methods allowing quantitative detection are highly desirable. Sensing devices yielding very low protein detection limits are required for many applications such as clinical diagnostics.

Label-free electrical protein detection with sub-picomolar detection limits has been achieved with the use of metal-oxide-semiconductor field-effect transistors (MOSFETs). The gates of the MOSFETs are connected to external gold electrodes, where the protein interactions take place. Upon biomolecular interaction, the induced variations in open circuit potential are measured by means of shifts in the transfer characteristics of the transistors.

Our protein test system involves the use of peptide aptamers that recognise highly related protein partners of the cyclin-dependent kinase (CDK) family. Using our technique, human CDK2 has been detected at 100 fM or 5 pg/ml, well within the clinically relevant range.

The target specificity, ease of fabrication and scalability of these FET arrays, further demonstrates the potential application of the multiplexable field effect format to protein sensing.

SI15

Bioaerosol Particle Detection by Flame Plasma Electrochemistry

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Real time detection and characterisation of bioaerosols is of interest to the health [1], security [2] and fabrication [3] industries. The majority of techniques in this field follow the capture and subsequent analysis methodology [4]. In addition to the long time duration between sampling and results, the collected sample may suffer from desiccation or chemical reaction that will affect the accuracy of the subsequent analysis.

The exception is single particle mass spectrometry [5] which is able to chemically analyse the particle online, however such devices remain relatively large and expensive.
In the approach presented here (Figure 1), the particle is directed into the heart of a laminar H_2/O_2 flame. A change in the open circuit potential is detected upstream by an array of electrodes. This has been shown [6] to correlate to the plume of gases given off by the particle as it burns in the flame. Further, the array collects spatial information on the plume.

The technique benefits from the particle remaining under the conditions in which it was sampled until the point of analysis. When introduced into the flame, a plume of gases of diameter *ca.* 10^3 times that of the particle is produced. This is an amplification effect, which allows sub-micrometer particles to be detected.

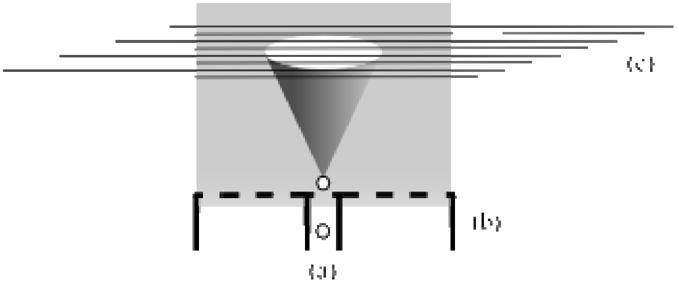

Figure 1. Particles are introduced to the separate central gas flow (a) of a Meker burner (b). Against the background flame (light grey) the particle combusts to produce a gaseous plume (dark grey). The front of this plume is imaged by an electrode array (c).

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SI16

Mechanical and Electrical properties of nanoclay and nanoclay based electrodes

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The present work introduces a comparative study on the use of nanoclay and nanoclay based electrodes containing clay minerals of different structures such as montmorillonite, hectorite, laponite, vermiculite, hydrotalcite and sepiolite. These minerals provide economic, green and smart sensor options using manufacture alternations such as nanoclay coatings, clay based nanocomposites, organoclays, hybrid materials and modified nano assemblies. Natural clay minerals are not electronically conductive [1]. However, colloidal clays idealized as a single layer of clay (nanoclays) behave very differently at the nanoscale [2]. Nanoclays have recently attracted attention because of their appreciable surface area, unusual intercalation properties and high ion-exchange ability. For example, clay added nanocomposite films with polymer and biopolymer matrix are of great interest for electrolyte membranes for the positive/negative electrodes separation in Li-batteries, thin layer capacitors and supercapacitors, membranes for electrocatalysis and membranes for modified electrodes in electrochemical sensors [3]. Nano-clay type gel electrolyte is used for dye-sensitized solar cells for green energy development which have considerable lower costs compared with amorphous silicon solar cells [4]. Hybrid materials, a typical example of organically modified nanoclay as surfactant-intercalated clay-modified electrode, are modified by ion exchange, metal/metal complex impregnation, pillaring and acid treatment to develop catalysts with desired [5]. Another modified assembly of ultrathin film by Langmuir Blodgett technique which is containing 1 nm thick clay particles allows significantly higher cation exchange capacity to higher sensing ability [6]. In particular, the well known concepts for nanoclays are described on the preparation of nanoclay based electrodes with application examples.

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SI17-Po

Mixed taste detection for LB film taste sensor

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A Langmuir Blodgett (LB) film taste sensor using an evaporated Au metal film as an electrode and used in mixed taste discrimination experiments is reported. The detecting parameter as the stability potential change depending on the disadsorption effect was used in addition to the conventional parameter as the maximum potential change depending on the adsorption effect. A new sensing film was deposited by stearic acid, with PAA-H-HCL as a polyion complex, using a vertical-dipping LB film fabrication system. Five mixed substances such as saltiness, sourness, bitterness, sweetness, and umami, were detected by analyzing response patterns. With these detecting parameters and new sensing film, mixed basic taste substances were clearly discriminated. Fig.1 shows a schematic of the detecting parameters. The maximum potential change is the conventional parameter, and the stability potential change is new one alternated by the response time in this measurement. The maximum potential change is the first response parameter after dropping point and the stability potential change is also the second response parameter after the maximum potential and 3 minutes later at the dropping point. These two parameters were very useful for discriminating mixed taste materials. Fig. 2 shows the dependence of the saltiness content of the mixture with other four basic taste materials such as sourness, sweetness, bitterness, and umami. In a mixed solution, for example 0.2 ml saltiness, was included with other same amount of the other materials, 0.2 ml each. The total amount of the mixtures was 1 ml. The stability potential change was proportional to the amount of the saltiness mixture, and the maximum potential change was also inversely proportional to it. The other dependences of the mixtures were measured simultaneously. By using these parameters, mixed solutions were clearly discriminated.

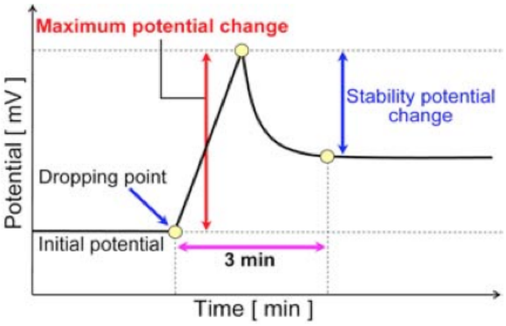

Fig.1 Discrimination parameters

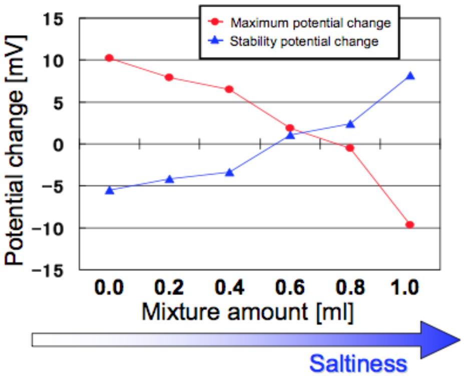

Fig.2 Dependence of the saltiness content of the mixture

SI18-Po

Multiplexed Open Circuit Potential Biosensing Instrumentation Testbed

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A detailed understanding of complex biological systems requires information about the functional state of proteins, which perform the bulk of work in the cell. Proteomics currently plays a major role in many areas of biomedicine, such as the identification of cancer biomarkers. The ability to directly interrogate protein interactions is therefore of major importance. In particular, label-free high throughput protein analysis methods allowing quantitative detection are highly desirable.

Field-effect devices are promising candidates for the development of inexpensive microarrays associated with portable instrumentation [1]. These stable semiconductor devices measure variations in the open circuit potential (OCP) that occur at the metal gate interface when the charge density and distribution of the immobilised biolayer changes upon interaction with a bioconjugate [2].

We here report on the parallel electrical detection of protein interactions using direct multiplexed OCP variation measurements. The OCP was measured in real-time using an ultra-low input bias current instrumentation amplifier providing an accurate differential measurement of voltage. An array of sensor inputs is switched in high speed via a multiplexer addressed by a microcontroller. The microcontroller converts the OCP differential measurements from analog to digital, displays real-time information on a LCD display, and transfers the captured data by User Datagram Protocol (UDP) / Transmission Control Protocol (TCP) through a WiFi module to other devices. A fully automated and accurate measurement system is hence achieved with direct computer interface for logging and analysis of the data. Apple Push Notification has also been incorporated to notify users' iOS devices of the measurement status.

The present work shows that high-throughput label-free electrical detection of protein interactions can be achieved by direct detection of the OCP with suitable multiplexed instrumentation.

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SI19-Po

Graphene-based Amperometric and Field-Effect Biosensing with Supramolecular Protein Complexes

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Graphene is one of the most promising materials for future nanoelectronic devices and a prime target for the electronics industry. Graphene can be employed in electronic devices such as atomically thin transistors, electronic waveguides, and is likely to lead to sensitive chemical and biological sensors. In fact, graphene has shown extreme (down to single-molecule) sensitivity to environmental changes. Progress in its synthesis now allows its growth on large areas, thus making it a potentially superior candidate for biosensing interfaces.

Here we are exploring graphene as a surface for enzyme immobilisation and activity detection. Protein immobilisation is central to the development of new bio-assays or sensing platforms as it is directly linked to such issues as protein conformation and subsequently to whether they remain active or not after immobilisation.

The 2-oxo acid dehydrogenase protein complex (2-OADHC) is one of the largest enzyme complexes, which is central to energy metabolism. It consists of a dihydrolipoyl acetyl-transferase (E2) protein core, on which 2-oxo acid decarboxylase (E1) and dihydrolipoamide dehydrogenase (E3) proteins bind non-covalently, but specifically. In this work we succeeded in immobilising both the E2 monomer and E2 supramolecular complexes directly onto the graphene surface, upon which the whole 2-OADHC complex can be assembled.

The immobilisation of the proteins was studied by atomic force microscopy, while the retention of their activity was tested through their redox electron transfer to the graphene. Binding of the whole complex was detected by amperometric and field-effect sensing.

The immobilisation onto graphene of a large, complex in structure, multi-function protein offers extensive flexibility for tailoring protein-protein interactions and resulting functions. The thermostable E2 protein constitutes a model system for scaffolding of complex, multidomain protein systems, which can be detected using graphene-based biosensors.

SI20-Po

BIOELECTROCHEMISTRY OF REDOX ENZYMES IMMOBILIZED ON MESOPOROUS GOLD ELECTRODES

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Nanoporous gold (NPG) is obtained by dealloying Ag-Au alloy in concentrated nitric acid for a certain period of time [1]. In the NPG layer the gold atoms assemble into a 3D-structure to form a large surface area material with tunable pore sizes ranging from a 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 and the NPG films have high electrical conductivity, indicating that NPG is a suitable material for the immobilization of redox enzymes for applications in biosensors and in biofuel cells. The creation of an efficient biofuel cell is dependent on 3 essential factors: choice of enzyme, choice of mediator, and choice of electrode material. The mesostructured electrodes allow 28 times higher enzyme loading compared to the polycrystalline gold electrode and can be utilised in the development of membraneless biofuel cells capable of generating high power densities. Currently the biofuel cells consisting of glucose oxidise as bioanode and bilirubin oxidise as biocathode are under developing.

[1] H. Qiu, C. Xu, X. Huang, Y. Ding, Y. Qu, P. Gao, *J. Phys. Chem. C* **2009**, 113, 2521.

SI21-Po

Enhanced Electrochemical Reduction of Hydrogen Peroxide at Surfactant/Salt Modified Electrodes

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Hydrogen peroxide (H_2O_2) is widely used in many biological systems and industrial processes in the textile, food, pharmaceutical and clinical sectors. The importance of hydrogen peroxide is related to its unique oxidising properties as well as decomposition, which plays a very important role in the manufacture of industrial water electrolysers, secondary metal-air batteries and fuel cells. Therefore, the accurate and rapid determination of H_2O_2 is extremely important.

Electrochemical H_2O_2 sensors are shown to be an appropriate alternative to the traditional methods (titrimetry, spectrophotometry and chemiluminescence) because they are rapid, low cost and easy for automation detection. Many metal materials such as Pt, Pd, Cu and Ag have been used as electrodes for the electrochemical determination of H_2O_2.[1] Recently, an improvement of the catalytic activity of silver screen-printed electrodes towards H_2O_2 reduction after electrode modification with a mixed surfactant/salt solution has been reported.[2] The combination of dodecyl benzenesulphonic acid and KCl led to changes in both the morphology and chemical composition of the silver paste electrode surface which enhanced the reduction of H_2O_2 at -0.1 V vs. Ag/AgCl up to 80-fold on such material.

In the present work, this phenomenon is further investigated with regard to the effect the type of metal electrode, surfactant and salt have on the reduction of H_2O_2. Silver paste electrodes were modified with a range of surfactants (dodecylbenzenesulfonic acid, sodium dodecyl sulphate, cetyl trimethylammonium bromide, Triton X-100) and chloride salts and their ability to reduce H_2O_2 was evaluated. The effect of the modification on the H_2O_2 reduction was assessed by cyclic voltammetry and amperometry. Scanning Electron Microscopy (SEM) measurements were performed to characterize the electrode surfaces before and after the surfactant-based modification. In addition, the surfactant/salt modifications were performed on a range of metallic substrates such as Au, Pt and other Ag-based electrodes. Comparisons of H_2O_2 reduction at these electrodes are shown and the effect of their modifications is also studied.

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4146.

SI22-Po

An integrated electrochemical sensor/biosensor platform for cell metabolism analysis

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This poster presents some results of investigations into the development of an integrated electrochemical sensing system for studying in real time the metabolism of mammalian cells under tissue culture assay conditions. Using a combination of MEMS technology and screen-printing, sensors and biosensors for pH, O_2, glucose and lactate were fabricated onto silicon substrate as microelectrodes compatible with a 96-well tissue culture format. Responses from the chemical sensors for pH and O_2 were obtained potentiometrically and amperometrically, respectively, while the glucose and lactate biosensors operated amperometrically. Strips of microwells containing sensors/biosensors were interfaced with a multipotentiostat to allow simultaneous monitoring of changes in the various parameters in buffer and culture medium over a period of up to 24h. This system has been applied to monitor variations in metabolite levels in the presence of mammalian cells. The potential for further development as a platform for the interrogation of cell metabolic activity and for toxicity testing will be discussed.

SI23-Po

Novel Redox Behaviour of the 1,4-Benzodiazepine Lorazepam and Its Analytical Application

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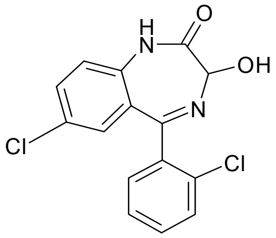
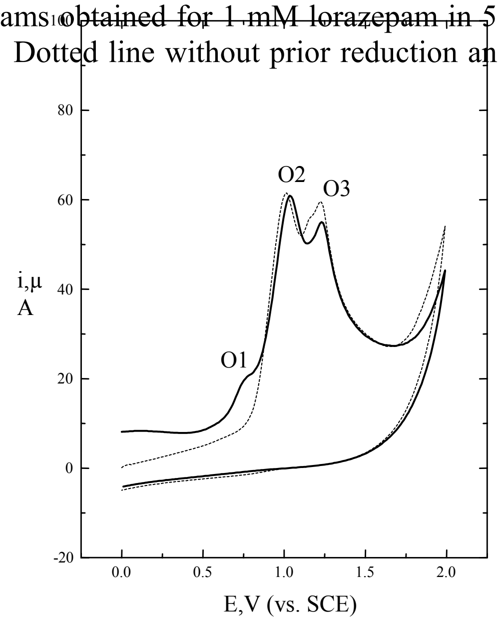
Lorazepam, 7-chloro-5-(2-chlorophenyl)-3-hydroxy-1,3-dihydro-2H-1,4-benzodiazepin-2-one, (I) is one of the most commonly administered and abused members of the 1,4-bezodiazepine class of drugs. Previous electrochemical investigations have focused on its cathodic behaviour showing two pH dependent reduction processes resulting from the 2e$^-$, 2H$^+$ reductions of the 4,5-azomethine and the 3-hydroxyl groups. However, to our knowledge there have been no reports on the redox behaviour of this molecule. In this present study we have identified several previously unreported oxidation processes (figure 1, O1, O2 and O3). The effects of both pH and scan rate on these were studied and mechanisms are given to explain these observations.



(I)

Figure 1. Anodic section of cyclic voltammograms obtained for 1 mM lorazepam in 50 % 0.2 M pH 8 phosphate buffer-50 % acetone. Dotted line without prior reduction and solid line with prior reduction.



SI24-Po

Development of a screen-printed uric acid biosensor, fabricated using a water-based carbon ink, for cell metabolism studies

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

Voltammetric studies were performed with these devices in the presence and absence of H_2O_2 and UA to characterise their redox behaviour under various solution conditions. The results indicated that a suitable oxidation peak could be obtained for H_2O_2 which was a pre-requisite for the operation of the proposed biosensor. In order to fabricate a UA biosensor, this transducer was coated with uricase.

Studies are underway to optimise the conditions for operation in culture medium containing cells in the presence of potential toxins.

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SI25-Po

Directly Heated Bismuth Film Electrodes Based on Gold Microwires

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Bismuth, as a nontoxic substitute for mercury electrodes, is an attractive electrode material in electroanalysis in particular for voltammetric and amperometric sensors. Stripping-analysis with bismuth film electrodes (BiFE) [1] offers well-defined and highly reproducible stripping signals. A favorable signal-to-background ratio in the negative potential range coupled with excellent resolution and reproducibility often makes BiFE superior to mercury. It is also possible to heat the bismuth film electrode directly by using a compact heating instrument comprising a filtering bridge for direct electric heating while performing undisturbed electrochemical measurements [2].

We describe the preparation of two different directly heatable bismuth-modified gold microwire electrodes [3]. We characterized the electrochemical behavior using cyclic voltammetry in acetate buffer and alkaline tartrate solution. The bismuth modified electrodes show a significantly wider potential window compared to bare gold wires. In the presence of picric acid as one example for the detection of explosives, the bismuth electrodes deliver higher signals.

By applying heat during the measurements, the signals can be enhanced further. We used the temperature pulse amperometry (TPA) technique [4] to improve the electrochemical response at the different types of electrodes. Here, we were able to detect 3 ppm traces of picric acid.

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SI26-Po

Electrochemical Detection of Fungal Infections in Clinical Samples

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Fungal infections of the respiratory system are one of the major problems for immunocompromised patients. The mortality is high and the diagnosis includes PCR and additionally sequencing of the products and cultivation of the fungi. Since this is a time-consuming process, we present the detection of *Candida albicans* and *Aspergillus fumigatus* from clinical samples by means of electrochemistry. Over the past decade, electrochemical detection of nucleic acids has become a powerful tool beneath classical molecular biological methods. Our group already reported on the electrochemical detection of a PCR-amplified sequence from *Clostridium acetobutylicum* [1] by means of labeling with [OsO_4(bipy)] using protective strands. In that preliminary work, PCR was performed with an artificial 136 base (b) single-stranded (ss) DNA oligonucleotide as template. Here we report first results on the detection of fungal DNA from clinical samples on gold electrodes. The gold electrode was modified with a capture probe organized in a self assembled monolayer (SAM). We used capture probes for *Candida albicans* and *Aspergillus fumigatus* [2]. DNA was isolated from clinical samples with identified fungal infections and cultivated fungi from agar plates. We used unpurified PCR-products for the detection experiments. After performing PCR, the covalent labeling of pyrimidine bases was performed by means of [OsO_4(bipy)]. The successful hybridization of the labeled target-DNA and the immobilized capture probes on the gold electrode resulted in square-wave voltammetric signals. This way, we were able to detect DNA from *Candida albicans* and *Aspergillus fumigatus* in the respective real samples.

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1818

SI27-Po

Study of lead ion complexation process with mercaptosuccinic acid on piezoelectric device

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High concentrations of toxic heavy metals such as lead and cadmium in landfill and other waste streams has lead to a keen and sustained interest in analytical techniques to monitor and quantify their presence in the environment. Particular attention has focused on reliable, portable and rapid sensing mechanisms for field measurements that require minimal calibration. Here we describe an approach for the determination of lead ions in aqueous solution using electrochemical quartz crystal microbalance methods. A gold coated QCM crystal surface is first modified with a self assembled monolayer of mercaptosuccinic acid (MSA). This has the ability to bind metal ions such as Cd^{2+} and Pb^{2+} enabling simultaneous detection of metals *via* frequency changes (Δf) associated with added mass, as well as the electrochemical redox response. Hence we describe an investigation of lead complexation behavior with MSA-modified gold electrodes conducted using electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry (CV) techniques. We investigate stability of the monolayer assemblies, preconcentration effects and the influence of pH on complexation and analytical performance. Thermodynamic parameters, such as the Gibbs energy and binding constant, were determined by fitting experimental data to selected adsorption isotherms.

The Evans Corrosion Symposium

EC1

Atmospheric Corrosion of Stainless Steel Studied with Inkjet-Printed Salt Deposits

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It has recently been shown that inkjet printing of salt patterns can be used to study atmospheric corrosion of metals.[1, 2] An inkjet printing method has been used to deposit salt patterns on stainless steel surfaces with controlled deposition area and chloride density. The samples are placed in a controlled humidity environment and undergo deliquescence, forming droplets where atmospheric corrosion can take place.

In this presentation, variation in the deposition area will be used to explore the effect of cathodic area and the effect of chloride deposition density at fixed relative humidity will be used to assess the effects of oxygen reduction and droplet resistance. A new technique for depositing mixed salt droplets by using two different cartridges will also be shown .

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EC2

Measurement and Modeling of Pitting Corrosion of Stainless Steel for Radioactive Waste Containers During Storage

Majid Ghahari[1*], Trevor Rayment[2], Nick Laycock[3], Donal Krouse[4], Cristiano Padovani[5], Rajmund Mokso[6], Marco Stampanoni[6,7], Alison Davenport[1]

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*speaker

Stainless steel containers are currently used for storage of intermediate level radioactive waste (ILW) in the UK. In order to support evaluation of the integrity of the containers during interim storage under atmospheric corrosion conditions, it is necessary to understand the mechanism of propagation of corrosion pits to underpin the development and validation of corrosion prediction models. In the first stage of this process, results from synchrotron X-ray imaging of 2D pits grown at the edge of 304 stainless steel foils under full immersion conditions are used to demonstrate that numerical simulations based on 2D finite element modeling are able to reproduce the characteristics of pit growth under potentiostatic and galvanostatic conditions. Stainless steel 304L is often used for relative thick parts of waste containers (e.g. lid flange), and prediction of its long term corrosion performance is likely to represent a conservative case relative to the more corrosion resistant grades (e.g. 316L) that are used for other parts of the containers.

The pit propagation model used in the present study is based on the work of Laycock and coworkers (1, 2), who have developed a 2D finite element model for pit propagation. The model calculates the local current density flowing at each point along the perimeter of the pit as a function of the potential and metal ion concentration in the adjacent solution. Anodic and cathodic kinetics (as functions of potential and chemistry), salt film precipitation, and ionic transport by diffusion and migration are each considered explicitly. In each iteration of the model, the simulation procedure is to calculate (or measure) the anodic current density on the pit surface at time t, allow ionic transport in the solution over a period Δt, move the pit boundary as a result of the dissolution, calculate the new pit solution chemistry at time $t + \Delta t$, and then repeat this sequence. Using this approach, the model is able to successfully simulate formation of the characteristic “lacy cover” found over stainless steel pits (3).

Ernst et al. (3) used video microscopy to demonstrate how 2D pits can propagate from the edge of stainless steel foils. In the present work, higher resolution images have been obtained using synchrotron radiography (at the TOMCAT beamline at the Swiss Light Source) to monitor pit propagation under both potentiostatic and galvanostatic control. Electrochemical data extracted from the radiographs are now being used to refine the model and provide improved input parameters.

Acknowledgements
This work was supported by the UK Nuclear Decommissioning Authority under contracts NR 3331 and NR 3274, EPSRC grant EP/E045464/1 and by the New Zealand Foundation for Research Science and Technology under contract 8X0409.

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EC3

Benzotriazole corrosion inhibition on nickel-aluminium bronzes

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Benzotriazole (BTAH) is an effective corrosion inhibitor for copper [1] and copper based alloys in aqueous chloride solution [2].

The mechanism by which BTAH inhibits corrosion on copper-based materials has been related to the formation of a complex-polymeric structure composed of BTA^- anions and Cu^+ ions. The high chemical affinity of BTAH molecule towards copper ions has been indicated as the main reason behind its superior anticorrosion properties [1], with reported values of adsorption free enthalpy energy ranging from 25 kJ mol^{-1} [1] to 47 kJ mol^{-1} [3] depending on the conditions of the investigated systems.

Nickel-aluminium bronze (NAB) has been extensively used for ship propeller and marine heat exchanger/condenser system. NAB has also been widely employed in the manufacture of values, tube plates, strainer, bodies and pump casting, shafts and impellers [4].

Few studies have been reported in literature concerning the corrosion inhibition of BTAH on NAB materials in aqueous chloride solutions. This work is focused on the BTAH corrosion inhibition on NAB by mean of potentiodynamic polarisation (PP), electrochemical impedance spectroscopy (EIS) and chronoamperometry (ChA) techniques in 0.6 M NaCl electrolyte solution. Mechanism of BTAH adsorption process was assessed considering a number of diverse adsorption isotherms, such as Langmuir, modified Langmuir and Frumkin isotherms. However, among them the best adsorption description was provided by the modified Langmuir isotherm.

In summary, in this research work, electrochemical techniques such as PP, EIS and ChA aimed to give a better understanding of the BTAH inhibition properties on NAB substrates in chloride environment.

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EC4-K

Title: Corrosion protection coatings for TATA Long Products

Dr Siva Bohm, Mr Phil Checkley & Dr Mallika Bohm

TATA steel produces steel plate for the ship industry, coated with a zinc-based primer. The primer provides corrosion protection, is over-coatable and does not interfere with welding and cutting processes in the shipyards. As Zinc price rocketing sky high cost reduction in zinc silicate pre-fabrication primer, one of very few coatings used by Long products was very attractive.

Replacing 5-10% of zinc without reducing its effectiveness as a pre-fabrication primer was an attractive idea. An ideal material should have enhanced connectivity between the zinc particles with the ability to charge transfer, and the environmentally friendly clay was there at low cost. Laboratory testing demonstrated an improvement in corrosion protection factor of two.

Development work showed very promising results; addition of ion-exchanged clay has significantly improved durability, weldability and cutting speed. Results were patented (EP 1479736 A1) and up-scaling was progressed. Both the exfoliation and cation loading of the clay particles influence the efficiency of coating. Conclusion is that the high surface area of clay particles play an important role on the corrosion protection of steel.

EC5

Castner Medal Presentation (SCI HQ, London, 4 August 2011)

The Castner medal and lecture are given biannually, to recognise the achievements of an authority on applied electrochemistry. The prize is named after Hamilton Castner, who was himself a pioneer in the field of industrial electrochemistry. He developed a better process for the manufacture of caustic soda, by electrolysis of brine in the mercury cell (patented in 1892).

The recipient of the 2011 Castner Medal is Prof Maria Skyllas-Kazacos of the University of New South Wales, Australia. Maria clearly demonstrates the attributes of a Castner Medal recipient, with interests spanning metal extraction, electrode materials, membranes, and perhaps most famously her work on the vanadium redox flow battery. This invention is now regarded as one of the most feasible technologies currently available for efficient energy storage, to help in the global reduction of fossil fuel consumption and greenhouse gas emissions.

From early in her research career, Maria had a particular concern about the environment. She has commented:

"I really wanted to do something that I could see as important for the environment and for society. As a physical scientist, I suppose that the most important social contribution you can make is to the environment – particularly from my own area of expertise as distinct from the medical or other social areas."

Prof Skyllas-Kazacos has a vast amount of research experience. Her work to date has led to the authoring and filing of 250 publications and patents.

For further information about the medal recipient, please see:
http://www.science.org.au/scientists/interviews/s/msk.html

The SCI Electrochemical Technology Group presented the Castner Medal to Prof Skyllas-Kazacos at a special ceremony held at SCI HQ (London, 4 August 2011). A video of her lecture will be shown at Electrochem 2011 (Bath, 5-6 September 2011).

Dr Pauline Allen
ViceChair, SCI Electrochemical Technology Group

EC6-Po

Combinatorial Electrochemical Corrosion Screening of Library Ni-Cr Thin Film Alloys Prepared by High-Throughput Physical Vapour Deposition

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In order to investigate the influence of alloy composition on the rate of corrosion, a combinatorial approach developed based on the high throughput physical vapour deposition (PVD) of the alloys combined with on chip (100 electrode) electrochemical screening methods. Results are presented for Ni-Cr alloys over wide compositional range. Films were characterized by using X-ray diffractometry (XRD) and energy dispersive X-ray spectroscopy (EDS). Evidence of the σ metastable phases in the Ni-Cr film alloys was found, and its composition range was defined. A preferred orientation was observed in Ni-Cr film alloys from nickel rich alloys. Corrosion measurements, conducted in phosphoric acid [pH 3], were made by a parallel combinatorial electrochemical screening of the polarization resistance and zero current potential. The σ metastable phases could be responsible for considerable enhancement in the corrosion resistance of Ni-Cr film alloys.

EC7-Po

Corrosion of some Ni-Cr dental alloys in artificial saliva containing various amounts of fluoride at different pH values.

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Nickel based alloys are used in dental industry for making dental prosthesis. The degradation of these alloys could have a potentially harmful effect on human health. The corrosion of dental alloys can be defined as the rate which the metal ions are released into the oral cavity. Corrosion also causes a reduction in mechanical properties in materials and shortens its lifetime. In dentistry, chromium is added to the nickel alloys, because increasing the amount of chromium in the alloys modifies the corrosion resistance of the nickel. In small quantities nickel is essential, but when the uptake is too high, it can become a danger to human health. An uptake of large quantities of nickel can have consequences such as lung embolism, heart disorders, birth defects, asthma and allergic reactions such as skin rashes (often from jewellery). Fluoride is very reactive and is a corrosive halide which is readily available in everyday life. Typical sources include toothpastes with fluoride additions for preventing tooth decay and mouth wash formulations. Regular contact of these ions with dental alloys have detrimental effects on the alloys and can cause increased corrosion and thus nickel ion release into the host body. This project is aimed at gaining a better understanding of the corrosion of a nickel-based dental alloy under the influence of aggressive halide ions, as well as several other conditions and/or alloy modifications that can influence the process.

Four different alloys with varying nickel and chromium contents were immersed in eight different concentrations of artificial saliva with sodium fluoride. These alloys were left immersed for periods of 1 day, 2 days, 7 days and 28 days in solutions of pH 5 and pH 7. The techniques that have been used to analyse the results include mass loss, graphite furnace atomic absorption spectroscopy (GFAAS), Raman Spectroscopy and potentiodynamic polarization methods. The mass loss technique included weighing the alloys before and after exposure to the artificial saliva solution for the set time period. These solutions were also analysed by GFAAS to see how much nickel had been released into the solution. Raman Spectroscopy was used to analyse sample surfaces after corrosion, while potentiodynamic polarization scan were employed to calculate the different rates of corrosion for each alloy.

The mass loss techniques in addition to the results of the GFAAS showed that alloy composition played a role in nickel release, while the potentiodynamic polarization results indicated that the alloy with the highest nickel concentration underwent the most corrosion or nickel release rate. Increased concentrations of fluoride and lower pH value solutions give higher corrosion rates. The higher chromium contents of alloys 1 and 2, as compared to 3 and 4, had a beneficial effect in lowering the corrosion rate.

Inorganic & Molecular Electrochemistry Symposium

IM1K

Donor-Acceptor Systems and Electron Transfer-Induced Reactivity

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Donor-acceptor systems based on d^8 metal centers have been studied due to their intriguing photophysical properties and their possible use in harnessing solar energy [1]. Catecholates/amidophenolates as well as phenylazopyridines are typical examples of non-innocent ligands [2]. In this contribution we will present donor-acceptor systems based on Pd(II) and Pt(II) as depicted in Figure 1 [3]. Results obtained from electrochemical and UV-vis-NIR and EPR spectroelectrochemical investigations will be presented and these data will be used to elucidate the electronic structures of the complexes. Additionally, studies on ligand redox-induced reactivity at metal centers will be discussed and the relevance of such studies for H_2 activation will be presented. Our efforts at using electrons from ligands for activating small molecules at metal centers will be the focus of this contribution. The use of DFT studies to corroborate the experimental results will also be discussed.

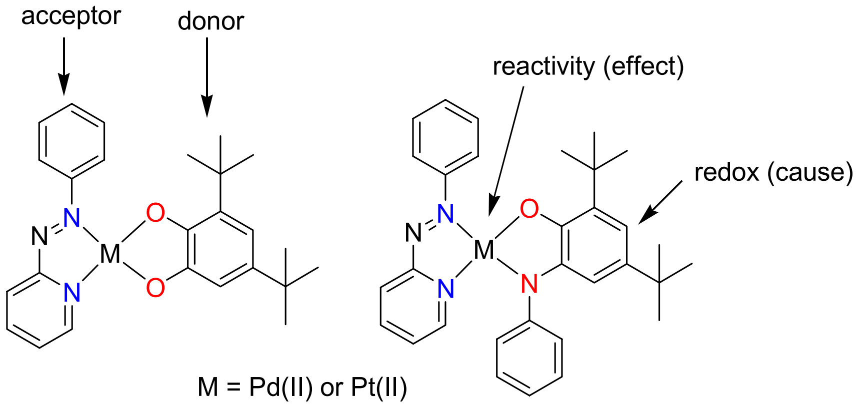

Figure 1. Sketch of molecules.

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IM2K

Attachment of redox-active Ru complexes to gold surfaces

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We describe a method of attaching $[Cp^*RuCl_2]_2$ derivatives to gold surfaces using dithiocarbamate bridging ligands. The method lends itself to producing not only redox active monolayers but also additional multilayers on top. We also describe theoretical calculations on the interaction of Ru complexes with gold surfaces.[1]

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IM3K

Polynuclear ruthenium(II) complexes displaying electrochromism and solvatochromism: redox and spectroscopic behaviour

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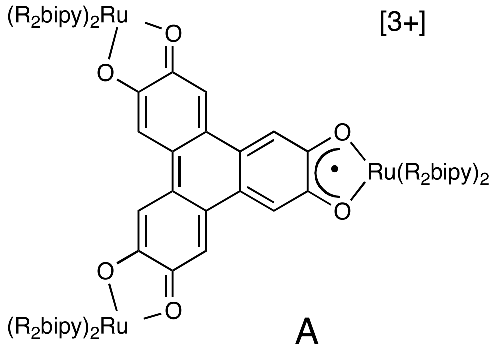
This talk will describe studies on two different classes of polynuclear Ru(II) complex. In the first (**A**), extensive ligand-centred redox behaviour results in redox chains containing up to seven members in which variations in near-IR charge transfer bands in the electronic spectra result in redox-switchable near-IR absorbance (electrochromism) in thin solid films [1]. In the second (**B**), the strong sensitivity of the Ru(II)/Ru(III) couple to changes in solvent results in a dinuclear complex in which the redox potentials and hence the degree of electronic coupling between metal centres is solvent dependent, such that the Ru(II)-Ru(III) mixed-valence state exhibits class II behaviour in water but class III behaviour in CH_2Cl_2 [2].



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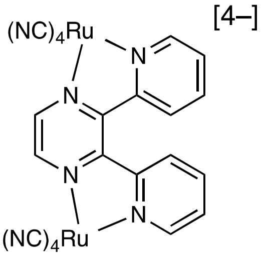

B

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IM4

Electrocatalytic CO_2 Reduction with Manganese and Osmium Carbonyl Complexes

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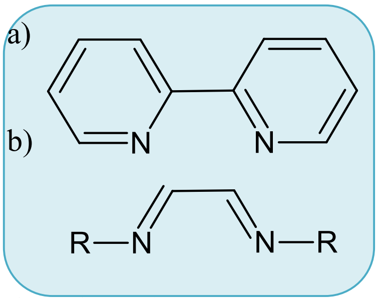
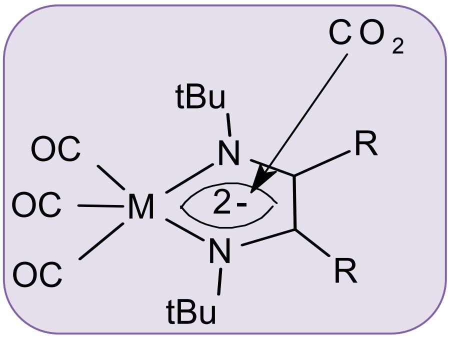
In our laboratory we study complexes that have applications in electro- and photocatalytic reduction of CO_2. These include novel mononuclear complexes which feature affordable and environmental-friendly metals centres and proton-bearing redox-active ligands, and oligonuclear systems with multiple reaction sites. Of these, we present the manganese equivalents of the well known *fac*-$[Re(CO)_3(\alpha\text{-diimine})X]$ (X=halide) catalyst precursors, and the osmium complexes, *trans*-(Cl)-$[Os^{II}(CO)(bpy)(PrCN)Cl_2]$ (PrCN = butyronitrile) and *mer*-$[Os^{III}(CO)(bpy)Cl_3]$.

Cyclic voltammetry and spectroelectrochemical experiments have shown that $[Mn(CO)_3(bpy)]^-$ is inactive toward CO_2, in contrast to $[Mn(CO)_3(tBu\text{-}DAB)]^-$. The non-aromatic nature of the formally 2e-reduced tBu-DAB ligand allows it to form a reactive π-delocalised metallacycle reacting with CO_2 to produce the formato complex, *fac*-$[Mn(CO)_3(tBu\text{-}DAB)(CO_2H)]$. Efficient CO gas development is observed upon further reduction of the formato complex. Preliminary results on the photochemical generation of the five-coordinate catalyst will also be presented.

trans-(Cl)-$[Os^{II}(CO)(bpy)(PrCN)Cl_2]$ and *mer*-$[Os^{III}(CO)(bpy)Cl_3]$ can both be electrochemically reduced to form chains $[\{Os^0(CO)(bpy^{\bullet -})(PrCN)\}^-]_n$ which are capable of catalysing the reduction of carbon dioxide. Comparative spectro-electrochemical studies reveal the true oligomeric catalyst nature.



butadiene (R-DAB; R = tBu, iPr)



IM5K

Ferrocenyl-Functionalised Catalysts for Redox Control and Switching

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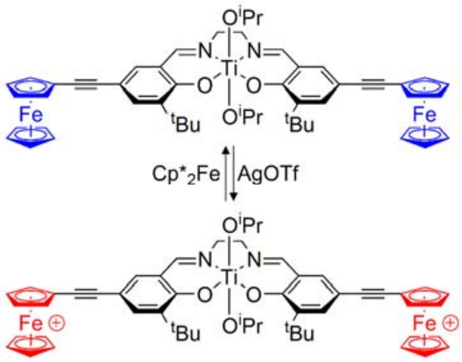
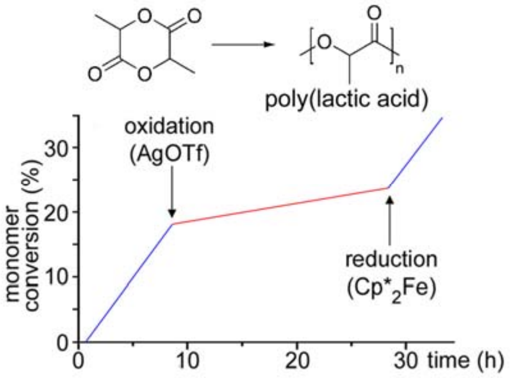
Incorporation of a redox-active functionality within a ligand framework potentially allows the reactivity and selectivity of complexed metal centres to be modulated through either chemical or electrochemical switching of the redox centre(s). [1] To date, the application of redox switchable catalysts in single-site polymerisation catalyst technology has not been fully demonstrated, yet it offers a number of attractive and potentially technologically significant advantages. For example, oscillating a catalyst through oxidised and reduced forms should allow the activity of the active site to be modulated, by changes to the electrophilicity of the active centres.

A key component of such a catalyst is a substitutionally inert redox-active ligand. We identified that ferrocenyl-functionalised derivatives would be suitable candidates and also rationalised that derivatisation of the bis(iminophenoxide) (salen) family could be important as this ligand class has enjoyed widespread usage in polymerisation catalysis. With these novel ligands and their subsequent metal complexes we have established that redox switches may be used to attenuate the activity of single-site polymerisation catalysts. Thus, a titanium-based lactide polymerisation initiator supported by a ferrocenyl-substituted salen ligand exhibits a substantially higher rate of propagation than its oxidised dicationic ferrocenium analogue. The reversibility of the redox event is demonstrated by treatment with chemical redox reagents. [2, 3] These, and other ferrocene-containing catalysts [4] (including diimines and phthalocyanines) will be discussed and expanded upon in the presentation.





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IM6K

Applications of weakly coordinating electrolytes in organometallic electrochemistry

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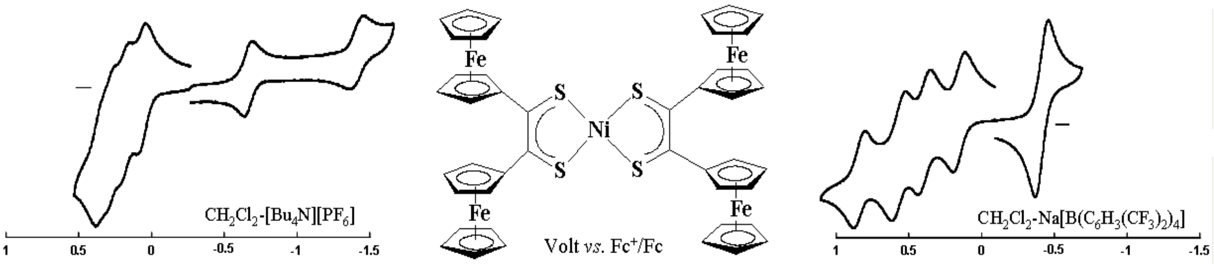
Organic electrolytes based on large, lipophilic, weakly nucleophilic and weakly coordinating anions of the perfluoronated aryl borates-type have opened an extended window for the study of electroactive molecules, in particular in organometallic electrochemistry. Selected examples from the literature will be discussed to illustrate the effects of this new generation of supporting salts in terms of thermodynamic, kinetic and practical applications.

The thermodynamic effects (see Figure) will be discussed with examples where the potential difference between two consecutive reversible electron transfer steps may be finely tuned and controlled with the properties of the electrolyte (solvent, anion and cation of the supporting salt).

The kinetic effects relates to the stabilization of positively charged species that were too reactive to be studied in usual, more nucleophilic, standard electrolytes.
The other practical applications of weakly coordinating anions for electrochemistry include solubilization of highly charged species and access to solvents of very low polarity for standard electrochemistry.
Finally, the quest for the most weakly coordinating medium for electrochemistry will be addressed with references to other salts and solvent properties.



W. E. Geiger, F. Barrière
"Organometallic Electrochemistry Based on Electrolytes Containing Weakly-Coordinating Fluoroarylborate Anions"
***Accounts of Chemical Research,* 2010,** 43, 1030-1039.

IM7K

Mark Whiteley

University of Manchester

Redox Chemistry and Electronic Structure of Molybdenum Alkynyl Complexes

The redox chemistry of organometallic metal alkynyl (acetylide) complexes, M-C≡CR, has attracted extensive current research directed towards the development of molecular materials with applications in electronic, magnetic and optical devices. Central to these applications is an understanding of the degree of electronic interaction between the metal centre and the alkynyl ligand; this can be controlled by the identity of the supporting metal group.

This presentation will review three related, half-sandwich metal alkynyl systems:

$[M(C\equiv CR)L_2Cp]$ (M = Fe, Ru, L_2 = P-donor ligand),
$[M(C\equiv CR)L_2(\eta\text{-}C_7H_7)]$ (M = Mo, W; L_2 = P-donor ligand), and
$[Mo(C\equiv CR)(CO)L_2Cp]$ (L_2 = P-donor ligand),

which illustrate the effects of variation of transition metal series, ring size and molecular geometry upon redox chemistry and electronic structure.

The redox chemistry of these systems will be outlined and compared using a series of experimental techniques (cyclic voltammetry, IR-spectroelectrochemistry, EPR spectroscopy) and the observed behaviour correlated with electronic structure as determined by DFT theory calculations.

IM8K

Ligand Redox Non-innocence in Open-Shell Transition Metal Catalysis

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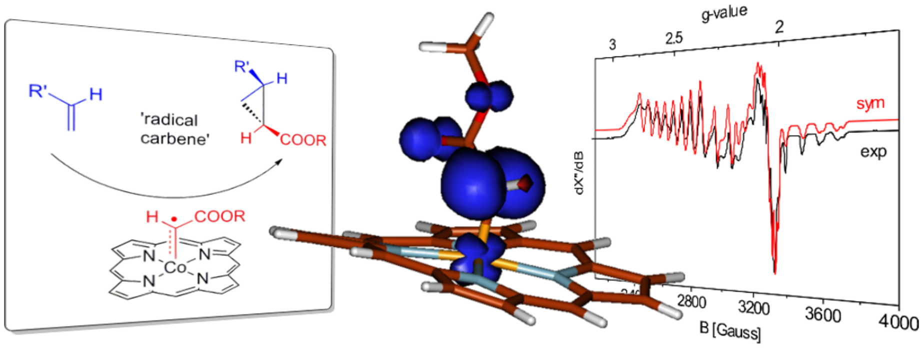
Organometallic compounds of Co, Rh, Ir metals are abundantly used as catalysts for a variety of important transformations in industry and academic research laboratories. Our current understanding of the organometallic reactivity of these metals is however mainly based on studies of diamagnetic complexes, while much less is known about the structure, reactivity and properties of their *paramagnetic* analogs.

Interest in the properties and reactivity of such paramagnetic species is rising within the organometallic community. This is triggered by the idea that such species might play an important and active role in the catalytic reactivity of these metals.[1] Special interest in open-shell organometallic species comes from their expected higher and different reactivity compared to their closed-shell counterparts, and these 'metallo-radical complexes' may well allow us to steer and control a variety of new radical-type reactions. This is partly inspired by the special bond-activation mechanisms of several metallo-enzymes, where ligand radicals actively participate in a catalytic cycle around the transition metal. [2,3,4]



This contribution focuses on the role of paramagnetic intermediates in the (catalytic) reactivity of (electrochemically generated) oxidation state +II group 9 transition metals, with a focus on the redox non-innocence of olefin-, carbene- and nitrene ligands. Reactivity studies, EPR spectroscopy and complementary DFT calculations are used to unravel the open-shell pathways of the paramagnetic Co^{II}, Rh^{II}, and Ir^{II} species.

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IM9K

How spectroelectrochemical techniques can help you

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In situ variable temperature spectroelectrochemical techniques are invaluable tools for probing the electronic character of the frontier orbitals of redox-active compounds. The spectroelectrochemical cell designs for use with uv/vis/nir spectrometers and for use in X-, Q- and W-band EPR spectrometers will be presented. The use of the cells will be demonstrated by the *in-situ* generation of organic free radicals in fluid and frozen media, transition metal ion complexes and biological enzymes.

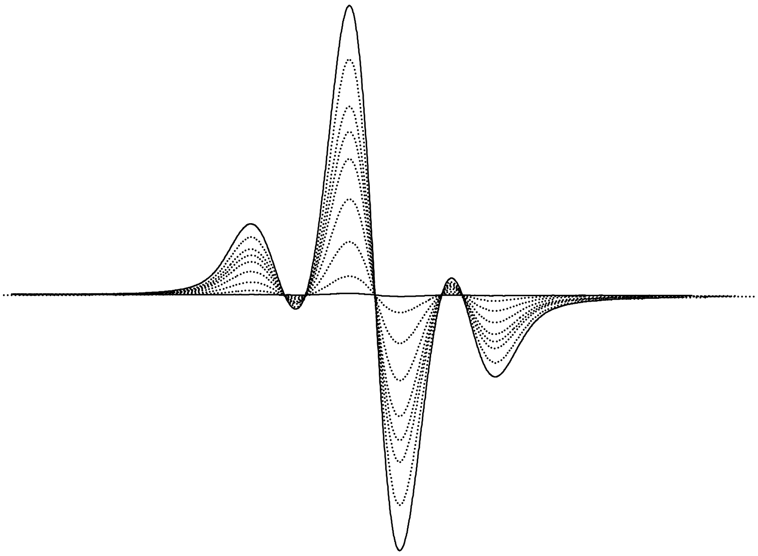

Figure 1. *In situ* electrogenerated EPR spectra of paramagnetic $[Pt(bpy)Cl_2]^{1-}$, bpy = 2,2’-bipyridine

IM10K

Proton-coupled Electron Transfers. Concerted processes in chemistry and biology: a joint electrochemical and photochemical approach

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Proton-coupled electron transfers (PCET) are omnipresent in natural and artificial chemical processes.[1] Understanding mechanisms and activation-driving force relationships, which underlie their practical efficiency, is a timely task in front of contemporary challenges concerning energy conversion, depollution and development of high-performance sensing. "CPET" reactions, in which proton and electron transfers are concerted, have the advantage of by-passing the high-energy intermediates of the stepwise pathways, even though this thermodynamic benefit may have a kinetic cost.[2,3]

In this context, a series of studies devoted to the oxidation of phenols, with, as proton acceptor, either an attached nitrogen base or water (in water as solvent), will be discussed.[2-4] The possibility that electron transfer, heavy-atom bond breaking and proton transfer may all be concerted will also be presented with the electrochemical cleavage of an O-O bond of an organic peroxide.[5] These examples reveal general features of PCET reactions that may serve as guidelines for future studies, among which emphasis should be put on new biological systems on the one hand and on molecular systems able to activate small molecules (e.g. H_2O, H^+, CO_2) on the other.

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IM11

Guilty as Charged: The case for redox non-innocence in bimetallic ruthenium complexes

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The 1,4-diethynylbenzene motif comprises one of the prototypical backbones used in the construction of conjugated organic and organometallic compounds and materials, and features prominently in early studies of ligand-bridged bimetallic complexes $[\{ML_n\}(\mu\text{-}B)\{ML_n\}]$. It is now well-established that the nature of the frontier orbitals in $[\{ML_n\}(\mu\text{-}B)\{ML_n\}]$ systems and associated redox products vary with the nature of the metal and supporting ligands from largely metal to predominantly ligand in character. Thus, it is possible to design complexes $[\{ML_n\}(\mu\text{-}B)\{ML_n\}]$ which undergo one-electron redox processes at a metal center to yield a mixed-valence system, or which exhibit redox non-innocence in the bridging ligand. Although mixing of orbital character between the metal and ligands can make clear assignments difficult, it is common for the redox products derived from $[\{ML_n\}(\mu\text{-}B)\{ML_n\}]$ systems to be described as belonging to either of these extremes. In the present work, a combination of UV-Vis-NIR and IR spectroelectrochemical methods and Density Functional Theory (DFT) have been used to demonstrate that one-electron oxidation of compounds $[\{Ru(dppe)Cp^*\}_2(\mu\text{-}C\alpha CArC\alpha C)]$ ($HC\alpha CArC\alpha CH$ = 1,4-diethynylbenzene; 1,4- diethynyl-2,5-dimethoxybenzene; 1,4-diethynylnaphthalene; 9,10-diethynylanthracene) yields solutions containing radical cations that exhibit characteristics of both oxidation of the diethynylaromatic portion of the bridge, and a mixed valence state. The simultaneous population of bridge-oxidised and mixed-valence states is likely related to a number of factors, including orientation of the plane of the aromatic portion of the bridging ligand with respect to the metal d-orbitals of appropriate π-symmetry.

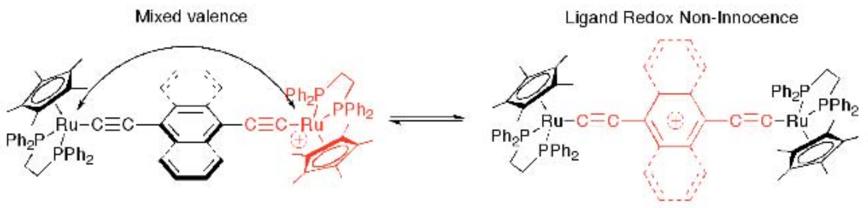

Figure 1. Bridging ligand orientation can play a substantive role in tuning the electronic properties of bimetallic radical cations.

IM12K

Ferrocenyl-based Transition Metal Complexes: Synthesis, Structure, Bonding and Spectro-Electrochemistry

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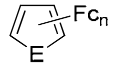
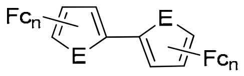
The synthesis, structure, reaction chemistry and reactivity of type A - E molecules featuring two or more redox-active organometallic termini will be envisaged. Main focus will be directed to the electrochemical and spectro-electrochemical properties of these molecules. Where appropriate, possible applications will be presented and mechanism for generation and reactions will be reported.

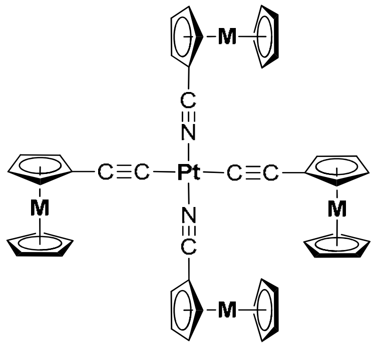


A [1]



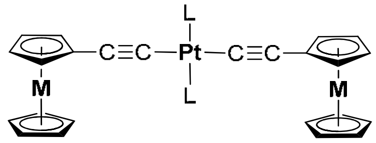
B [2]

E = O, S, NR, **Ti**Cp_2, **Zr**Cp_2
Fc = **Fe**(η^5-C_5H_4)(η^5-C_5H_5)
n = 1, 2, 3, 4



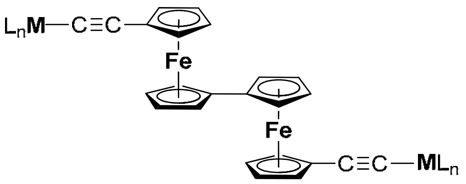
M = **Fe**, **Ru**

C [3]



L = $P^nBu_{3-n}Fc_n$ (n = 1, 2, 3)
M = **Fe**, **Ru**

D [4]



L_nM = **Ru**(η^5-C_5H_5)(Ph_3P)$_2$, **Os**(η^5-C_5H_5)(Ph_3P)$_2$,
Ru(η^5-C_5H_5)(dppf), **Fe**(η^5-C_5Me_5)(dppe)

E [5]

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IM13K
Density Functional Theory: A Tool for the Prediction of Redox Properties for Heteroaromatics

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Redox-active and photoactive oligomers and polymers based on heteroaromatics such as pyrroles, indoles and carbazoles have received a great deal of attention in recent years. Typically these form extended π-conjugated thin film materials which can display semiconducting to conducting electronic conductivity, efficient luminescence and redox activity combined with relatively low cost, good processability and mechanical properties and the ready tuning of properties through chemical functionalisation. This makes them suitable for a variety of applications, including the active film in organic electronic devices, sensors and supercapacitors and in electroluminescent materials.

The traditional synthesis of novel heteroaromatics can often be a complex process, with large expenditure in lab hours and chemical costs. The continuing advance in computational power at affordable cost levels now provides the opportunity to consider using computational methods as a screening method for the calculation of heteroaromatic properties, allowing a quick analysis of e.g. the redox properties to identify candidates for electrochemical applications, without the need for synthesis.

A DFT computational method for the calculation of redox properties of heterocycles will be discussed. This has been shown to enable the calculation of redox potentials of heteroaromatics in solution with excellent accuracy [1]. The method has also been used to determine heteroaromatic electron spin density distributions and enable the successful prediction of coupling positions [2]. The extension of this method to as yet unsynthesised heteroraomatics could allow the prediction of their oxidation potentials and the nature of the materials formed from their coupling. This method may in future provide a powerful tool in the identification of monomers best suited to the formation of useful redox-active materials without the need for extensive trail and error organic synthesis.

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IM14K
π-Dimerization of Pleiadiene Radical Cations

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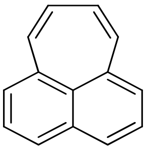
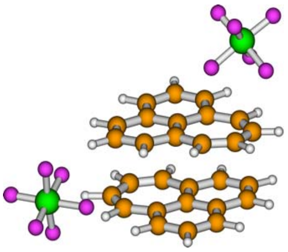
One-electron oxidation of the non-alternant polycyclic hydrocarbon pleiadiene in THF produces corresponding radical cations detectable in the temperature range of 293-263 K only on the subsecond time scale of cyclic voltammetry. Although the EPR-active red coloured pleiadiene radical cation is stable, according to the literature, in concentrated sulfuric acid, our spectro-electrochemical measurements provide a convincing evidence for its facile conversion into the green coloured, formally closed shell and hence EPR silent π-bound dimer dication stable in THF at 253 K. The unexpected formation of the thermally unstable dimeric product featuring a characteristic intense low-energy absorption band at 673 nm (1.84 eV; $\log\varepsilon_{\max} = 4.0$) is substantiated by *ab initio* calculations on parent pleiadiene and the PF_6^- salts of the radical cation and dimer dication. The latter is stabilized with respect to the radical cation by 14.40 kcal mol^{-1} (DFT-B3LYP) [37.64 kcal mol^{-1} (CASPT2//DFT-B3LYP)]. An excellent match has been obtained between the experimental and TD-DFT calculated UV-Vis spectra of the PF_6^- salt of the pleiadiene dimer dication, considering the solvent (THF) effects. Our results present a new view on the anodic behaviour of non-alternant polycyclic hydrocarbons.


pleiadiene


pleiadiene π-dimer dication (PF_6^- salt)

IM15

Redox Non-innocence in Ruthenium Vinyl complexes

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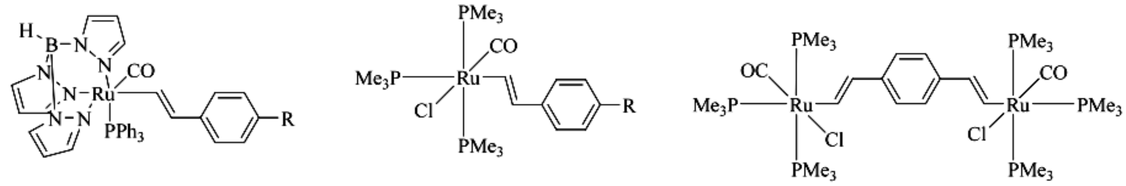
In the emerging field of molecular electronics, complexes with two or more transition metal moieties bridged by a π-conjugated carbon rich ligand have received a lot of attention as models of wire-like systems.[1] The examination of electronic interactions between redox sites have led to extremes of behaviour being reported. For example, in [{Fe(dppe)(Cp*)}2(μ-C≡CC6H4C≡C)] a metal oxidation occurs,[2] whilst a ligand oxidation has been reported in [{RuCl(dppe)2}2(μ-C≡CC6H4C≡C)].[3]

These contrasting differences arise from differences in the nature of the M-C≡C bond, and consequently attention is now being paid to alternate metal-bridge linkages.[4-5]

We report here ruthenium vinyl complexes of the general form
Ru(CH=CHC6H4R)(CO)(PPh3)Tp (**1**) [R = Me, NO2, CO2Me, OMe],
Ru(CH=CHC6H4CH3)(CO)Cl(PMe3)3 (**2**)
and bimetallic [{Ru(CO)Cl(PMe3)3}2(μ- CH=CHC6H4CH=CH)] (**3**).

Results from IR spectroelectrochemistry and DFT studies are consistent with extensive ligand redox character in both cases.[6]



(1) (2) (3)

Figure 1. Complexes synthesised in this study.

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IM16-Po

Metal dithiocarbamates: investigating their potential as mediators for microbial fuel cells

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Microbial Fuel Cells (MFC) use microbes such as bacteria as catalysts to extract electrons from biomass for power. In a MFC, electron transfer from microbes to the anode can occur directly or via a mediator. The mediator is reduced by the microbe and oxidized at the anode. The initial focus of this investigation was to study the electrochemistry of a variety of metal dithiocarbamate (dtc) compounds in the hope of identifying one or more that may be suitable for use as a MFC mediator.

In a MFC the mediator must be soluble in aqueous environment but also hydrophobic enough to penetrate cell membranes in order accept electrons from enzymes within the membrane. These different environments may influence the redox potentials of the dtc complexes as well as electron transfer rates and relative stabilities of oxidized and reduced forms of the mediator. This prompted us to study the electrochemical response of the metal dtc complexes in various solvents.

Thus, as well as attempting to find an ideal mediator in terms of suitable potential, a study was conducted using cyclic voltammetry to gain an insight into:

i. How solvent identity affects metal dtc electrochemical behaviour, in particular how this may influence how these complexes behave both in polar (aqueous) and non-polar (intra-membrane) environments.
ii. How the identity of the metal centre (e.g. Cu, Ni, Fe) affects metal dtc electrochemical behaviour in terms of electrode potential, reaction mechanism and stability.
iii. How the chemical identity of the dtc ligand influences the electrochemical response of the complex and whether we can use this information to tune the redox potential of the mediator.

As well as meeting the above objectives, it was hoped that this study would shed more light on more fundamental chemical principles such as the reasons why metal dithiocarbamates show varying electrochemical behaviour in different solvents.

IM17-Po

“Inverse” Mixed Valence Complexes

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Over recent decades the study of conjugated organic and organometallic systems has become an important topic of chemical research. One of the major contributing factors in this interest is the redox active nature of these systems, and the ability for such systems to undergo facile inter- and / or intra-molecular electron transfer (ET) processes as well as their non-linear optical properties [1]. Introduction of one or more metal centres in the conjugated system provides further redox active sites and opportunities to moderate or augment ET processes. Such systems have been studied for many different applications including photochromic systems [2], as components in future molecular electronics technology [3], and in present day and near-future technology in the form of charge transport and injection materials.

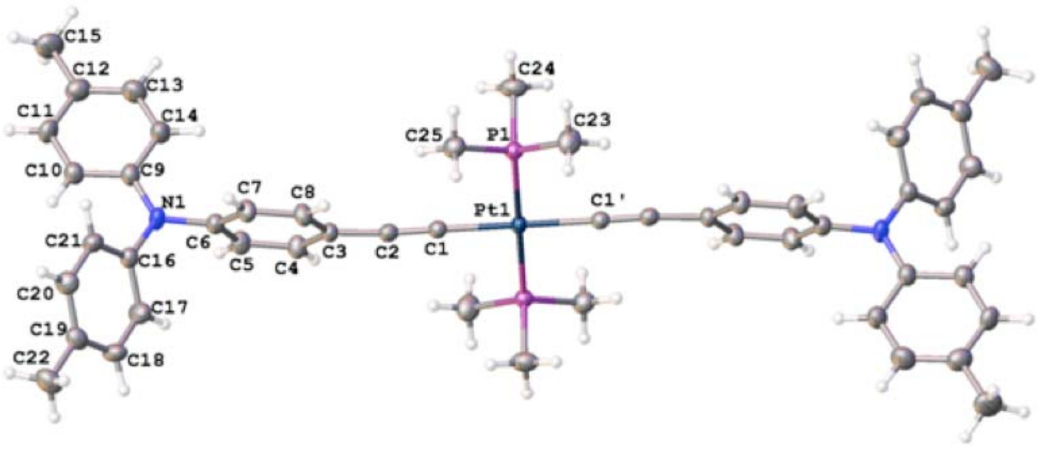

Figure 1: Molecular structure of *trans*-Pt(PMe3)2(C2C6H4NTol2)2 as determined by X-ray crystallography

We report here the electrochemical analysis of *trans*-Pt(PR3)2(C≡CC6H4Ntol2)2, (PR3 = PMe3, PEt3, PPh3; tol = tolyl) and *cis*-Pt(dppe)(C≡CC6H4Ntol2)2. We have investigated the effect of changing the phosphine ligand on the oxidation potentials of the wire like systems.

Comparative studies with structurally related *trans*-Ru(C≡CC6H4Ntol2)2(dppe)2 highlights the critical role of the metal atom in determining the nature of the oxidation events in these systems.

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IM18-Po

Structural and Electrochemical Characterization of Some Bis(ferrocenyl)alkynyl Complexes

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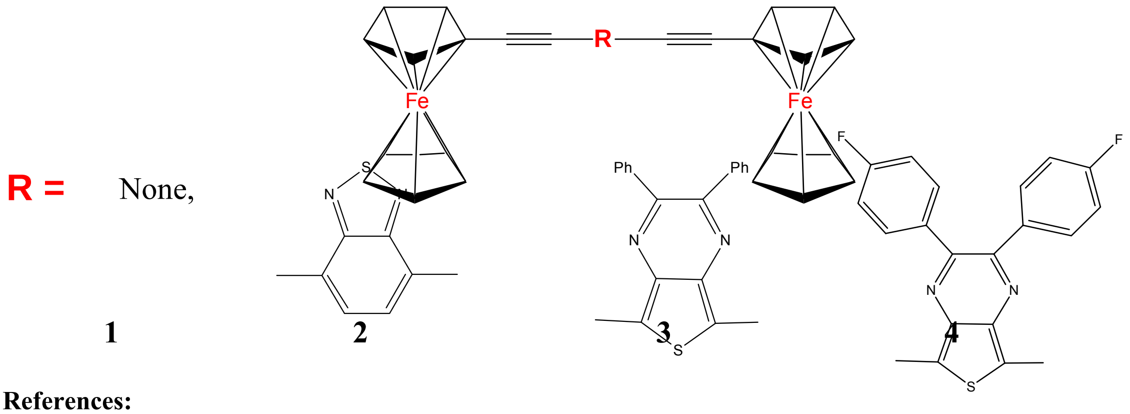
Alkynyl ligands with conjugated spacer groups are well known to generate extensive delocalization [3] between metal centers of similar oxidation potential [4]. Variation of the conjugated spacer groups in Bis(ferrocenyl) complexes allow tuning of the electronic and steric features[1-2]. We have synthesized a series of new bis(ferrocenylethynyl) complexes Fc-C=C-R-C=C-Fc where R = none (1), benzothiadiazole (2), theienopyrazine (3) and diflurothienopyrazine (4). The cyclic voltammograms of **1-4** were recorded at various scan speeds (10-2000 mV s^{-1}) over the range from -1000 to 2000 mV. All the complexes can be reversibly oxidized and reduced with position of the oxidation and reduction peaks only slightly dependent on scan speed. In the case of **1** two overlapping oxidation waves were observed at all scan speeds (Fig 1: anodic shoulder and peak + cathodic shoulder and peak) with a separation of 0.09 V ($\Delta E = {}^{2}E^{0}_{1/2} - {}^{1}E^{0}_{1/2}$). This indicates relatively weak interaction between Fe centers. Cyclic voltammograms for **2** and **3** show one reversible wave for each complex. In the case of **2** the oxidation peak is resolved into two at very low scan speeds (< 50 mV/s – see Fig 2). Their separation was found to be 0.06 V at 20 mV/s. Such a resolution was not observed for **3**. These findings allow us to arrange the complexes in the order of decreasing Fe-Fe interactions: **1** > **2** > **3**. As for the $E^{0}_{1/2}$ values, these are similar for all complexes and more anodic compared to ferrocene (0.44 V) due to the presence of ethynyl bridges and spacers that remove the electron density from the ferrocene moieties. These results have important implications in investigating the charge delocalization in the metal-containing polymers.



References:

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Nano-Carbon Technology Symposium

NC1K

Nanocarbons: An Overview

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In this presentation I will give a brief overview of the chemistry of carbon nanotubes and graphene. I will touch upon current synthetic methodology, surface chemistry modification, properties and some potential applications.

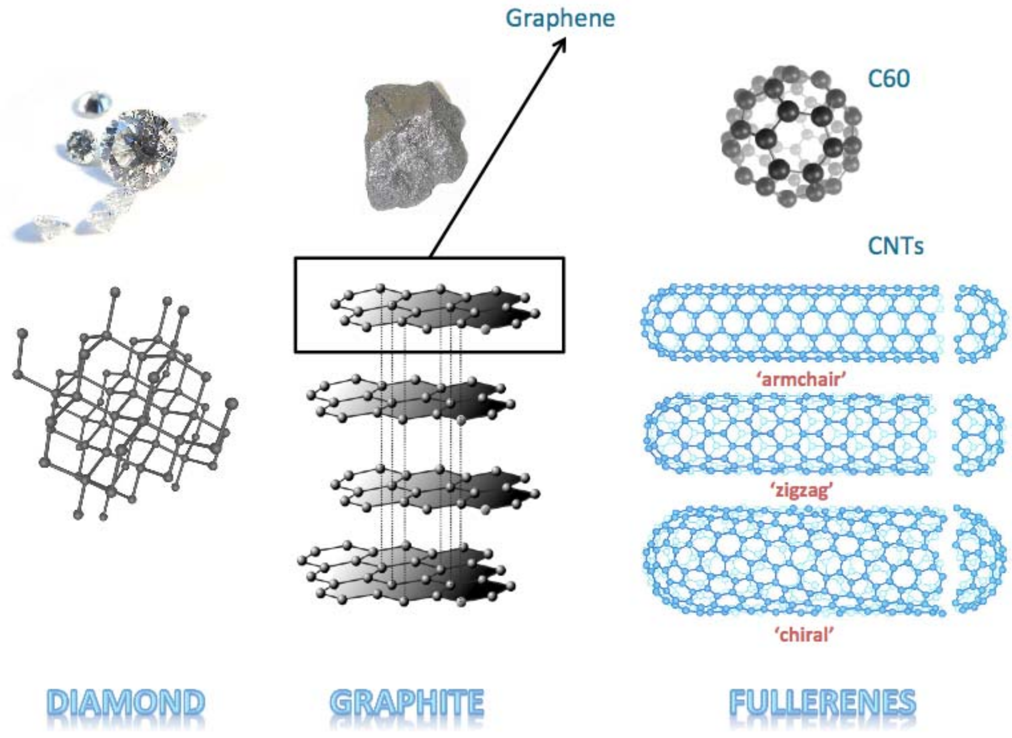

Figure 1. Forms of Carbon.

NC2K

Carbon Nanotube Electrochemistry: Fundamentals and Applications

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The electrochemical properties of carbon nanotubes continue to attract a great deal of interest, although the roles of defects and residual growth catalyst in promoting electron transfer have been debated.

Our recent work on carbon nanotube electrochemistry will be presented, spanning fundamental aspects (electron transfer kinetics) and applications in hydrogen storage [1] and redox flow batteries. Data using both commercially sourced nanotubes and those grown in house (*see Figure*) will be presented.

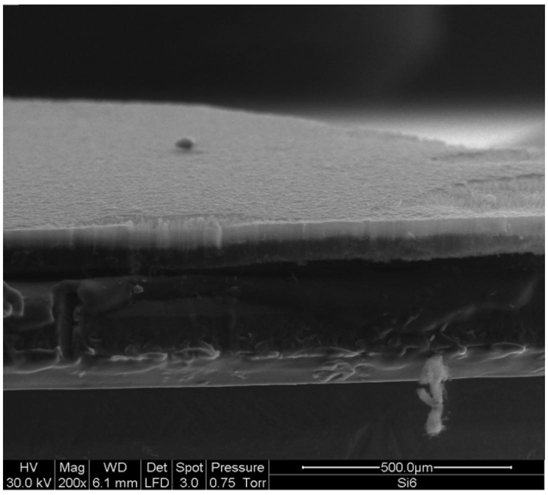

Figure 1. Electron micrograph of a carbon nanotube array grown, for use as an electrode, by chemical vapour deposition on a silicon wafer. (The scale bar is visible in the lower right hand corner of the figure.)

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NC3K

Transport and kinetics at carbon nanotube – redox enzyme composite modified electrode biosensors : modelling redox enzymes dispersed in nanotube mesh films of finite thickness

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In a recent feature article Li, Wang and Chen [1] described nano-bioelectrochemistry as a new interdisciplinary field which provides scope for much exciting development, innovation and new discovery over the next few years. This emerging field combines interfacial electrochemistry, biochemistry and biocatalysis and nanoscience and has as a central aim the full understanding and use of biological electron transfer processes in well defined nanostructured environments which can be used as platforms for emerging biosensor and bioelectronic applications and devices. In a recent review by Willner and Katz [2] it was stated that 'integration of redox enzymes with an electrode support and formation of an electrical contact between the biocatalyst and the electrode is the fundamental object of bioelectronics and optobioelectronics'. More generally the nanoscale will define the region where the physical and engineering science of the 21st century will be pursued, elaborated and utilized . Since their discovery by Iijima [3] in 1993, carbon nanotubes (both multiwalled and single walled, designated MWNT and SWNT respectively) have attracted enormous international interest because of their perceived unique structural, mechanical and electronic properties . In addition the redox and catalytic properties of electrodes modified with both MWNT and SWNT have recently been examined . These types of nano-heterogeneous systems have been typical exemplifiers of chemically modified electrodes which have been extensively studied for over 30 years .

Of course the attractive feature of chemically modified electrodes lies in the fact that the deposited chemical microstructure or bio-recognition element can be the subject of bottom up rational design and be tailormade to perform a specific task. The 'bottom up' construction of nano- structured assemblies using catalytic enzymes, small molecule redox mediators and immobilized matrices can be challenging, and the successful combination of all three components to form a successfully operating biocatalytic system necessitates a detailed understanding of the fundamental kinetic and transport processes which may occur within the surface immobilized nanostructure. This is best accomplished by developing a mathematical model which captures the essential physics and chemistry which encompass the key happenings in the process of biosensor operation namely, the transport of reactant (often called analyte or substrate) to the surface immobilized biorecognition element, and the chemical reaction dynamics between the substrate and the latter. It is usually assumed that the substrate transport mechanism can be ascribed to diffusion (transport in a concentration gradient). The rate law governing the interaction between substrate and biocatalyst can then be specified. Hence the modeling procedure involves problem formulation in terms of specifying a particular differential equation which involves diffusion and chemical reaction components. This reaction-diffusion (RD) equation may in general be time dependent and the chemical term may well be of a form such that the net RD equation is non-linear. It is solved subject to specific initial and boundary conditions to obtain an expression for the reaction flux or equivalently, the current flow and hence the amperometric response in terms of pertinent experimentally measurable parameters such as substrate and mediator concentration, enzyme loading, layer thickness and so on. The mathematical solution may sometimes be analytical, or more often, numerical. This type of analysis has been described for a variety of model systems [4].

In a recent communication describing amperometric glucose detection at SWNT mesh modified glassy carbon and gold electrodes incorporating dispersed immobilized glucose oxidase, Lyons and Keeley [5] have reported that catalytic activity with respect to glucose oxidation is observed only when a soluble mediator such as oxygen or ferrocene monocarboxylic acid is present in the solution. Catalytic glucose oxidation does not occur if adsorbed glucose oxidase is only present. The homogeneous mediator is required to ensure efficient charge shuttling between the flavin active site buried deep within the protein sheath and the underlying carbon nanotube sidewall. It was suggested that mediator molecules such as oxygen or ferrocene monocarboxylic acid molecules are of the correct size to enter the glycoprotein sheath effectively and interact with the flavin group. It is important to note that the carbon nanotube and the enzyme molecule share a similar length scale and so the enzyme is able to adsorb on the nanotube sidewall without losing its biologically active shape, form and function. Indeed Baughman and co-workers [6] have suggested the striking analogy of piercing a balloon with a long sharp needle such that the balloon does not burst. Instead by a gentle twisting action the needle can be made to enter the balloon without catastrophe. Similarly it was proposed by Lyons and Keeley [5] that some number of nanotubes are able to pierce the glycoprotein shell of glucose oxidase and gain access to the flavin prosthetic group such that the electron tunnelling distance is minimized and consequently electron transfer probability optimized. Such access is not generally afforded with traditional smooth electrodes.

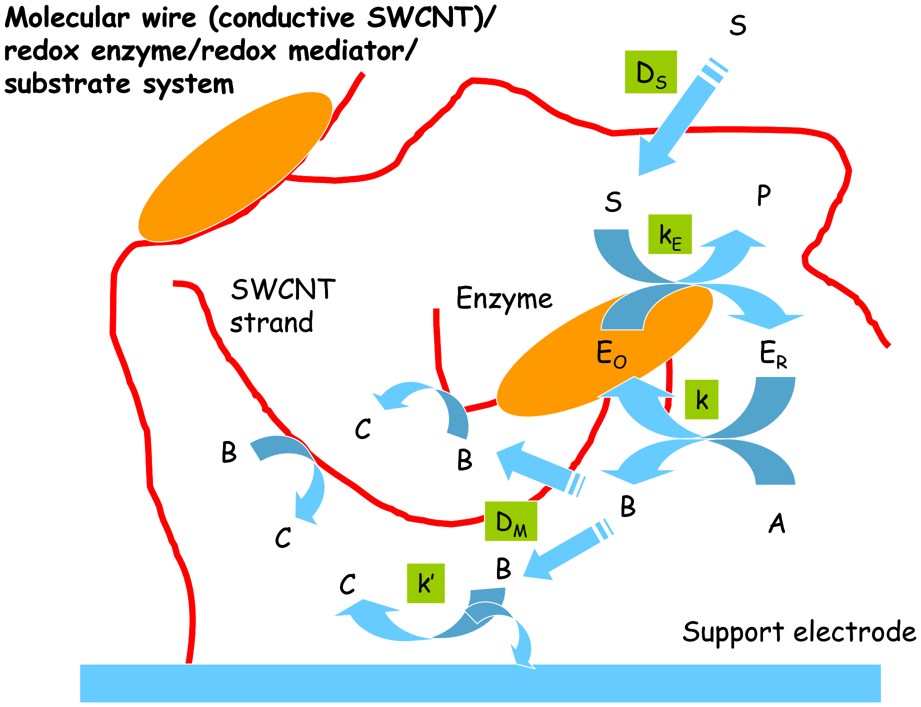

Figure 1. Schematic representation of reaction and diffusion of substrate and mediator within an immobilized nanotube mesh. The nanotube acts as a molecular wire and the mediator reacts at the underlying support electrode surface

In the present communication a mathematical model describing the transport and kinetics of substrate and redox mediator in surface deposited films of finite thickness is described [7]. These bio-catalytically active chemically modified electrodes comprise redox enzymes immobilized in a highly dispersed mesh of single walled carbon nanotubes (SWNT) which are in turn immobilized on a support metal surface. A small molecule redox mediator is used to both regenerate the reduced enzyme and to transfer electrons either to the carbon nanotube surface or to the underlying support electrode surface thereby generating a current which can be measured. The pertinent transport and kinetic differential equations of both substrate and redox mediator are formulated along with suitable boundary conditions and are solved analytically to derive suitable approximate analytical expressions for the current response expected for the system under steady state batch amperometric conditions. The kinetics of substrate and mediator within the nanotube layer are summarized in terms of a kinetic case diagram.

Acknowledgements

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NC4

Electrochemical behaviour of exfoliated single and multi layer graphene microelectrodes

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Results of a study on the electrochemical properties of exfoliated single and multi-layer graphene flakes will be presented. Graphene flakes were deposited on silicon/silicon oxide wafers to enable fast and accurate characterization by optical microscopy. Conductive silver paint and silver wires were used to fabricate contacts; epoxy resin was employed as masking coating in order to expose a stable, well defined area of graphene. Multi-layer graphene microelectrodes showed a quasi-reversible behaviour during voltammetric measurements in potassium ferricyanide; the standard heterogeneous charge transfer rate constant, k°, was estimated by following the method described by Mirkin and Bard [1]. On the contrary, as-prepared mono-layer microelectrodes exhibited a reversible behaviour. Raman spectrometry mapping revealed a defect-free surface, even after the electrochemical measurements, proving that defects are not necessary to make the graphene surface electrochemically active.

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NC5K

How to get the most out of Boron Doped Diamond in Electroanalysis

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Polycrystalline boron doped diamond (pBDD) is, and has been, the subject of considerable interest as an electrode material due to exceptional properties such as a wide potential window, low background currents, chemical inertness, high electrical conductivity and hardness.[1,2] On a local scale the properties of the surface vary heterogeneously due to the variations in boron uptake grain to grain. We show how, using high resolution electrochemical mapping techniques, this variation can be quantitatively mapped and linked unambiguously to the underlying grain structure and boron uptake. Implications of these finding on the use of pBDD in electroanalytical applications are discussed. A major challenge in the use of pBDD as an electrode material, especially in drodynamic applications is both ncap-ulation of the material in an insulating support to produce a co-planar structure and retention of the wide range of applications facilitated by the use of BDD as an electrode material. In this talk the fabrication, characterisation and application of the first *all-diamond* hydrodynamic electrodes will be described,[3] in particular, the tubular flow microelectrode (TFME) and the dual band electrode (DBE).

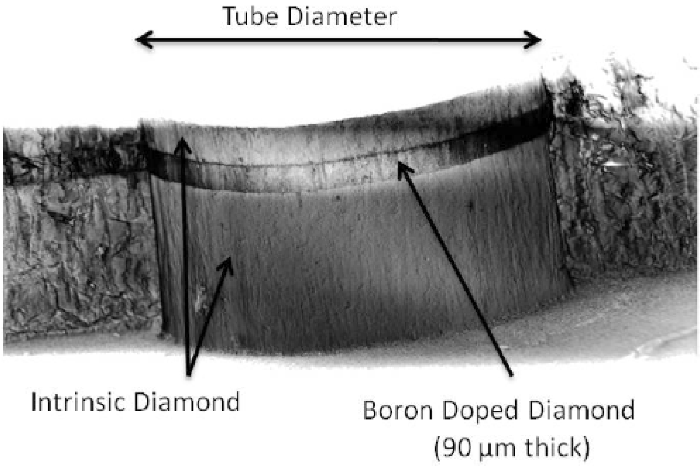

Figure 1: FE-SEM image of an all-diamond TFME[3]

Laser machining is used to define the electrode geometry either by cutting a hole through sandwiched intrinsic-pBDD-intrinsic layers, as shown in Figure 1, or by patterning insulating diamond and then overgrowing with pBDD. The electrodes were characterised and found to give well-defined mass transport over a wide range of flow rates, consistent with a co-planar geometry. The TFME was used for the electrochemical detection of dopamine, and in contrast to the majority of other electrodes, did not passivate as a result of electrode fouling. The DBE was used for hydrodynamic flow and solution conductivity measurements and was shown to be stable in harsh acidic environments.

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NC6K

Electrochemical and sensing properties of reduced graphene oxide

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Graphene-based materials have received significant attention in recent years due to their unique electronic, mechanical and thermal properties since their discovery in 2004.[1] Graphene has shown great promise for applications in different areas such as electronics, energy storage and conversion, and in the development of biosensors.[2]

Among the synthetic approaches, the chemical vapor deposition technique on metal or silicon surfaces has provided a means to investigate graphene physical, optical and electronic properties. Exfoliation of graphene oxide sheets and a subsequent deoxygenation treatment is another route to prepare graphene suspensions.[3]

In this presentation, I will discuss a photochemical-based reduction method for the synthesis of graphene nanosheets from graphene oxide. Three different reduction processes were investigated. The first is based on the direct illumination of an aqueous solution of graphene oxide at λ=312 nm. The resulting graphene nanosheets were characterized using atomic force microscopy, X-ray photoelectron spectroscopy (XPS) and electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy). The results obtained were compared to those of graphene nanosheets synthesized in the presence of hydrogenated silicon nanowires (Si NWs) and silicon nanowires decorated with copper nanoparticles (Cu NPs) under UV irradiation. We found that graphene nanosheets synthesized using SiNWs/Cu NPs exhibited superior electrochemical charge transfer characteristics. This is mainly due to the higher amount of sp^2-hybridized carbon in these graphene sheets as evidenced by XPS analysis.

In the second part of my talk, I will focus on some applications of reduced graphene oxide in biosensing.

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NC7

Redox Reactions at Nanodiamond Surfaces Revealed by Attenuated Total Reflectance InfraRed Spectroscopy

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Nanodiamond (ND) is formed by detonation of carbon-based explosives and consists of individual diamond nanoparticles of ~ 5 nm in diameter. This material is attracting much interest at present in possible biomedical applications such as drug delivery, intracellular imaging and biosensing. Our interest lies in its unexpected redox properties [1,2] as we find that when immobilized on an electrode it is able to undergo direct oxidation and reduction and can also undergo electron transfer with solution redox molecules such as $IrCl_6^{2-}$. As undoped diamond is an insulating material, with a band gap of 5.5 eV we have suggested that this redox activity must be associated with its surface. By necessity bonding at the surface is unsaturated and due to the acid treatment used in purification highly oxidized. The ND surface contains an array of different surface functionalities, such as carboxylic acid, alcohols, quinones and ketones etc. As these groups can undergo redox transformations they may be responsible for the observed redox activity.

This talk will discuss recent experiments to elucidate the mechanisms behind electron transfer at the ND surface. This study uses Attenuated Total Reflectance InfraRed (ATR IR) spectroscopy to monitor changes in the vibrational frequencies of the surface functional groups of the ND in the presence of redox probes. In ATR IR the IR beam is directed through an internal reflection element (IRE), on top of which a thin layer of the nanomaterial is immobilised. The IR beam is reflected internally at the surface of the IRE, but the beam also penetrates the immediate environment above the prism surface as an evanescent wave. An IR vibration spectrum of the material within range of the evanescent wave can therefore be obtained and as only a thin layer is probed, solvent absorption is minimised. Use of nanomaterials ensures that a high surface area is available to be probed, allowing good quality IR spectra of the redox-active surface functional groups to be obtained.

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NC8

Carbon Nanoparticle Surface Modification for Sensor Development

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Emperor 2000® carbon nanoparticles are a form of carbon black with surface sodium sulfonate groups. This negative surface coverage is initially converted to positive amine functionality with reaction with a diamine. [1] The aminated carbon nanoparticles can then be subjected to further synthetic reactions.

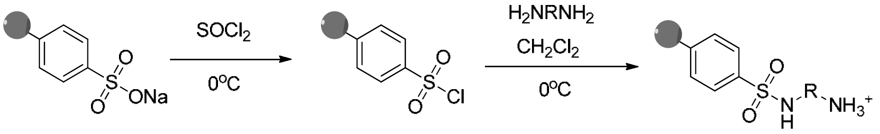

Figure 1. Diamine functionalisation of Emperor 2000® CNPs [1].

Carbodiimide mediated peptide coupling reactions were employed and a range of small organic molecules were reacted with the aminated surface of the carbon nanoparticles. This resulted in a range of carbon nanoparticles with new surface functionality created *via* amide bond formation.

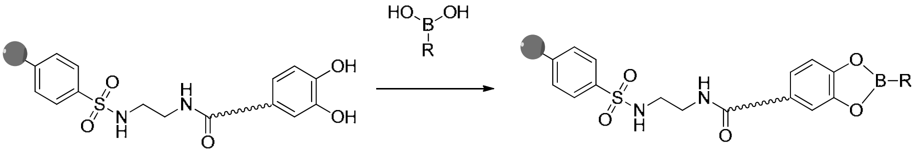

Figure 2. Boronic acid binding to terminal diol

By appending molecules with a free catechol unit to the carbon nanoparticles, there is the potential to detect boronic acids as the reaction of catechols and boronic acids is very favourable. [2]

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Green Electrochemistry Symposium

G1K

The Development and Application of Microflow Electrolytic Reactors for Synthesis

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The design of microflow electrolytic cells is a challenge that, if successfully overcome, could rejuvenate electrosynthesis as a routine procedure in the organic synthetic laboratory. The lecture will stress the characteristics for a useful microflow cell, particularly the selective and complete conversion of reactant to product combined with a product formation rate that provides sufficient mass of isolated product for further chemistry or determination of properties.

It will also be emphasized that the syntheses attempted must match the capabilities of the cell design. So far, we have operated with the cell in undivided mode and then balanced cell chemistry is imperative. The difficulties in developing divided cells lies in the properties of membranes rather than the cell design.

Two cells will be described. A ‘cheap’ cell fabricated in the laboratory and a pre-production commercial cell (Syrris), see figure 1. The mass transport in the cells will be characterized using the reduction of ferricyanide and the performance in synthesis will be demonstrated using the methoxylation of *N*-formylpyrrolidine. The cells can achieve > 95% conversion with the formation of only a single product being formed. Furthermore, it is possible to form product at a rate of > 1 g/hour. This performance makes electrolysis comparable with other microflow chemistries. The application of the cells to some other reactions will be reported.

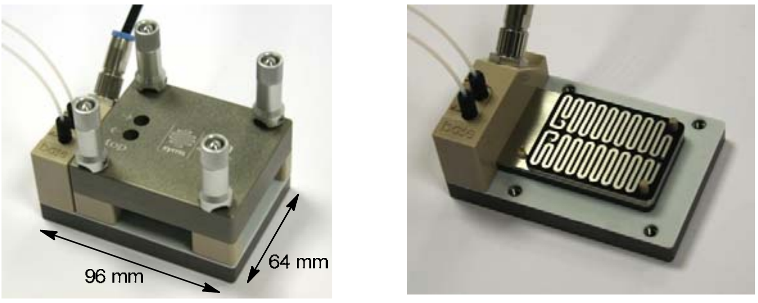

Figure 1. The microflow cell.

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2. J. Kuleshova, J.T. Hill-Cousins, P.R. Birkin, R.C.D. Brown, D.Pletcher, M. Hawes, P. Homewood, T.J. Underwood, submitted.

G2

Hydrogen from Sunlight at textured $ZnFe_2O_4$ electrodes

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To make a hydrogen economy feasible the energy used to decompose water must come from a renewable, abundant, and clean source. Photoelectrochemical water decomposition removes the need for inefficient electrolysers by creating hydrogen in situ, but the requirements on the photoelectrode material are exacting[1].

Zinc ferrite ($ZnFe_2O_4$) is a worthy material for investigation based on these requirements predominately because its band gap (1.9 eV) is ideal for the photolysis of water (1.8 – 2.0 ev)[2,3], metal oxides are highly stable, and $ZnFe_2O_4$ is an easy material to synthesis at a low-cost.

In order to enhance the photoelectrochemical performance of $ZnFe_2O_4$ its light absorption, interfacial charge transfer and charge transport properties require improvements by optimising the nanostructure. A highly uneven and porous nanostructure increases the internal surface area of the $ZnFe_2O_4$ film and minimises recombination, significantly improving the light harvesting properties.

In this work aerosol assisted chemical vapour deposition was used to obtain thin films of $ZnFe_2O_4$. As the electrode performance depends on the deposition conditions, the effect of choice of solvent on the nanostructure was investigated. A series of $ZnFe_2O_4$ electrodes were prepared by changing the deposition parameters (i.e. composition of deposition solvent). The electrodes were characterised by XRD, SEM, I-V, and IPCE. The SEM revealed that films deposited using ethanol were more highly structured and porous than those deposited using methanol. The photocurrent density and IPCE were found to increase with increasing the concentration of ethanol in the deposition solvent, which was also related to the decrease of aerosol droplet size. This improved performance has been attributed to ethanol having a relatively high combustion enthalpy and providing the necessary heat for the decomposition of precursor, and then aid in the formation of a highly structured and porous $ZnFe_2O_4$.

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G3

Ionometallurgy – Properties and Applications of Metal Ions in Ionic Liquids

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The deposition, dissolution and reprocessing of metals has classically been carried out using strong acids and bases. Water and hydroxide ligands dominate the reactivity of metal ions in solution and this has coloured the extent of metal processing over the last century. The use of ionic liquids allows the control of speciation and reactivity, which in turn affects all aspects of metal processing. This presentation discusses the relationship between speciation and redox properties. It also highlights fundamental aspects such as solute activity. The practical application of this fundamental information is demonstrated through the deposition of nanostructured materials and composites and the micromachining of surfaces. Results from pilot-plant and commercial scale processes are also presented.

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G4

Tuning of channels in 3D inverse bicontinuous cubic Fd3m-type nanostructured platinum films

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Tailoring the surface of conventional electrodes with a wide variety of nanostructures has emerged as a powerful tool to enhance the performance of electrochemical devices. Metallic nanostructures with highly ordered 3-D networks of channels show very high surface area, high conductivity and chemical stability, ideal for use in the fields of batteries, solar cells, capacitors, and electrocatalysis [1]. Here we demonstrate surfactant templated growth of 3D inverse bicontinuous cubic nanostructured platinum films at the surface of an electrode. The objective of this research is to broaden the utility of these bicontinuous cubic films, by gaining control over the pore size throughout the entire network of channels. This was achieved by using different additives along with phytantriol, a structure directing agent. Ultrahigh surface area porous electrodes were obtained through electrochemical reduction of a platinum salt dissolved in the aqueous domains of the cubic phases. Based on small angle X-ray scattering (SAXS) experiments, Fd3m symmetry was assigned to the nanostructured platinum films thus obtained. In addition to SAXS, transmission electron microscopy was used to investigate the morphology of the nanostructured platinum films and cyclic voltammetry was applied to determine the electro-active surface area of these films.

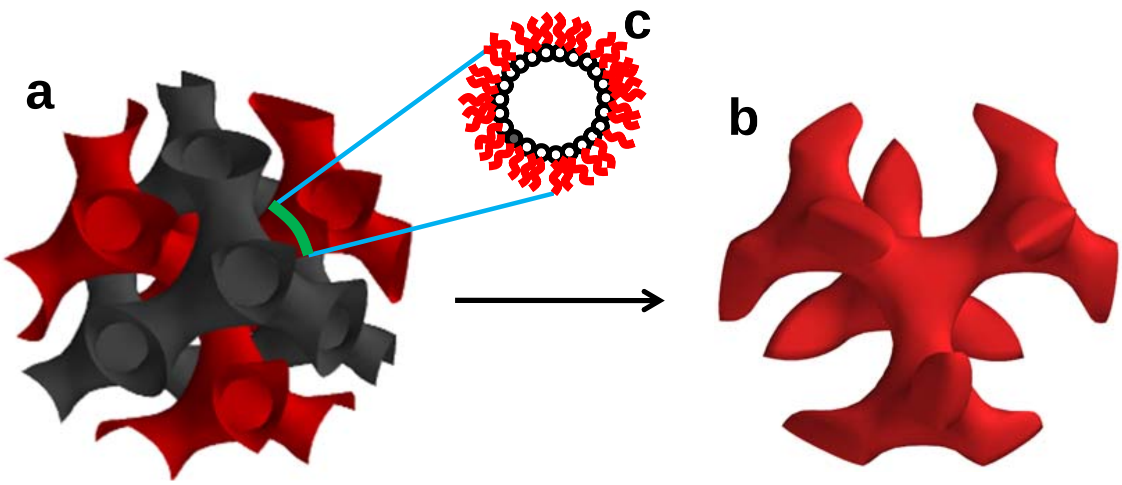

Figure 1. 3D representation of inverse bicontinuous cubic structure with a) Pn3m and b) Fd3m symmetry whereas c) showing internal pore size

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G5

Electrochemical Characterisation of Mixed Poly(pyrrole-thiophene) Films Immersed in Choline Chloride Based Ionic Liquids

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Electronically conducting polymers based on functional pyrroles and thiophenes have continued to attract academic interest as well as develop in practical applications and uses. The application of mixed pyrrole-thiophene systems for energy storage has recently become the focus of the PolyZion [1] consortium (EU FP7 funded framework programme). The PolyZion project aims to create a new class of fast rechargeable zinc-polymer battery for hybrid and small electric vehicles applications, utilising the novel properties of choline chloride based ionic liquids. These liquids are especially attractive because of their good electrochemical windows, high stability and low toxicity.

In such energy storage devices the movement of ion and solvent through the polymer film during the oxidation and reduction cycles is critical to both application and function, e.g. charging rate, metal ion permeability or adhesion stability. We have compared several films grown from mixed monomer precursors in conventional organic (or aqueous) media, with that of choline chloride based ionic liquids. This fundamental work has explored the electrochemical characterisation, DC capacitance behaviour and ion-solvent transport properties of thiophene-pyrrole copolymers using a range of electrochemical methodologies in combination with acoustic impedance quartz crystal microbalance techniques.

[1] www.polyzion.eu

G6K

Electrochemistry and Biomass - Backwards to the Future?

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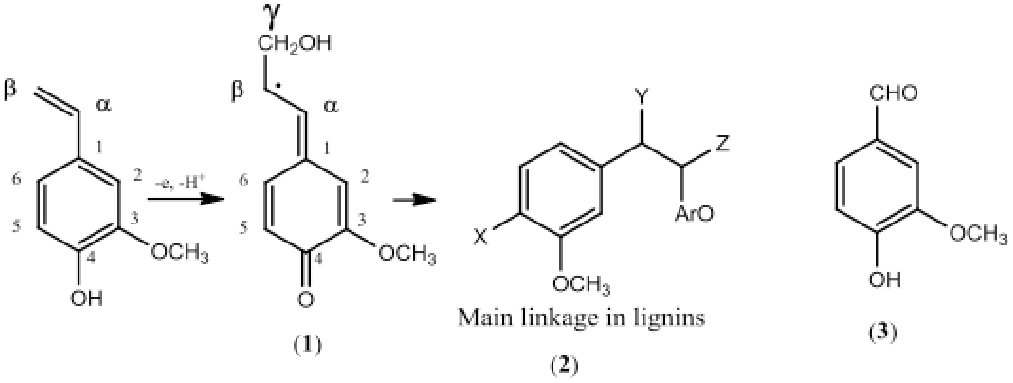
Background. Organic chemicals were originally obtained by biomass conversion involving pyrolysis, distillation and fermentation of, e.g. wood, bone, sugars. The age of coal followed, but by the 1950s oil was the main source of carbon for volatile fuels and (petro)chemicals, including polymers. In 1973 OPEC proclaimed an oil embargo and oil prices rose from about US$3 per barrel to above US$10, prompting searches for alternative, renewable, sources of fuels and chemicals. The success of the Monsanto adiponitrile process stimulated interest in electrochemical conversions, including that of biomass and biomass-derived materials for new feedstocks or reduced compounds useful as fuel additives[1;2]. Renewability was then an issue but minimizing production of greenhouse gases was not! Criteria have changed and we present an example of a relatively clean electrolytic conversion of a renewable, but polluting, feedstock.

Lignins to vanillin. Lignins are mixtures of polyphenols comprising 15 – 30% of (renewable) lignocelluloses (ca. 10_7 tonnes p.a.). In nature, oxidation of e.g. coniferyl alcohol gives quinonemethides (1) that polymerise, typically with β-O4 coupling (2). This can be demonstrated in the laboratory[3]. The food additive vanillin (3) is produced industrially by treatment of lignins in alkaline solution with oxygen at ca. 150 $_o$C in the presence of copper or cobalt catalysts, probably also via involvement of quinonemethides[4]. To examine the process on a realistic scale, and in previously unobtainable detail, Ultrazine NA sodium lignosulfonate was electrolysed in a a flow cell (FM01), equipped with nickel anodes, that operated at conditions (145 $_o$C/500 kPa/3M NaOH) similar to those used in the industrial chemical process. Up to 150g of the lignosulfonate could be electrolysed in 2-3 hours at cell voltages of ca. 1.3 – 1.6V and currents in the 6 – 12A range. Samples could be taken without interrupting the reaction and the profiles obtained point to vanillin formation in a steady state concentration[5].



(1)

Main linkage in lignins

(2)

(3)

[1]Chum,H.L. & Baizer,M. (1985) The Electrochemistry of Biomass and Derived Materials. ACS, Washington DC ; [2] Ellis,K.G., Nazar-ul-Islam, Sopher,D.W., Utley,J.H.P., Chum,H.L., & Ratcliff,M. (1987) Electro-Organic Reactions .30. Cleavage and Coupling of Some Biomass-Derived Organic-Compounds. Journal of the Electrochemical Society 134, 3058 ; [3] Chum,H.L., Johnson,D.K., Palasz,P.D., Smith,C.Z., & Utley,J.H.P. (1987) Reactions of Quinomethides - Stereoselective Oligomer Syntheses by Michael Additions. Macromolecules 20, 2698 ; [4] Pardini,V.L.,Smith,C.Z., Utley,J.H.P., Vargas,R.R., & Viertler,H. (1991) Electroorganic Reactions .38. Mechanism of Electrooxidative Cleavage of Lignin Model Dimers. Journal of Organic Chemistry 56, 7305 ; [5] Smith,C.Z., Utley,J.H.P., & Hammond,J.K. (2011) Electro-organic reactions. Part 60[1]. The electro-oxidative conversion at laboratory scale of a lignosulfonate into vanillin in an FM01 filter press flow reactor: preparative and mechanistic aspects. Journal of Applied Electrochemistry 41, 363.

G7

Electrosynthetic Processes at the Carbon Membrane Stabilised Triple Phase Boundary Interface

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Electrosynthetic processes are becoming more widely established as a tool in organic synthesis with some processes seeing success at the industrial scale, most notably the production of adiponitrile in the Monsanto process[1]. The advantages of electrosynthesis over traditional synthesis are that less harsh reagents and conditions generally need to be used for simple redox processes. With fewer reagents involved processes can generally be made cleaner and more efficient.

However there are disadvantages holding back electrosynthetic processes from being more widely accepted as a synthetic tool. One such disadvantage is that the choice of solvents is limited to only very polar ones such as acetonitrile. Water would be the optimal choice but so often synthetic reagents are not soluble in it. Electrolyte is also required in large excess to ensure conductivity and is often problematic to separate post-reaction creating wasteful purification steps.

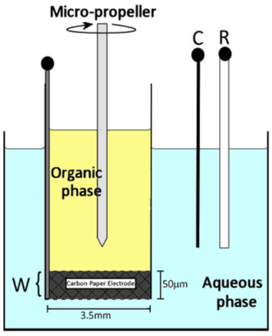
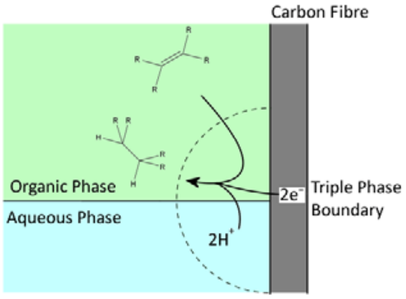


Figure 1. A carbon fibre stabilized triple phase



Scheme 1. A typical Triple phase boundary reaction occurring within the carbon membrane.

This work presents a new synthetic system which utilises a triple phase boundary process[2] (scheme 1.) utilizing the high conductivity of water containing all intentionally added electrolyte whilst keeping all organic reagents separated in an immiscible organic phase in which the reactions occur and from which products may be extracted directly (Figure 1). This also leaves the aqueous phase unaffected by the reaction meaning it can be recycled over multiple reactions.

[1] Danly, DE *Journal of the Electrochemical Society,* 131 (1984) 435
[2] Marken F.; Webster R.D. *et al. Journal of Electroanalytical Chemistry,* 437 (1997) 209

G8

Formation of Electrochromic PTFA Films Utilizing Room Temperature Ionic Liquids

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Conducting polymer (CP) materials, in conjunction with room temperature ionic liquids (RTILs) have been utilised to fabricate new energy-efficient electrochromic films. [1] An electrochromic material is one where a reversible colour change takes place upon reduction or oxidation, on passage of electrical current after the application of an appropriate electrode potential. Electrode substrates typically used are glass coated with an optically transparent electrically conductive film such as fluorine-doped tin oxide (FTO) or indium-doped tin oxide.

Electrochromic films of polymeric 2,3,5,6-tetrafluoroaniline (PTFA) were prepared with the RTILs 1-butyl-3-methylimidazolium (BMIM) hexafluorophosphate and BMIM trifluoro-methanesulfonate (TFSI). PTFA films formed on FTO glass from aqueous electrolytes were stable in air. Yellow films were formed utilising the ionic liquids, but they were easily removed when washed with deionized water due to the strongly hydrophobic nature of the PTFA. In aqueous solution poly-(2,3,5,6-tetrafluoroaniline) films deposited on FTO glass were orange and pink in the oxidized and reduced forms. [2] The films were characterised using a range of spectroscopic, microscopic and electrochemical techniques.

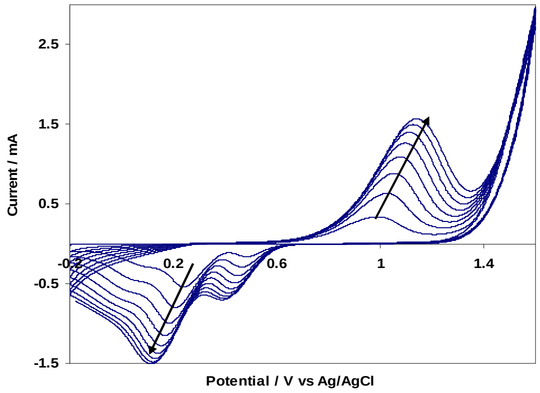

Figure.1. Cyclic voltammograms of PTFA film deposited on FTO glass from 50 mM TFA/ 2 M $HClO_4$ in deionized water. ν= 40 mVs^{-1}, number of cycles: 10.

[1] (a) F. Endres, Andrew P. Abbott, D. R. Macfarlane, *Electrodeposition from ionic liquids*, Wiley-VCH Verlag GmbH & Co. KGaA, **2008**; (b)R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays* **2006**, *27*, 2.
[2] J. Niessen, U. Schroder, M. Rosenbaum, F. Scholz, *Electrochemistry Communications* **2004**, *6*, 571.

G9

Effect of anode materials on wastewater denitrification and TOC removal in an upflow electrochemical reactor

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Abstract

Electrochemical treatment of wastewater has been studied extensively in the literature. However, an investigation of anode materials on simultaneous electrochemical denitrification and organic matter oxidation in wastewater samples hasn't been investigated in much detail. In this study, a continuous undivided up flow electrochemical reactor (UER) is employed for the same. Anode materials such as titanium, carbon felt, nickel, copper and lead have been used and inter-electrode gap has been varied to investigate removal efficiencies. The cathode material is made up of activated carbon granules (GAC) from waste palm shells in Malaysia. From preliminary experimental runs, it was found that only titanium and carbon felt showed effective oxidation of organic matter. About 90% of organic matter could be oxidized at the anode at optimum electrode spacing of 1 cm whereas only 7% of nitrate was removed at the cathode. The results prove that effective denitrification is possible mainly with an up flow bio-electrochemical reactor (UBER) in which an autohydrogenotrophic denitrifying bacteria is employed on GAC (this functions as a bio-carrier as well as the cathode material). Further work on simultaneous denitrification and organic matter oxidation is recommended for a UBER system.

Keywords: Electrochemical; denitrification; activated carbon; electrodes; UER

G10

Carbonized Layer-by-Layer Cellulose-PDDA-TiO$_2$ Composite Thin Films: Carbon enhanced surface conductivity

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Mesoporous TiO$_2$ (anatase) materials immersed in aqueous electrolyte are known to behave as bulk electrical conductors at applied potential negative of the apparent flat band potential, whilst exhibiting insulator properties at more positive potentials. Here we present a versatile vacuum carbonisation method for cellulose nanowhiskers [1] that induces surface conductivity making TiO$_2$ surface states and surface reactions accessible to direct electrochemical control also in the positive potential range. A layer-by-layer electrostatic deposition process with cellulose nano-whiskers, TiO$_2$ nanoparticles, and PDDA (poly(diallyldimethylammonium)) allows well-defined levels of cellulose to be added to the TiO$_2$ thin films. Dopamine binding at the anatase surface and redox cycling aided by the thin carbon film in mesoporous TiO$_2$ are demonstrated and dopamine is detected at micromolar concentration.

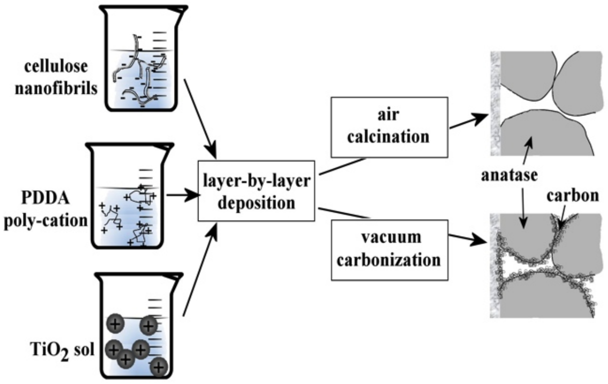

Figure 1. Schematic drawing of the formation of TiO$_2$ – cellulose films and their conversion into mesoporous films of carbon-modified anatase [2].

[1] Vuorema A, Sillanpää M, Rassaei L, Wasbrough MJ, Edler KJ, Thielemans W, Dale SEC, Bending S, Wolverson D, Marken F, Electroanalysis 22 (2010) 619.

[2] Vuorema A, Shariki S, Sillanpää M, Thielemans W, Nelson GW, Foord JS, Dale SEC, Bending S, Marken F, PCCP 13 (2011) 9857.

G11-Po

Characterization of Oxide Films Formed on Al-Alloy for Aerospace Applications, Prepared via Plasma Electrolytic Oxidation in Alkaline Solutions

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Abstract

Aerospace application and energy saving strategies in general boosted the interest and the research in the field of light weight materials, typically on alloys based on aluminium. Plasma electrolytic oxidation (PEO) improves surface properties of light metals like hardness, corrosion stability, chemical resistance and wear behaviour, therefore it is an attractive topic in the field of metal protection. In this work, especially PEO processes of Cu, Zn, Mg, Si containing Al-alloys were investigated. As rectifier two different power supplies were used. The composition of the coating can be modified by the incorporation of anionic components like silicate or phosphate contained in the bath or by the incorporation of cationic species (alloy elements) like silicon, magnesium or copper from the substrate. As an example, mullite (Al8[(O,OH)|(Si,Al)O4]4) can be formed during spark discharge anodization of aluminium when the bath contains silicate anions, and/or the substrate is a silicon- containing alloy.

Morphology and film composition studies of layers produced on different aluminium alloys with different concentration of aluminium, magnesium, silicon, copper, zinc have been carried out using techniques such as optical and electron microscopy (ESEM), EDX, together with XRD investigation of the phase composition. Additionally research deals with the characterisation of layer thickness and porosity, layer hardness and surface energy. The paper will summarize the results and process strategies for optimization of treatment parameters for different alloys of Al.

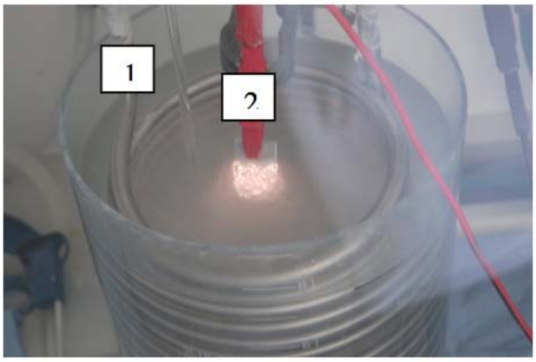

Figure 1. Experimental setup. 1) Cathode: stainless steel, 2) anode: Al-alloy

G12-Po

Using White Bronze as a Potential Replacement for Nickel in the Decorative Chromium Plating Application.

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Research carried out at the University of Wolverhampton, is investigating viable commercial alternatives for nickel replacement as underlayer for chromium plating. White bronze (copper tin alloy) also known as speculum has been found to be the most promising alternative, and is currently being used in the jewellery industry but as a topcoat.

Colorimetric analysis using the L*a*b* colour space indicates there is a distinct difference in appearance between nickel and white bronze but when used as an underlayer for chromium plating there is no significant difference between the two.

Linear polarisation technique used to obtain corrosion current density figures showed that the white bronze deposit would corrode at a rate of 0.232 mils per year whereas nickel corroded at a rate of 0.285mils per year. However, when used as an underlayer for chromium plating white bronze corroded at 0.034 mils per year while nickel corroded at 0.024 mils per year. It was therefore concluded that the white bronze corrodes slower than nickel and would provide better corrosion resistance, with the application of chromium on top the corrosion would be a lot slower and of similar rates between the white bronze and nickel undercoats.

Accelerated corrosion testing were used to support results obtained from the electrochemical experiments however, white bronze appear to corrode significantly faster than nickel within the same time scale.

Atomic Force Microscopy experiments indicated that the nickel deposit to be the smoothest of all the deposits characterised with an RMS and Rmax values of 3.08nm and 18.6nm respectively. The Cu-Sn deposit is the roughest of all deposits studied with the following RMS and Rmax values of 8.30nm and 73.0nm respectively. White bronze deposit therefore provided corrosion sites, whereas the nickel deposit did not.

To conclude, the white bronze has the potential to replace nickel in applications where appearance is the primary objective and used within low corrosive atmospheres. Further experiments are underway to produce a non porous deposit allowing white bronze to be used in more corrosive atmospheres.

Electrochemical Processes in Exotic Media Symposium

EM1K

Electrical double layer in ionic liquids: from fundamentals to applications

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This *keynote lecture* will overview the current status of understanding of the structure and properties of the electrical double layer at electrode/electrolyte interfaces. Existing theories and computer simulations will be confronted with available experimental observations.

The presentation will cover:

1. Results for flat electrodes
2. Results for more 'realistic' electrodes, used in various applications, including nano-templated electrodes, and, generally, the properties of the double layer in confined geometries.
3. The link between the structure and dielectric response of the double layer and the properties of supercapacitors, electroactuators, and lubricants

It will focus not only on equilibrium properties, but will discuss also some features of the dynamic response to the double layer charging and discharging, including the ion transport dynamics in confined geometries.

Overview-like in character, the talk is intended to compare different, sometimes contradicting, as well as complementary achievements of different groups worldwide. At the same time, it will also focus on a set of original results, based on the cooperation projects of the presenter's group at Imperial and the groups of Maxim Fedorov (Max Planck Institute, Leipzig), Martin Bazant (MIT), Yuri Gogotsi (Drexel University), and some others (for References see Ref.1-8 on Web of Science page http://apps.webofknowledge.com/summary.do?SID=W1EAjmEiG3O%40i%40gICMG&product=WOS&qid=1&search_mode=GeneralSearch)

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EM2K

The “Electrochemistry” of Emergent Magnetic Monopoles

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The analogy between spin configurations in spin ice materials like $Ho_2Ti_2O_7$ and proton configurations in water ice, H_2O, has been appreciated for many years (see Ref. [1] for a review). However it is only in the last few years that this equivalence has been extended into the realm of electrodynamics [2]. In this talk I shall describe our recent experimental work that identifies emergent magnetic charges ("monopoles"), transient magnetic currents ("magnetricity") and the universal properties expected of an ideal magnetic Coulomb gas (magnetic electrolyte - "magnetolyte"). These universal properties include the Onsager-Wien effect, "corresponding states" behaviour, Debye-Huckel screening and Bjerrum pairing [4-6]. I will describe experimental results for both traditional spin ice materials ($Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$) and a recently discovered system ($Dy_2Ge_2O_7$).

[1] Bramwell and Gingras, *Science*, **294** 1495 2001
[2] Ryzhkin, JETP **101** 481 (2005); Castelnovo et al., *Nature* **451** 42 (2008)
[4] Bramwell et al. *Nature* **461** 956 (2009): Fennell *et al.,* & Bramwell *Science* **326** 415 (2009); Giblin, Bramwell *et al.*, *Nature Physics* **7** 252 (2011)

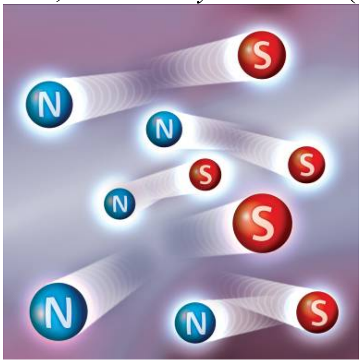

Figure 1. Emergent magnetic monopoles in spin ice form the magnetic equivalent of an electrolyte

EM3

Mass Transport in Room Temperature Ionic Liquids

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In this presentation, the use of chronoamperometry, cyclic voltammetry and scanning electrochemical microscopy to study the mass transport of redox-active species in room temperature ionic liquids (RTILs) is described. The rate of ferrocenemethanol diffusion in imidazolium-based RTILs decreases with increasing RTIL viscosity and analysis of the data reveals that the simple Stokes–Einstein equation is not applicable in these systems. The "correlation length", estimated from diffusion coefficient data, corresponds very well to the average size of holes (voids) in the liquid, suggesting that a model in which the diffusing species jumps between holes in the liquid is more appropriate in these liquids. Cyclic voltammetry at ultramicroelectrodes was also used to study mass transport in RTILs and demonstrates that the ability to record steady-state voltammograms during ferrocenemethanol oxidation depends on the voltammetric scan rate, the electrode dimensions and the RTIL viscosity. Similarly, the ability to record steady-state SECM feedback approach curves depends on the RTIL viscosity, the SECM tip radius and the tip approach speed. As I will show, steady-state SECM feedback approach curves can be recorded in RTILs, even when moderately viscous, provided that the tip approach speed is low enough to maintain steady-state diffusion at the SECM tip. In those cases where a very viscous RTIL is used as the electrolyte, tip-induced convection can contribute significantly to the SECM tip current. However, our results will show that this effect can be accounted for theoretically using mass transport equations that include both diffusive and convective terms.

EM4

Control of Redox reactions at the Solid/Gas interface

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The presence of ions in plasma presents a realistic prospect for controlling redox reactions at an electrode by considering ionised gaseous environment of a flame as a dilute electrolyte. The focus of this work is to apply the well-established principles of electrochemistry in liquid and solid phases, to the gas phase. In the past we have presented zero current potentiometric measurements between two inert metallic electrodes in a gaseous electrochemical cell.[1,2] A specially designed burner producing a flame split into two compartments enabled us to manipulate the concentration and identity of ionised species in a two-compartment cell to produce a controllable concentration gradient. We have extended this work by systematically designing an electrode system for dynamic electrochemistry by considering the flame flow characteristics, temperature, and flame conductivity. In this paper evidence for reproducible cyclic voltammograms will be presented showing for the first time that redox chemistry at the solid gas interface can is indeed possible.

The ability to control chemical reactions at the surface of an electrically conducting substrate in gaseous plasma opens avenues for academic research and applications such as electroanalysis, electroplating etc. in the gas phase.

[1] Hadzifejzovic, E.; Galiani, J. A. S.; Caruana, D. J. *Physical Chemistry Chemical Physics*, *8* (2006) 2797.

[2] Sanchez Galiani,J., Hadzifejzovic,E., Caruana,D.J., *Electrochimica Acta* 53 (2008) 3271-3278.

EM5-Po

Plasma electrochemistry: Electron Transfer at the Solid/Gas Interface

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To date all electrochemical measurements are confined within a potential window defined by the solvent, but typically no larger than -3 to +3 V. Only redox reactions within these limits can be studied in liquid phase, however, there are a plethora of redox reactions which lie outside these limits and will may only be accessed in the absence of solvent. The presence of ions in flames presents a realistic prospect for performing electrochemical reactions at an electrode in a flame plasma environment. [1,2]

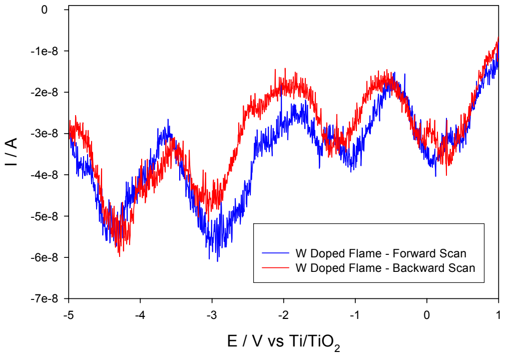

Figure 1. Cyclic voltammogram between +1 and -5 V, at scan rate 1 V s^{-1}, in a hydrogen/oxygen/nitrogen flame doped with ammonium metatungstate hydrate, with forward scan in blue and backward scan in red.

A specially designed burner producing a flame split into two compartments enabled us to control the concentration and identity of ionised species in our system. The ionised gaseous environment of a flame acts as a dilute electrolye, enabling us to apply well-established principles of the liquid phase to the gas phase. In this paper, we will illustrate the set-up used to perform cyclic voltammetry in the gas phase. The introduction and subsequent characterisation of reducible species in the flame will be highlighted. We propose that the features shown in the CV in Figure 1 are due to electrochemical redox reactions at the surface of a graphite electrode in the gas phase. The ability to measure and control redox reactions in gaseous plasma provides an exciting gateway for research and applications of electrochemistry

[1] Hadzifejzovic, E.; Galiani, J. A. S.; Caruana, D. J. *Physical Chemistry Chemical Physics* **2006**, *8*, 2797.

[2] Hadzifejzovic, E.; Stankovic, J.; Firth, S.; McMillan, P. F.; Caruana, D. J. *Physical Chemistry Chemical Physics* **2007**, *9*, 5335.

EM6-Po

Electrode Processes at Gas | Salt | Pd Nanoparticle | Glassy Carbon Electrode Contacts: Salt Effects on the Oxidation of Formic Acid Vapor and the Oxidation of Hydrogen

Fengjie Xia [a,b], Sara E.C. Dale [b], Richard A. Webster [b], Mu Pan [a], Shichun Mu [a], Shik Chi Tsang [c], John M. Mitchels [d], and Frank Marken [b]
[a] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070, China*
[b] *Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK*
[c] *Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, UK*
[d] *Microscopy and Analysis, University of Bath, Claverton Down, Bath BA2 7AY, UK*
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The electrochemical oxidation of formic acid to CO_2 is facile at nano-palladium catalysts. In conventional electrochemical systems this process is conducted in aqueous phase and the resulting formation of poorly soluble CO_2 gas can limit the kinetics. Here, an alternative electrochemical system with the gas phase in closer contact to the palladium nanoparticle catalyst is investigated based on a glassy carbon electrode and a solid $(NH_4)_2SO_4$ salt electrolyte [1]. It is demonstrated that the reaction zone of salt, palladium nanoparticle catalyst, and gas phase, is where the electrochemical oxidation process occurs. The effects of the type of salt, the partial pressure of formic acid, and the gas flow rate are investigated. Preliminary data for the oxidation of hydrogen gas at the salt | palladium | electrode contact are reported. A significant salt effect on the palladium catalysed reactions is observed.

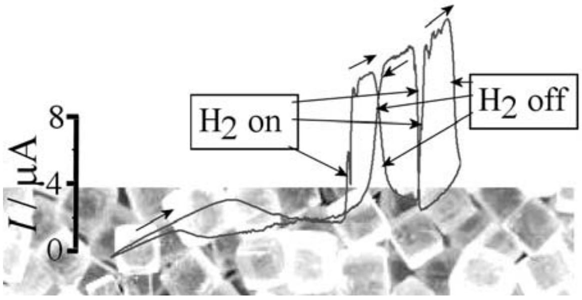

Figure 1. Schematic drawing of a cyclic voltammogram recorded at an ammonium sulphate – Pd nanoparticle contact under flow of humidified nitrogen and with hydrogen pulses generating immediate hydrogen oxidation responses.

[1] S.E.C. Dale, C.Y. Cummings, F. Marken, Electrochem. Commun., 13 (2011) 154.

EM7-Po

Astroelectrochemistry: Cosmic Dust Electrochemistry

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We propose that redox reactions on the surface of interstellar dust particles contribute to the synthesis of some polyatomic species that have been identified in the interstellar medium (ISM). Most of the dust is found in clouds along with a rich abundance of molecular and atomic species, creating a thermodynamically distinct region in the ISM where chemistry can be supported.

The involvement of dust particles in the synthesis of complex polyatomic molecules is generally accepted to be important in astrochemistry. For example molecular hydrogen, H_2, the most abundant molecule in the ISM, is formed on the surface of particles. However, to date dust particles have been included in chemical models only as benign surfaces, where reactants are adsorbed on the surface where they can react.

We propose a hypothesis that connects chemical synthesis on the surface of dust particles with electrical charging of the particles by known physical phenomena in the ISM. Individual particles can be negatively charged by attaching to electrons in areas of the gas that is ionised, or positively charged in the periphery of dust clouds where electromagnetic radiation is powerful enough to eject electrons from particles. Using knowledge of redox process at the solid/liquid and solid/gas interfaces; a hypothesis is presented for processing mechanisms involving electron transfer between surface adsorbed species and the solid dust particles found in the ISM. The hypothesis is based on the interaction of dust particles with electromagnetic radiation and plumes of ionised gas, which electrostatically charge dust particles leading to an adjustment of the Fermi energy of electrons on the surface of individual particles. Here the individual particles act as „single electrode electrochemical reactors in the gas phase.

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EM8-Po

Electrosynthetic Processes at the Carbon Membrane Stabilised Triple Phase Boundary Interface

John Watkins, Sunyhik D. Ahn, James E. Taylor, Steven D. Bull, Frank Marken
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Electrosynthetic processes are becoming more widely established as a tool in organic synthesis with some processes seeing success at the industrial scale, most notably the production of adiponitrile in the Monsanto process[1]. The advantages of electrosynthesis over traditional synthesis are that less harsh reagents and conditions generally need to be used for simple redox processes. With fewer reagents involved processes can generally be made cleaner and more efficient.

However there are disadvantages holding back electrosynthetic processes from being more widely accepted as a synthetic tool. One such disadvantage is that the choice of solvents is limited to only very polar ones such as acetonitrile. Water would be the optimal choice but so often synthetic reagents are not soluble in it. Electrolyte is also required in large excess to ensure conductivity and is often problematic to separate post-reaction creating wasteful purification steps.

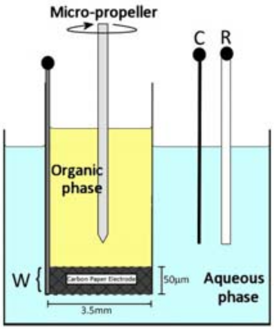
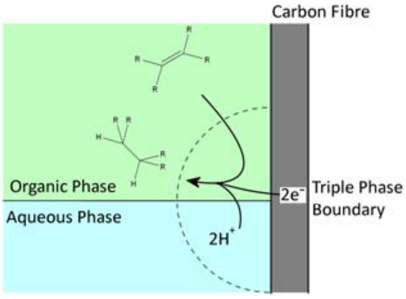


Figure 1. A carbon fibre stabilized triple phase



Scheme 1. A typical Triple phase boundary reaction occurring within the carbon membrane.

This work presents a new synthetic system which utilises a triple phase boundary process[2] (scheme 1.) utilizing the high conductivity of water containing all intentionally added electrolyte whilst keeping all organic reagents separated in an immiscible organic phase in which the reactions occur and from which products may be extracted directly (Figure 1). This also leaves the aqueous phase unaffected by the reaction meaning it can be recycled over multiple reactions.

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EM9-Po

Immersion Coating of Copper from a Deep Eutectic Solvent: A Novel Method for the Protection of PCBs

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The deposition of precious metals, including Ag and Au, onto a Cu substrate is an important process in the printed circuit board industry. This is to prevent oxidation of Cu preventing reflow of solder alloys during the joining of circuit components [1]. Commercial methods still suffer serious technological problems resulting in defects and failures in assembled devices. Here we investigate the application of a deep eutectic solvent (DES) as a replacement for the commercial aqueous galvanic and autocatalytic processes. A DES offers unique solvent properties; galvanic processes in DES systems do not require strong inorganic acids or toxic co-ligands and reducing agents [2]. The deposition of Ag, Pd and Au from a choline chloride: ethylene glycol based DES, (*Ethaline 200*), on to Cu has been studied and demonstrates a sustained growth. Such coatings are not available from corresponding galvanic aqueous processes [3]. The electrochemical properties of Ag, Pd and Au in Ethaline 200 has been studied and metal surface of the deposits have been characterised using spatial X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

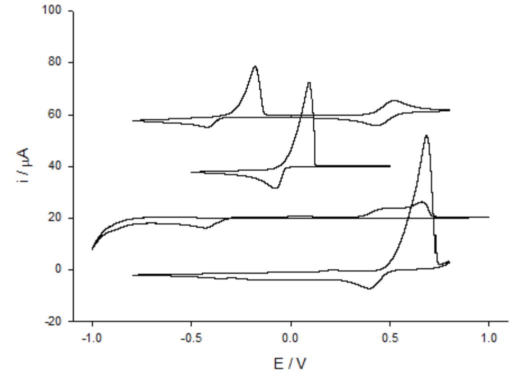

Figure 1: Cyclic votammograms of metal salts in Ethaline 200: (a) 0.02 M $CuCl_2$, (b) 0.02 M AgCl, (c) 0.02 M $PdCl_2$, (d) 0.02 M AuCl. Electrodes: working - 2mm Pt disc, counter - Pt flag, reference - Ag wire. $\nu = 10$ mV s^{-1}. CVs offset for clarity.

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Nano-Electro-Crystallization Symposium

NM1K

The dynamic copper electrode: growth and additive interactions on the atomic scale

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Since the successful implementation of copper as an interconnect material in modern ULSI microchips, copper electroplating gained major importance in the microelectronics industry. Current applications range from the defect-free filling of sub-50 nm features to micro scale structures with extreme aspect ratios. This is achieved in industrially used copper electroplating bathes by a combination of additives, which lead to Cu filling of these features from the bottom up. The simplest additive combinations that lead to such superfilling consist of chloride, a growth-inhibiting water-soluble polymer such as polyethylene glycol (PEG) and a growth-promoting short-chain aliphatic organosulfur species. Although the synergistic action of these additives is well documented, the underlying microscopic mechanisms are still under debate. Furthermore, the atomic-scale growth mechanisms at the high deposition rates employed in industrial processes are even unknown in additive-free electrolytes.

In my talk I will discuss how progress in increasing the temporal resolution of surface-sensitive *in situ* methods can help to unravel the growth mechanisms and additive-surface interactions in these complex systems. Specifically, I will present atomic-scale studies on millisecond time scale by fast scanning tunnelling microscopy (Video-STM) [1,2] and surface X-ray diffraction methods [3], using Cu(100) in chloride-containing electrolyte as an example. Starting from the interface structure in the double-layer regime, which exhibits characteristic differences to Cl-covered Cu(100) under ultrahigh vacuum conditions [4], the pronounced influence of the potential-dependent Cl adlayer structure on the Cu growth behaviour is illustrated. Furthermore, these studies reveal growth induced surface strain, which can be attributed to the presence of steps and adatoms. Similar studies in electrolytes containing PEG provide insight into the structure of the inhibiting layer and the growth inhibition. As a model for the accelerator species methyl thiolate on Cl-covered Cu(100) was investigated by *in situ* Video-STM. Quantitative statistical analysis of the observed surface dynamics allows determining the intermolecular interactions between these organosulfur adsorbates as well as reveals pronounced interactions with Cu adatoms.

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NM2K
DNA-templated conductive nanowires

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DNA is a chemically-robust, well-defined template on which a variety of conductive materials can be grown under mild conditions. We have described the synthesis of smooth and uniform metallic, semiconducting and polymer-based nanowires by mild aqueous routes at room-temperature [1]. The nanowires have been chemically characterized by FTIR, XRD, XPS and their conductivity measured by cAFM, scanned conductance microscopy and direct two-terminal I-V measurements. All the nanowires show some common features in their growth morphology and we have developed a simple model based on considerations of surface tension and line energy that accounts for the main aspects of the templating reaction.

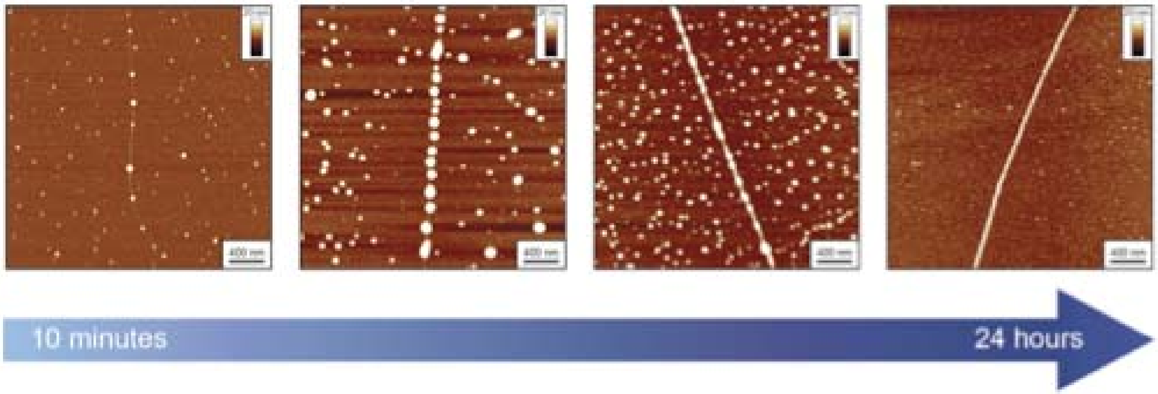

Figure 1. Atomic force microscopy time course of the formation of poly(dithienylpyrrole) nanowires on ⌊-DNA.

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NM3
Growth of Pt films on Au(111) via Surface Limited Redox Replacement (SLRR)

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Here we will present the Surface Limited Redox Replacement (SLRR) protocol implemented and optimized for growth of Pt films on Au(111) using sacrificial underpotentially deposited (UPD) layer. The growth was done in *one-cell configuration*, different from protocols previously reported in literature, which use either multiple immersions [1] or flow-cell setup [2]. The SLRR method has two well decoupled steps: (1) formation of the epitaxial UPD layer under potential control and (2) surface-limited redox replacement of that UPD layer by a more noble metal at open circuit potential (OCP) i.e. electroless step. So far this method has been successfully applied in synthesis of functionalized Pt fuel cell catalysts [3, 4] and thin film growth [5] using Cu UPD sacrificial metal.

In present work we explore deposition of Pt films obtained by SLRR of Pb UPD [6]. Even after the first displacement by SLRR of Pb UPD, STM reveals homogeneous and dense Pt clusters network with the roughness that does not change with the number of replacement as illustrated in Figure 1A. We used OCP chronopotentiometry and electrochemical quartz crystal microbalance (EQCM) to follow displacement kinetics. The EQCM measurements show excess of Pt deposition that could be attributed to additional reduction power due to oxidative adsorption of OH_{ad} [7] taking place during Pt deposition or H-adsorption/ partial desorption [8] expected to take place upon Pb UPD layer formation. This surprising result has motivated the study of Pt deposition films based on SLRR of H-UPD layer. Our work clearly demonstrates that it is indeed possible to deposit Pt films using the H reduction power. The accordingly grown Pt films show roughness increase with the number of replacement events, Figure 1B. All SLLR deposited Pt films are characterized by H-UPD, X-Ray diffraction, EDS and ex-situ scanning tunnelling microscopy (STM). Moreover, the structure and roughness of SLRR grown Pt films will be compared to Pt films grown by overpotential deposition (OPD) at different potentials.

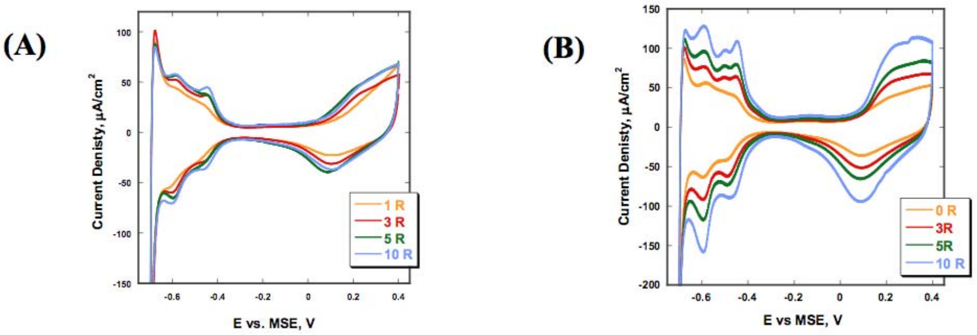

Figure 1. Cyclic voltammetry in 0.1 M H_2SO_4 (50 mV/s) on Pt films deposited after different number of replacements using (A) SLRR of Pb-upd on Au-films, (B) SLRR of H-upd on Pt-films (deposited on Au using SLRR of Pb UPD)

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NM4

Electrodeposition of platinum from lyotropic liquid crystal mixtures

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The aim of this research project is to prepare surfaces with controlled size and dispersion of small size particles by using electrochemical deposition. Small size particles are reported to enhance catalytic performance thus, reduce the amount of expensive metals such as platinum loaded onto an inert substrate.[1]

The electrodeposition of platinum from H_2PtCl_6 has been studied using cyclic voltammetry and chronoamperometry in varying mixtures of octaethyleneglycol monohexadecyl ether $C_{16}EO_8$ and water. $C_{16}EO_8$ is known to form liquid crystalline phases depending on its concentrations in water. The mixtures were chosen to explore the micellar and hexagonal phase of the crystal. Pt films were electrodeposited on Au microdisic electrodes for a range of conditions such as the deposition potential and the charge density. In each case voltammetry in H_2SO_4 was used to characterize the deposited platinum films. The electroactive area, roughness factor and the specific catalyst area of the platinum were systematically calculated. The poster will present an overview of the experiments conducted and results obtained.

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NM5K

Electrocrystallisation of Silver in Deep Eutectic Solvents; an Electrochemical Kinetic Study Using Real Time *in-situ* Holographic Imaging

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Metallisation technology has been used for surface coatings as a means of enhancing or changing the substrate appearance and/or functional attributes such as abrasion, wear resistance, corrosion protection, lubricity or for improving the aesthetic qualities. Electrochemical (electrolytic or galvanic) metallization or plating processes involve the nucleation and subsequent growth of the nuclei resulting in isolated islands; thin film coatings then develop from further growth and coalescence of these isolated islands. The structure, functional properties and appearance of the thin films depends on the nucleation and growth mechanism. Usually the island growth occurs through Volmer-Weber growth, resulting in the formation of three dimensional (3D) islands. The island growth controls the morphology of the deposited films such as grain size, film thickness and electrical conductivity of the film. [1] The control of the island shape and the nuclei density is of great importance in material synthesis. Whilst most of the established literature is devoted to aqueous processes, recently we have been interested in the electrochemical nucleation and growth of metal films in non-aqueous media, particularly Deep Eutectic Solvents (DES type ionic liquids) based on quaternary ammonium salts and we have described the challenges associated with *in-situ* imaging of nucleation process using probe microscopy. [2-4]

Here we describe for the first time a totally new approach and will present preliminary results of an investigation into the early stages of electrochemical nucleation and the kinetics of island growth for silver deposition using *Digital Holographic Microscopy* (DHM) in a choline chloride / ethylene glycol DES electrolyte. DHM is several orders of magnitude faster than probe microscopy and is a non-contact imaging tool. Normalisation of the data has allowed kinetic information of thin film formation to be established. The study reveals that the silver electrocrystallisation at small over-potentials takes place through the formation of non-facet hemispherical islands with a random distribution on the surface.

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NM6K

Nucleation of gold nanoparticles at the water|1,2-dichloroethane interface

Yvonne Gründer, Sven L.M. Schroeder, Robert A.W. Dryfe

The formation of nanoparticles has been widely investigated due to their broad potential applications in many areas such as catalysis, electronics and coating applications. However, the initial nucleation and growth process of nanoparticles is not well understood, particularly in liquid solution, although this is crucial to optimise their physical and chemical properties for the required functionality.

The deposition process at an interface between two immiscible liquids can be considered as an intermediate case between purely homogeneous deposition through electron transfer between redox couples in the same phase, which on its own is difficult to control, and heterogeneous deposition at the (conventional) solid electrode-electrolyte interface.

Therefore, the liquid-liquid interface is ideal for interfacial nucleation studies as it should be free from defects, which serve as preferential nucleation sites and therefore a metastable state of the system should exist. With the two reactants, the oxidised metal precursor and a reducing agent separated in the two phases, the driving force of nucleation can be controlled through electrochemical control of the interfacial potential.

The electrochemically controlled reduction of tetrachloroaurate at the water|1,2-DCE interface was investigated. We have revisited this system previously investigated by Cheng and Schiffrin[1], since it is possible that the "random"[2] nature of the deposition process may be related to the presence of contaminants, which in turn may drive the nucleation process.

We find that the formation of a solid phase is hindered in a clean, defect-free environment and that the reduction to metallic gold can only be observed through addition of artificial nucleation sites. Although the interfacial electrochemical potentials indicate that the formation of a third phase by reaction is thermodynamically feasible, the lack of nucleation sites and/or anion-anion repulsion in a very clean system can stabilise a metastable state in which no nucleation through applied overpotential is possible at the liquid/liquid interface.

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NM7

Ultra Thin Layer Deposition of Low Band Gap semiconductors onto ZnO Nanowires for Photovoltaic Applications

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ZnO nanowire assemblies show great potential for use as photoanodes in excitonic solar cells. The well defined crystal structure, high aspect ratio and charge mobility render ZnO nanowires an attractive alternative to mesoporous TiO_2 nano particle films commonly used in dye-sensitized solar cells. Another attractive aspect of ZnO nanowires is the possibility of generating radial depletion layers by careful tuning of their cross section and doping density, these properties may enhance the efficiency of charge separation and collection upon excitation of the ETA layer.

Various means of sensitizing ZnO nanowires for photovoltaic applications have already been investigated, including the use of quantum dots [1] and photoactive dyes [2]. One promising approach is to electrodeposit thin shells of low band gap semiconductors such as CdTe and CdSe onto the nanowires, leading to a device commonly known as an Extra Thin Absorber (ETA) cell [3]. The nanowire morphology results in effective absorbance of diffused light by the thin absorber layers. Such an approach could lead to high efficiency photovoltaic devices which could be manufactured at a low cost.

The present contribution will focus on our initial investigation of the deposition of low band gap layers of CdSe and CdTe onto ZnO nanowires, including the use of ionic liquid electrolytes.

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NM8

Electrodeposition of Core-Shell Superconducting-Ferromagnetic Mesocrystals

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We have fabricated three dimensional superconducting-ferromagnetic core-shell structures by electrodeposition onto B-doped diamond electrodes, and probed the magnetic properties of individual mesocrystals using Hall array magnetometry. The superconducting core is a highly facetted single crystal of either lead or tin, and its magnetic properties do not suffer from complications associated with flux pinning. Different shapes of superconducting core can be achieved by tuning the concentration of the depositing metal in solution or by changing the overpotential applied to the working electrode [1]. The magnetic shell was electrodeposited on top of the superconducting core. Nickel was chosen as the shell material because of its ferromagnetic properties and the ability for it to electroplate [2]. Magnetisation measurements on individual mesocrystals exhibit superconductivity at applied fields well in excess of the bulk critical field of the core due to field compensation effects associated with the ferromagnetic shell. The magnetic response can also be tuned from net ferromagnetic to net diamagnetic by varying the applied magnetic field.

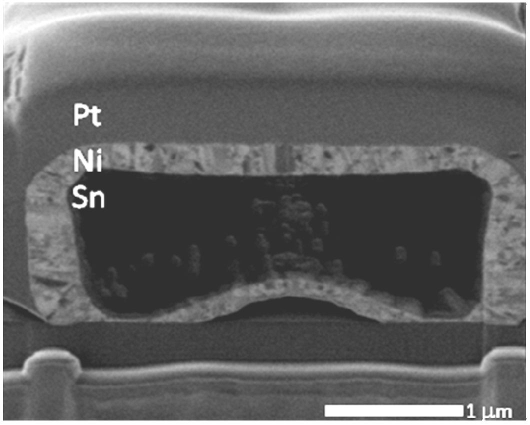

Figure 1. FIB image of the cross section of a tin-nickel core-shell crystal [2].

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NM9-Po

NANOSTRUCTURED HEATABLE GOLD WIRE ELECTRODES

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For Electrochemistry, temperature is one of the most important parameter along potential, current and time. Typically, the whole electrochemically measuring cell with electrodes and bulk solution is tempered to achieve the required temperature. Alternatively, research has developed various methods for heating only the electrode but leaves the temperature of the bulk solution unaffected. Causing a fast adjustment of the desired temperature and leading to extremely short measurement periods, heated electrodes offer a series of novel and unique advantages. Beside the acceleration of electron transfer processes and the thermal convection towards and back from the electrode surface, the heated electrodes enable the enhancement of the sensitivity in electrochemical analysis [1]. In view of the growing trend towards miniaturized sensors, signal amplification is an important strategy to decrease the detection limits.

In this work a gold nanostructure is generated on heatable wire electrodes [2]. With the heated electrodes it is possible to enhance analytical signal in several applications. The gold nanostructures were generated by template-free electrodeposition at room temperature and lead to the enlargement of the electrochemically active electrode surface [3]. The time for the deposition is varied between 300 and 1200 seconds. A scanning electron microscopy image shows the structure of the gold wire electrode before and after electroplating (Figure 1). The new structures were investigated by performing electrochemical measurement with and without heating. We observed an increasing voltammetric signal compared to unmodified and unheated electrode surfaces.

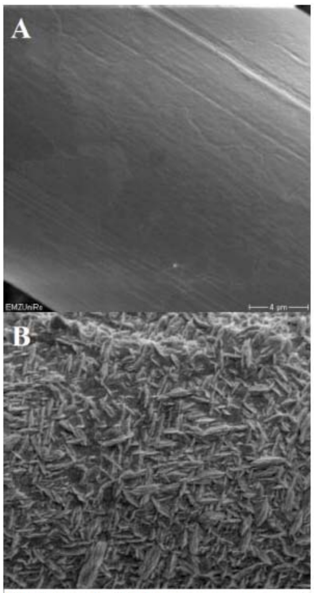

Figure 1 SEM micrographs of A) plain and B) nanostructured Au wire electrode in five thousand fold magnification

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Nano-Electroanalysis Symposium

NE1K

Covalent Chemical and Electrochemical Modification of Carbon Nanotubes by Redox Probes for Biosensor Applications

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The surface modification of carbon nanotubes (CNT's) with monolayer of specific chemical functional groups has received great interest for potential applications in molecular electronics, biosensors, surface adhesion and electrocatalysts. In this work, electrochemical and solid phase synthesis methods have been used to covalently bond an organic monolayer linker and redox probe to the surfaces of carbon nanotubes[1]. After abrasive immobilization of CNT's to the glassy carbon electrode, the linker layer was covalently attached to the CNT's either by electrochemical reduction of $PhCH_2NHBoc$ diazonium salt or oxidation of Boc-EDA. After the Boc group deprotection, a selection of organic redox probes such as anthraquinone (Fig.1), nitrobenzene and dihydroxy benzene are attached to the spacer layer by amid coupling reaction using solid-phase synthesis. The surface coverage, stability, electron transfer coefficient and rate of the tethered probe have been investigated by electrochemical techniques. The resulting dihydroxy benzene modified CNT's were evaluated as a mediators for the oxidation of NADH. The combination of electrochemical attachment of protected linkers and subsequent modifications using solid-phase synthesis provides a very versatile approach for attaching a wide range of organic moieties onto different types of carbon surface.

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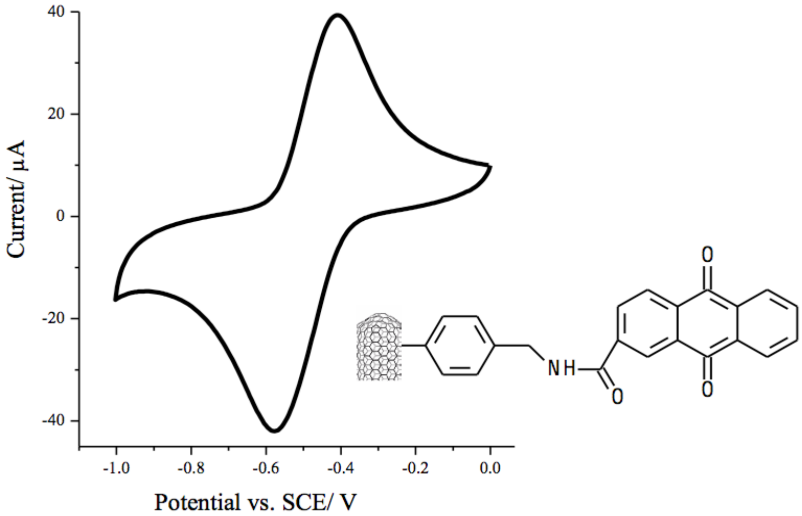

Fig.1. Cyclic voltammograms at scan rate of 50 mV s_{-1} in 0.1 M PBS, pH 7, NH for CNT's modified by AQ through $PhCH_2NH$ spacer layer.

Acknowledgment: This project is funded by National Plan for Science and Technology (NPST), King Saud University, Project no: 10-NAN101402.

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NE2
Trace Metal Electroanalysis in Cotton Films

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Natural cellulose is an abundant raw material and of interest in many fields of technology. Natural cellulose in the form of cotton is a widely used textile with the ability to absorb humidity. In electrochemical studies cotton has been employed either (i) dissolved and re-precipitated onto electrodes [1] or (ii) in the natural state as discs in contact to suitable working electrodes [2]. Here, a cotton textile is employed as a versatile sample pre-concentrating substrate for trace metal sensing in a new electroanalytical procedure.

It has recently been shown [3] that a solid electrolyte salt such as ammonium chloride or ammonium nitrate can be employed in direct contact to an electrode surface resulting in an array of contact points where electrochemical processes occur. In order to visualize the electrochemically active zone in this type of measurement cell and in the presence of humidified argon (ca. 80% relative humidity), the cotton disc was immersed into Aurofab gold plating solution, dried, and then placed into the humidified "salt cell" (see Figure 1).

Next, cotton discs pre-impregnated with aqueous sample solution containing 0.1 M $NaNO_3$ and trace levels of Hg^{2+} (1 hour immersion) were dried and placed into the measurement cell. At very low Hg^{2+} concentrations (5 nM = 1 p.p.b) DPV stripping responses are obtained. A mechanism for this high level of sensitivity will be discussed.

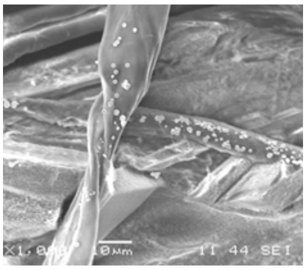

Figure 1. Scanning electron microscopy image of a cotton surface with deposits of gold. The cotton was dipped into gold plating solution (Aurofab BP RTU II, Rohm and Haas), dried, and placed into the humidified electrochemical cell for gold deposition. Gold micro-discs signify "active" cotton-electrode contacts.

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NE3

Development of Au nanorods arrays in alumina for SERS substrates

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There has been growing interest in the properties and uses of metal nanorod arrays due to their anisotropic nature with respect to strong surface plasmonic resonances. The spectroscopic, photochemical and electromagnetic properties of particularly gold nanorods arrays make them an ideal substrate in applications such as SERS and Dark Field Imaging [1]. Studies into optimizing their preparation conditions, overall dimensions, and controlling the level of exposure of the nanorods from their alumina template support are essential in developing these substrates for tailored applications.

The nanorod arrays here were produced by *a.c.* electrodeposition of gold into the pores of a hexagonally ordered alumina film grown on an aluminum substrate using a two stage anodisation process in oxalic acid followed by barrier layer thinning. FTIR specular reflectance (Exoscan FTIR 4100) provided a new and rapid method of determining the porous film thickness as shown in Figure 1. The results were verified by *in-situ* ellipsometry monitoring and modeling of the film growth in oxalic acid.

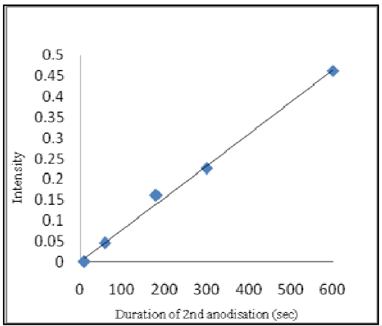

Fig.1. Intensity of the bayerite alumina FTIR peak *vs* anodisation time.

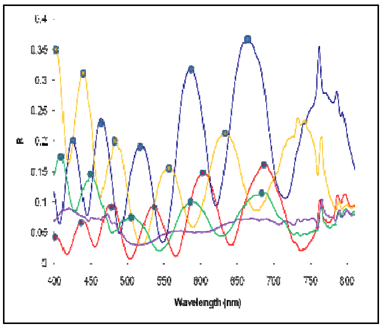

Fig.2. *S*-polarized specular reflectance of Au/alumina composite film showing effect of rod exposure.

Specular reflectance measurements over the range 400 – 820 nm with both *s* and *p* polarised light showed pronounced interference fringes. From the s polarized light interference pattern the depth of the gold within the pores and therefore the amount of alumina to be etched back to expose the gold was calculated. The conditions for etch back were optimized using reflectance spectra data, as shown in Figure 2, and SEM imaging. Once the rods had been exposed the spectra obtained showed no fringes but a distinct transverse plasmonic resonance at *ca.* 510 nm. In addition a weak 'higher order' transverse plasmonic resonance [2] at ~450nm was observed.

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NE4

Modelling the amperometry of AFM-SECM systems

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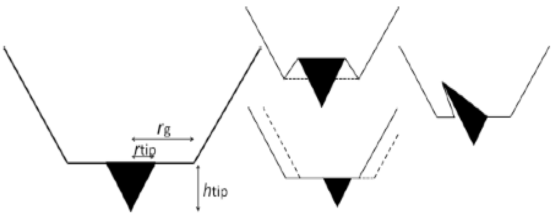
Scanning electrochemical microscopy (SECM) is used to image the reactivity of a surface by scanning an electroactive probe above the sample of interest. However, the experiment is run at constant height and the topography influences the current measured at the electrode. The combination of atomic force microscopy (AFM) with SECM, achieved by integrating a microelectrode into an AFM cantilever, relies on the atomic force keeping the sharp tip of the probe at constant distance from the substrate. The influence of the topography on the current is thus minimized.
The probes are fabricated by coating a commercially available cantilever with a layer of conductive material, followed by a layer of insulation. Focused Ion Beam is then used to remove the insulation from the tip apex. The insulation layer is then further etched to reveal the electroactive region. This results in conical electrodes with conical insulation[1]. The fabrication of these probes is difficult and defects occur. The process is also expensive. The work had two main aims: firstly to model and study the behaviour of "perfect tips" both in the bulk and close to a surface; secondly to investigate the influence of the tip geometry on the behaviour of the electrode. 2D and 3D finite element modelling of the diffusion controlled amperometric response of both perfect tips and tips presenting defect were simulated and their influence quantified.

An expression was derived to predict the limiting current in the bulk of these electrodes as a function of three parameters: r_{tip} the radius of the electrode, h_{tip}, the height of the electrode and r_g, the radius of the insulation sheath. Typical defects encountered were modelled and tables of their influence derived to enable the adjustment of the equation for a more accurate bulk limiting current estimation[2]. Approach curves and line scans were used over various substrates to determine the sensitivity and resolution of the electrode. Guidelines are derived showing the electrode geometry with the best imaging capabilities. The study of the defects enables their classification in terms of their influence and users can now decide which tip should be discarded or what loss in resolution is to be expected.



Left: The perfect tip, with the electroactive area in black; right: Typical defects such as insulation forming a crater around the electrode, off centered tip and gap in the insulation

This lecture will present the results obtained for tips in the bulk, approach curves, line scans and the guidelines for choosing the best AFM-SECM tip geometries.

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NE5K

Quantitative Visualization of Electrocatalysis at Individual Metal Nanoparticles

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Electrocatalysts are of ubiquitous importance and can be found in a large array of research fields and applications, including corrosion science, development of electroanalytical sensors, waste water treatment, electro-organic synthesis and energy conversion devices (*e.g.* batteries, fuel cells and solar cells). Of particular interest is the development and optimisation of electrocatalysts for low temperature fuel cells, which are expected to play a vital role in fulfilling future energy demands.

Fuel cell electrocatalysts generally consist of noble metal (platinum, rhodium, ruthenium) nanoparticles (NPs) immobilized on a carbon support to optimise metal utilisation. Current understanding is mainly derived from studying large ensembles of nanoparticles, in which there may be a large dispersion in size, shape and support effects. As such, the results drawn from these studies reflect the average electrocatalytic behaviour of an ensemble, even though electrocatalytic properties of individual nanoparticles may vary widely.

In this work we demonstrate how the novel scanning electrochemical cell microscopy (SECCM) technique [1] can be combined with conventional high resolution imaging techniques (AFM and FE-SEM) to locate and address the electrochemical characteristics of individual NPs on a surface. In particular, we have studied the electrocatalytic behaviour of small NP ensembles and individual NPs within an ensemble on carbon-based support materials. The approach described allows the electrocatalytic behaviour of individual particles to be linked to their physical characteristics, opening new avenues in NP electrocatalysis research and nanoscale electroanalysis.

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NE6K

Electrochemistry in nanopore/electrode structures - from pore fabrication to DNA sequencing-by-tunneling

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Solid-state nanopores have recently attracted much interest as ultrafast and robust DNA fragment sizing and sequencing devices. Other, perhaps equally attractive applications include the detection of proteins, RNA, protein/protein and protein/DNA interactions [1, 2]. These sensors combine the features of true single-molecule sensing with the prospects of working in rather concentrated solutions, for example under physiological conditions. One of the challenges in nanopore sensing is however rooted in the lack of spatial resolution and specificity of the pore, and the poor control over the translocation speed. For example, with a view on DNA sequencing, even thin solid-state membranes of, say 30 nm in thickness, are still contain many DNA bases at the same time and any detected signal is a convolution from many bases.

Integrating electrode structures with the nanopore is one way to overcome (some of) these issues and also offers new routes to nanopore device fabrication, including small metallic nanopores [3, 4]. We have fabricated a range of different electrode structures, including ‘large’ membrane electrode devices, ‘small’ □-electrode/nanopore architectures, and multi-electrode/nanopore devices (e.g. tunnelling junctions aligned with the nanopore) [5]. I will present a selection of these nanopore/electrode structures, their electrochemical characterization (current flow in the cell, pore conductance), and how they can be used for single-molecule biosensing applications [4]. Detection of single molecules can be based on electric current, optical spectroscopy or a combination of both, offering a unique set of tools for biomolecular sensing.

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NE7

The electrochemistry of single silver nanoparticles via nanoparticle-electrode collision processes

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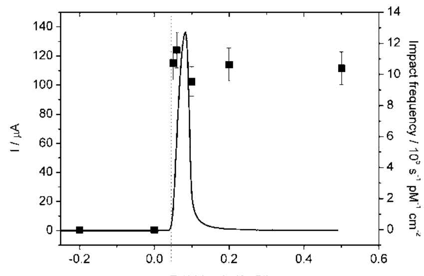
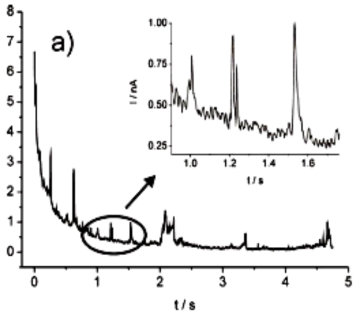
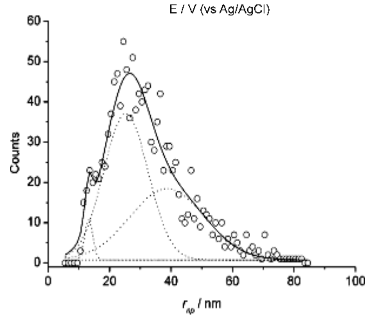
To characterize the risk posed to ecosystems by increased release of silver nanoparticles (AgNPs) and their environmental fate, the development of detection techniques is urgently required. Here we investigate for the first time the anodic particle coulometry (APC) method based on the faradaic charge transfer during the direct electro-oxidation of AgNPs while they collide with an electrode. Using this method we can quantitatively detect and characterize AgNPs in aqueous solution as well as monitor AgNPs aggregations. Furthermore, the underpotential deposition of Tl (Tl UPD) is also observed during the AgNPs – electrode collision process.







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NE8

Simultaneous determination of paracetamol and dopamine using thin film pyrolytic carbon electrodes

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This work describes the electrochemical properties of thin (150 nm) pyrolytic carbon (PyC) films created using a reliable, non-catalytic chemical vapour deposition process. After deposition, the electron transfer characteristics of the films are optimised using a simple oxygen plasma treatment. The resulting material is endowed with a large electrochemi cal surface area and outstanding electron transfer properties. PyC represents a new class of carbon electrode, and its large density of edge-plane graphitic sites makes it an ideal candidate for electrochemical sensor applications. In particular, it has been used for the simultaneous determination of paracetamol and dopamine. This is an issue of considerable importance, as the former is known to interfere with dopamine measurements in biological samples. Pyrolytic carbon exhibits excellent electro-catalytic activity towards the oxidation of these two compounds, and the sensor shows high sensitivity and low detection limit. It has been applied to the determination of paracetamol and dopamine in commercial pharmaceutical samples.

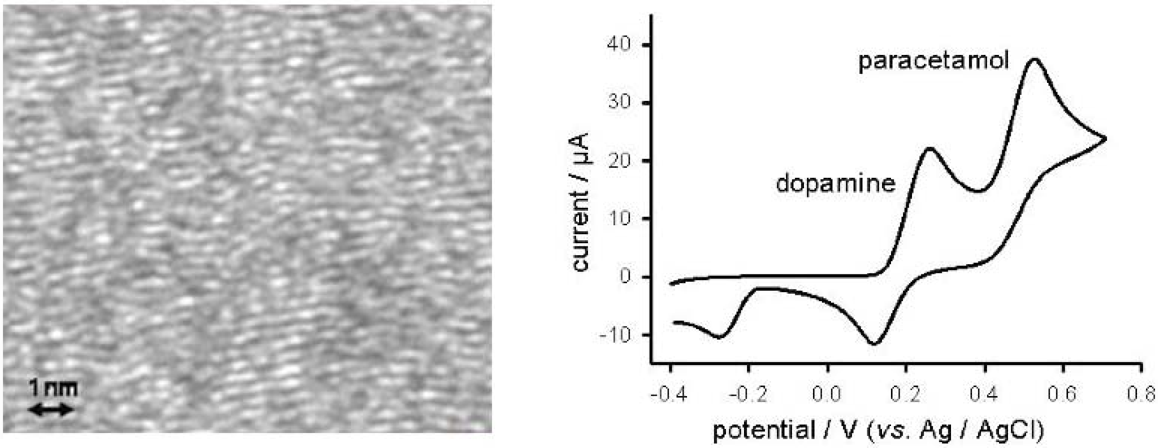

Image showing the nano-crystalline graphitic structure of PyC films, along with a cyclic voltammogram recorded at a PyC electrode in the presence of 1 mM dopamine and 1 mM paracetamol in 0.1 M phosphate buffer (pH 7). Note the large separation between the oxidation peaks for the two compounds.

Ref: Keeley *et al.*, *Electrochem. Commun.* **2010**, *12*, 1034-10

NE9

Single Walled Carbon Nanotubes (SWNTs) as a Template for the Controlled Deposition of Functional Gold Nanostructures

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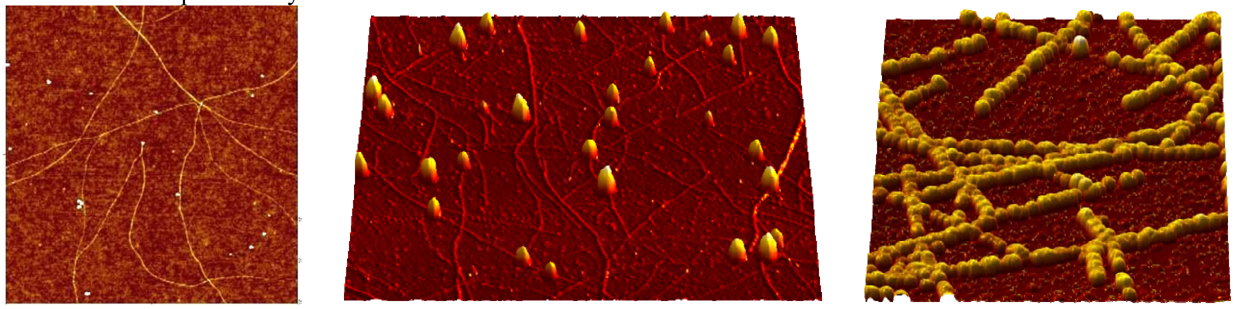
Random networks and individual isolated pristine single-walled carbon nanotubes (SWNTs) can be decorated electrochemically with Au nanoparticles (NPs). By using a sparse surface coverage (typically less than 1%) of pristine SWNTs on an insulating substrate electrodeposition of NPs is highly directional. By varying electrodeposition driving force (potential) and time one can control the NP density and size. Our findings suggest that nucleation of Au on SWNTs is 'instantaneous', and the nucleation density increases with increase of the deposition driving force[1]. This knowledge has enabled us to synthesize a range of different nanostructures, from isolated Au NPs to Au nanowires (NWs), which we have used as expedient platforms for analytical [2] and electrocatalytical purposes [3]. In particular, we show that such devices are particularly attractive for the measurement of fast electron transfer kinetics.



(i) SWNTs (ii) Au Nanoparticles on SWNTs (iii) Au NWs

Figure 1. AFM images of
(i) a random SWNT network [1],
(ii) a random SWNT network decorated with Au NPs [1],
(iii) Au NWs electrochemically deposited onto a random SWNT network.

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NE10

Facile preparation of nanogold in solution or on solid surfaces for electrochemical applications

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Over the last two decades, different kind of gold nanomaterials have been used tremendously in electroanalysis due to its unique properties e.g. electrocatalytic, conductivity, stability etc. However, the preparation methods of gold nanomaterials should be more simplified for wide applications. In this conference we will show (1) a facile preparation of carboxylate-functionalized gold nanoparticle (CAuNPs) and their attachments on indium tin oxide (ITO) electrode, (2) simple preparation of gold nanowire (AuNW) seeds, their attachments on ITO electrode and followed by growth of seed with various kind of growth solution for comparison studies, (3) one step chemical preparation of AuNP/ITO electrode and (4) comparisons studies of electrochemical properties among the different types nanogold-modified electrodes and conventional electrodes.

To prepare CAuNPs, simply an aqueous solution of $HAuCl_4$ was added to alkaline solution of 2,2'-dihydroxy-1,1'-dinaphthylmethane-3,3'-dicarboxylic acid (aq.) under sonication and continued sonication for 15 min. Afterward, the synthesized CAuNP was characterized by UV, TEM and XPS. TEM images confirm the mean size of CAuNPs was 10.8 ± 1.2 nm. For apply as electrode materials, the CAuNPs were immobilized on amine terminated ITO (AITO) electrode. The FE-SEM images confirmed the homogeneously immobilization of CAuNPs on AITO. The CAuNPs/AITO has better electrocatalytic property toward the electrooxidation of dopamine than that of conventional CAuNPs/amine terminated ITO electrode. In different experiment, AuNWs were prepared by same methods of CAuNPS preparation except using 2-naphthol instead of 2,2'-dihydroxy-1,1'-dinaphthylmethane-3,3'-dicarboxylic acid. Afterward, the AuNWs were immobilized on AITO. Next, AuNWs/AITO was immersed in three kinds of growth solutions individually for comparison studies in terms of morphology and electrochemical properties. The different growth solution allowed growing the AuNW with different shape, size and density. Moreover, different growths solution treated AuNW/ITO electrode showed different electrocatalytic property toward the electroxidation of glucose. Besides, the bare ITO electrodes was treated with $HauCl_4$ (aq.) and ascorbic acid (aq.) and followed by heating at 75 ^{0}C for 15 for one step preparation of AuNPs/ITO. The FE-SEM images demonstrated that the sizes of AuNPs were changed with changing the ratio between $HAuCl_4$ and ascorbic acid. Next, the modified electrode was subjected to check the electrochemical properties. The impedance data indicated that our developed AuNP/ITO has much lower charge transfer resistivity than that of bare ITO, or commercially available AuNP/AITO electrode. Moreover, our AuNP/ITO showed best electrocatalytic properties toward the electrooxidation of hydroquinone or catechol among the tested electrodes.

Electrochemical CO_2 Conversion Symposium

CO1K

Solar driven fuel synthesis: Opportunities and Challenges

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The world is facing a tremendous energy challenge, and solar energy harvesting is indispensible for a sustainable energy supply in the near future. Production and demand need to be balanced both in time and across different locations, which requires the scalable conversion of solar energy into fuel, preferably a (transportable) hydrocarbon.

Process options for artificial solar to fuel (S2F) systems can roughly be divided in two. One option is to use advanced photovoltaic solar panels, converting solar energy into electricity, while the generated electricity can be used in a second step to convert water and CO_2 into thermodynamically uphill products such as methanol. This is viable if a highly selective electrode for CO_2 reduction is developed. Direct electrochemical reduction of CO_2 in aqueous solutions has been studied with many different metals as a catalyst. Copper shows to be unique in that it forms detectable amounts of methane (CH_4) and C_2 products [1-3], while certain copper electrodes were found to produce Fischer-Tropsch-like products up to C_4 [4]. Recent progress in understanding of electrochemical CO_2 reduction over Cu-electrodes will be highlighted, including details of the morphology of the copper electrodes which influence their catalytic performance.

An alternative process would be to directly convert solar photons into chemical products by photocatalysis[5]. Its advantage compared to (photo)-electrochemical cells lies in the absence of a proton transfer membrane, while at the same time an external circuit is not necessary. Also here several bottle-necks need to be solved before direct photocatalytic conversion of CO_2 and H_2O can be practically applied, one being the high recombination probability of the photo-excited state. This is related to the inefficient transport of the electron and hole pairs to the catalytic promoters and surface adsorbed reagents, i.e. CO_2 and H_2O, respectively. Downscaling of the chromophore particles to the atomic level will be demonstrated to be a way forward, with particular emphasis on the function of Ti-O-sites in the silica scaffold SBA-15[6].

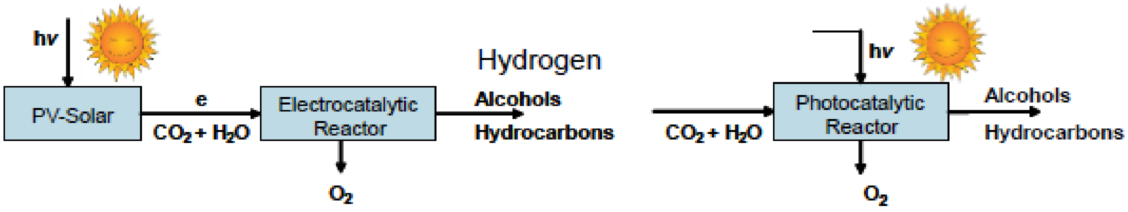

Fig. 1. The two process options to be discussed: left, electrocatalysis; right, photocatalysis

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CO2

The Importance of Surface Morphology in Controlling the Activity of Polycrystalline Copper towards CO2 Electroreduction

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Electrochemical reduction of CO_2 into hydrocarbons is an interesting route for capturing CO_2 and producing chemical fuels [1]. The most attractive metal for CO_2 electroreduction is copper since it is the only metal known that efficiently produces hydrocarbons [2]. However, it has been shown that the efficiency and the selectivity of this catalyst are dependent on many different reaction conditions such as the choice of electrolyte, the working potential, and the electrode pretreatment. The present study is on three different polycrystalline copper electrode morphologies: an electropolished surface, a surface covered by copper nanoclusters and a sputtered surface

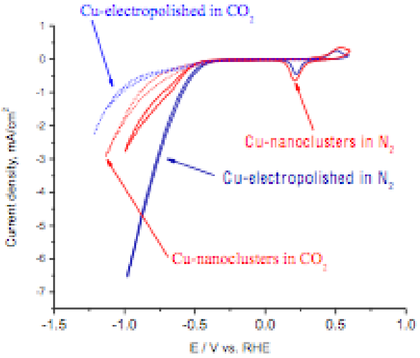

Figure 1. Cyclic voltammograms of electropolished and Cu-nanocluster covered surfaces in N_2 and CO_2.

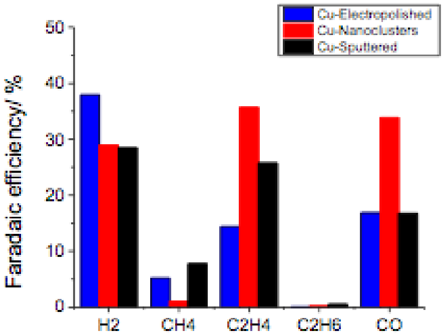

Figure 2. Product distribution and related Faradaic efficiencies for the three Cu surfaces at -1.1 V vs.RHE.

Cyclic voltammograms of electropolished and Cu-nanocluster covered surfaces in N_2- and CO_2-saturated electrolyte (0.1M $KClO_4$) on Fig.1 show different onset potentials of the reduction reactions. Lower onset current densities in CO_2 environment indicate the blocking of active sites by intermediates of CO_2 reduction reaction.

Fig. 2 shows Faradaic efficiencies for each of the products for all three types ofelectrode at -1.1 V vs. RHE. The trends observed here are in a good agreement with theoretical predictions, that the undercoordinated sites are more active for obtaining hydrocarbons from CO_2 [3].

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CO3

Bio-inspired Metal Sulphide Electrocatalysts for CO_2 Reduction

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The threat of climate change has put the development of carbon capture, storage and utilisation technologies firmly on the scientific and political agenda. Iron-nickel sulfide membranes formed in the warm, alkaline springs on the Archaean ocean floor are increasingly considered to be the early catalysts for a series of chemical reactions leading to the emergence of life. The anaerobic production of acetate, formaldehyde, amino acids and the nucleic acid bases – the organic precursor molecules of life – are thought to have been catalyzed by small cubane (Fe,Ni)S clusters (for example Fe_5NiS_8), which are structurally similar to the surfaces of present day sulfide minerals such as greigite (Fe_3S_4) and mackinawite (FeS).[1] Contemporary confirmation of the importance of sulfide clusters as catalysts is provided by a number of proteins essential to modern anaerobic life forms, such as ferredoxins, hydrogenases, carbon monoxide dehydrogenase (CODH) or acetyl-coenzyme A synthetase (ACS), all of which retain cubane (Fe,Ni)S clusters with a greigite-like local structure, either as electron transfer sites or as active sites to metabolise volatiles such as H_2, CO and CO_2.[2]

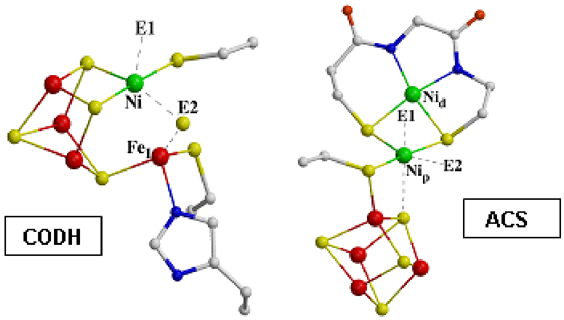

Figure 1 (Fe,Ni)S cubane clusters in enzyme active sites.

This talk will describe our recent attempts to model the electronic structure and redox properties of bulk iron sulphide materials and to identify the preferred sites of CO_2 adsorption. Alongside this we have investigated two approaches to the synthesis of FeS nanomaterials, namely via single source precursor routes or by continuous hydrothermal synthesis. Finally initial investigations into the electrochemical properties of these materials and their stability under experimental conditions will be discussed.

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CO4

Electrocatalytic Carbon Dioxide Reduction

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The energy efficient reduction of carbon dioxide to generate useful products is highly desirable for environmental and economic reasons. Due to the high potential required for the direct reduction of CO_2, catalysis is crucial in order to offer a reaction pathway of lower energy. Although vast arrays of CO_2 reduction catalysts have been identified the understanding required to implement an intelligent design of catalysts is not yet available, due to knowledge gaps in the mechanisms as well as efficiency and durability[1].

The electroreduction of CO_2 in the presence of $Mo(CO)_4$bipy and structurally similar compounds has been investigated. The group of compounds used were found to lower the overpotential necessary compared to the uncatalysed system as seen below (figure 1).

Experiments were carried out in a non-aqueous environment in order to take advantage of the enhanced solubility of CO_2 and avoid the competing hydrogen evolution reaction HER, which often hinders the interpretation of data gathered using aqueous electrolyte[2].

The mechanism of the reaction is being investigated.

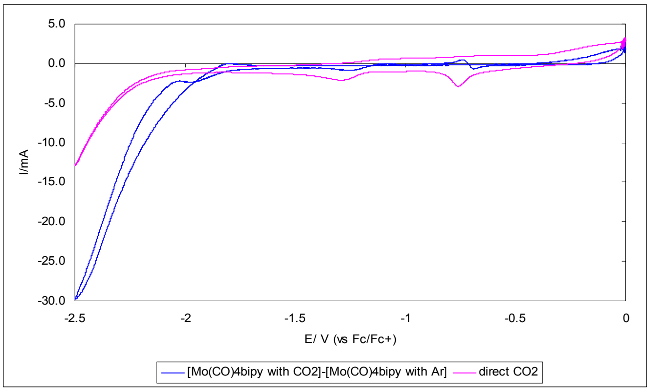

Figure 1: Cyclic Voltammograms, in THF with 0.1M $TBA(BF_4)$, showing direct CO_2 reduction and CO_2 reduction in the presence of 0.5mM $Mo(CO)_4$bipy. Scan rate: $200mVs^{-1}$, at room temperature and pressure. Fc based RE, Au (2mm diameter) WE.

References:
[1] Saveant, J. M. *Chem. Rev.*, 2008, 108 (7), pp 2348–2378
[2] Y. Hori, in *Electrochemical CO_2 Reduction on Metal Electrodes, Modern aspects of Electrochemistry No.42*, ed. C. Vayenas et al., Springer, New York. pp 89-189.

CO5
Cu and Au Electrocatalysts for CO_2 Reduction

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The electrochemical conversion of carbon dioxide into small hydrocarbons, with potential use as fuels, has generated considerable attention in recent decades.[1] One of the most pressing issues is the development of good electrocatalytic materials, which effectively reduce CO_2, while avoiding poisoning effects due to the production of carbon monoxide. Copper has been found to be a promising electrode material, due not only to its catalytic activity towards CO_2 reduction, but also to its high tolerance towards CO poisoning.[2]

In this contribution, we describe the performance of electrocatalysts for CO_2 reduction based on metallic nanoparticles (Cu, Au and Cu@Au), supported on carbon black powders (Vulcan XC 72R). The metallic nanostructures are prepared by colloidal synthesis methods, electroless deposition and a combination of both approaches. Metal loading, crystalline structure, as well as particle size and distribution, were characterised using XRD, EDX and TEM (see Figure 1). Preliminary electrochemical studies suggest that the reduction of CO_2 is dependent on the electrolyte and pH, as well as on the nature of the electrocatalyst. The results also indicate that there is a marked influence of both mass transport and surface processes on the overall reaction.

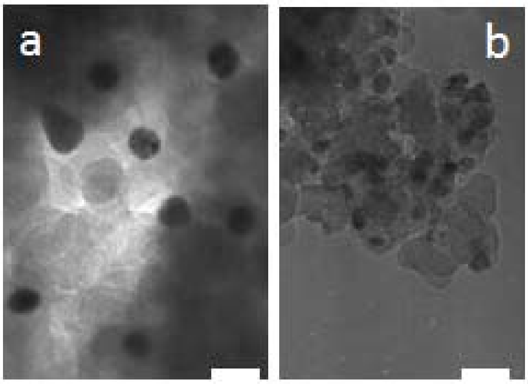

Figure 1. TEM images of Au (a) and Cu (b) nanostructures on Vulcan. The scale bars represent 20 and 50 nm in (a) and (b), respectively.

References:
[1] E. Barton Cole, P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev and A.B. Bocarsly,
J. Am. Chem. Soc., 132 (2010) 11539.
[2] M. Gattrell, N. Gupta and A. Co, J. Electroanal. Chem., 594 (2006) 1.

CO6-Po

Electrochemical Activation and Incorporation of Carbon Dioxide into Organic Compounds

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Carbon Dioxide is the main contributor to the increased concentration of gases present within the atmosphere. The main cause being combustion of fossil fuels (coal and oil). Therefore green methods which involve reducing the amount of CO2 in the atmosphere are currently of much interest to industry.
Current methods involve capture of CO2 using an amine based species post combustion. [1] Pre-combustion methods also exist in which fuel is firstly converted to H2 and CO2 followed by capture. Once captured storage of CO2 is required, however CO2 has possible use as a C1 building block in organic synthesis, and if effectively activated it can allow for the carboxylation of organic molecules referred to as fixation. For example, reaction of epoxides with CO2 affording cyclic carbonates. These types of organic molecules have various uses and applications within industry such as in the manufacture of paint-strippers, anti knocking agents and bio-degradable packaging.[2] Generally this type of reaction is carried out at high temperatures (>100oC) and elevated CO2 pressures (>10 atm) in the presence of an organo or metal catalyst.
Electrochemical activation of carbon dioxide and incorporation into epoxides forming cyclic carbonates provides a mild route to the activation and fixation of carbon dioxide. Our work shows the implementation of a catalyst free electrochemical system for the carboxylation of epoxides using alternative Bu4NBr supporting electrolyte and user friendly acetonitrile solvent. This system works well for a range of epoxide substrates giving corresponding cyclic carbonate in good to excellent conversion and yield (Figure 1).[3]

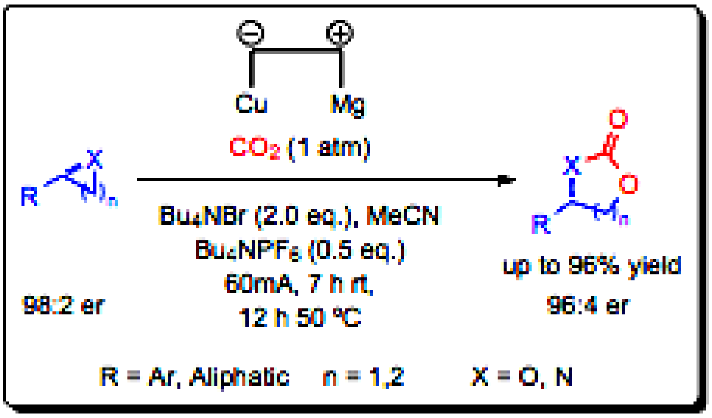

Figure 1: Electrochemical CO2 incorporation to form cyclic carbonates and carbamates

[1] P. H. M Feron and Hendricks, Rev.IFP., 60 (2005) 451.
[2] J. Melendez , M. North and R. Pasquale, Eur. J. Inorg. Chem. (2007) 3323.
[3] B. R. Buckley, A. P. Patel and K. G. U. Wijayantha (2011) Article in preparation.

CO7-Po

Electrochemical Routes to CO_2 Reduction within Metal Aggregates

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Processes at carbon nanofibre membrane electrodes are investigated. The carbon nanofibre material is based on ca. 50 nm diameter carbon fibres compressed into ca. 50 μm thickness discs (from Nanolabs Ltd.). When investigated as working electrode immersed in aqueous solution, these carbon nanofibre membrane electrodes exhibit high surface area and increased capacitance. The membrane structure is well suited for the immobilisation of metal catalyst nanoparticles.

Next, membrane electrode assembly (MEA) structures based on commercial Nafion membrane coated both sides with carbon nanofibre electrodes are produced and investigated. These electrode assemblies can be employed in aqueous media with or without supporting electrolyte (Nafion acting as electrolyte) and provide a versatile tool for Electrocatalytic processes in liquid or gas phase environments.

In order to develop a CO_2 electro-reduction protocol, the carbon nanofibre MEAs are employed in a humid gas environment under potentiostatic control and products are detected online in real time with a mass spectrometer. Progress towards electro-catalytic CO_2 conversion is described and discussed with the aim of improving efficiency and product selectivity.

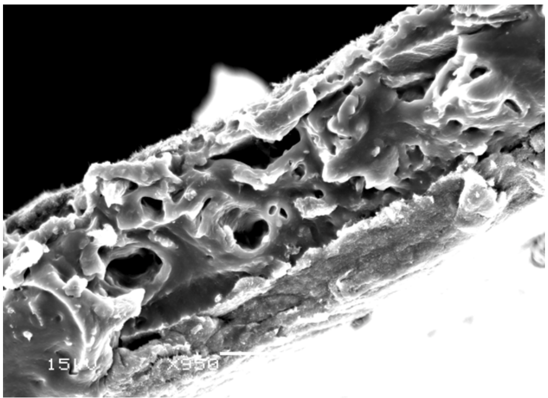

Figure 1. SEM image of a carbon nanofibre paper | Nafion^{TM} | carbon nanofibre paper membrane electrode assembly.

CO8-Po

Redox Reactivity of Methylene Blue in the Pores of UMCM-1 Metal-Organic Frameworks

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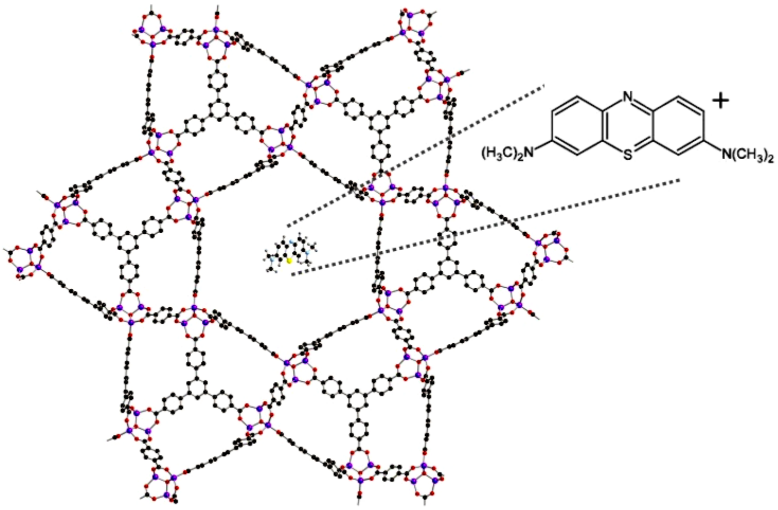
Redox processes are studied in the molecular pores of a crystalline UMCM-1 metal organic framework (MOF) material [1,2]. Methylene blue is employed as an absorbed redox active dye component. From the change in coloration during dye adsorption, it can be concluded that an essentially irreversible adsorption process with high pore loading of the resulting MOF structure occurs. The adsorbed methylene blue remains redox active in the MOF pores and there is no evidence of losses during extended redox cycling. Due to the size of the pores, the reactivity of the pore-bound methylene blue is closely related to that expected for methylene blue in aqueous solution. A study of the effect of solution pH on the voltammetric responses reveals an interesting gradual change in electrical pore conductivity form poorly conducting under acidic conditions to highly conducting under alkaline conditions and this is interpreted in terms of charge transport via single-electron hopping conduction in pores.



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[2] J.E. Halls, A. Hernán-Gómez, A.D. Burrows, F. Marken, Dalton Trans. (2011) in print.

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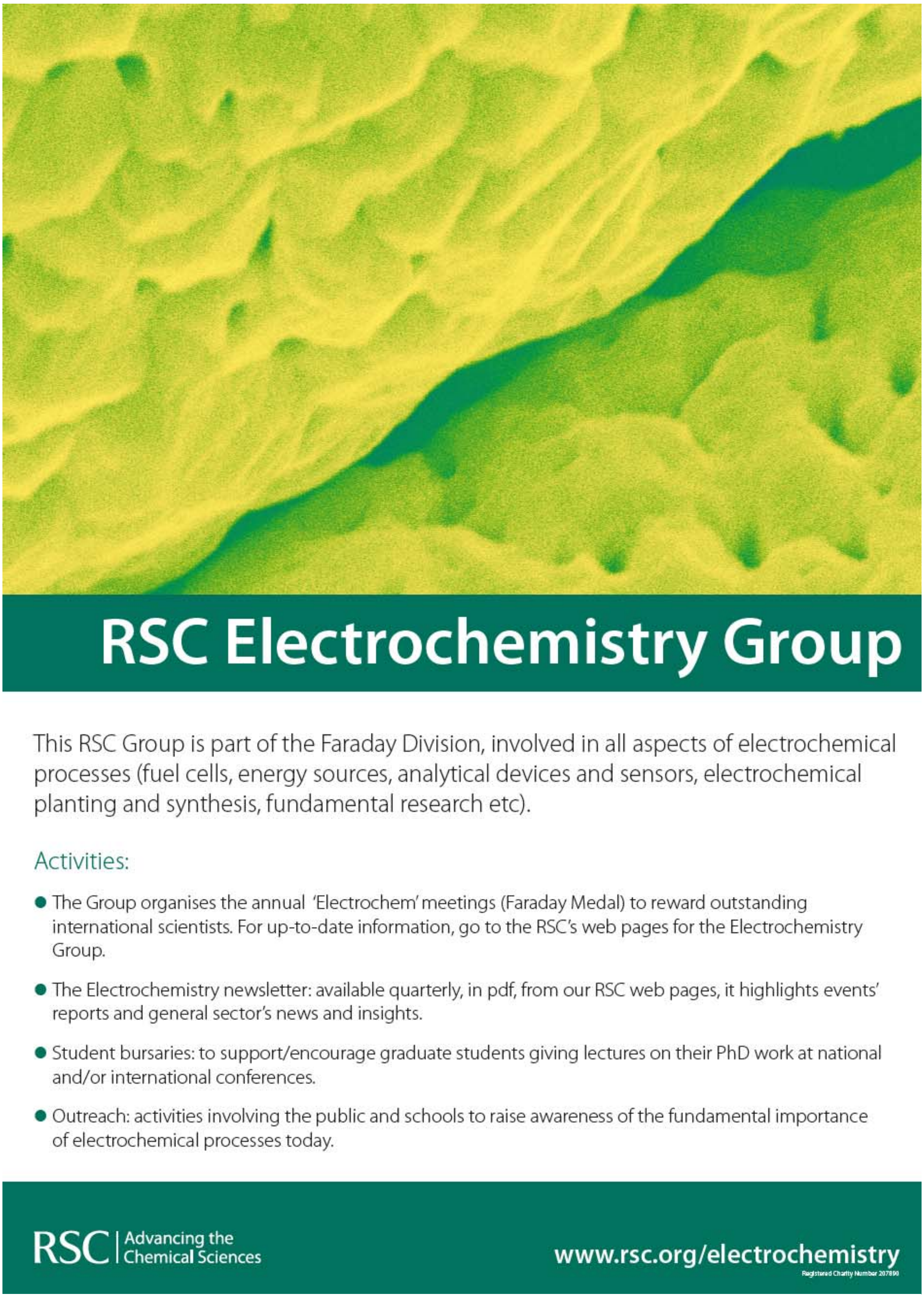

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Activities:

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