No. 1 January 2018

NEWSLETTER

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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

ROYAL SOCIETY OF CHEMISTRY | ELECTROCHEMISTRY GROUP

SCI
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Contents

Editorial

Welcome to the first issue of the Electrochemistry Newsletter in 2018. Last year was a busy year full of activities for the members of the electrochemical community. In particular, in the area of batteries, we welcomed the government's creation of the Faraday Institution on Monday 02 October 2017. This ambitious initiative will provide many opportunities for the electrochemical community in the UK.

This first issue of the Newsletter of 2018 also includes a number of reports from students and postgraduates who assisted or organised a conference. Students should be encouraged to apply for a contribution to the cost of presenting their work at a national or international conference or organising a postgraduate conference. The Electrochemistry Group of the RSC and the Energy Technology Group of the SCI provide the funds if the application is accepted.

This issue also includes a report on the Castner Medal award to Prof Frank Walsh and, as usual, information on conferences and details of upcoming events. The electrochemical calendar and product information are also included.

I welcome any feedback and suggestions or contributions from readers for future issues. Many thanks to Oliver Rodriguez Martinez, who helped to put together the Newsletter.

Carlos Ponce de Leon

If you wish to notify the editor with your view on the material or the content of any item in this issue, or if you wish to contribute to the newsletter, please write to the Editor-in-Chief (Carlos Ponce-de-León, Faculty of Engineering and the Environment University of Southampton) at:

capla@soton.ac.uk

Missed a copy? You can catch up on all the news *via* our web-space hosted by the Royal Society of Chemistry at the following URL.

http://www.rsc.org/Membership/Networking/InterestGroups/Electrochemistry/news.asp

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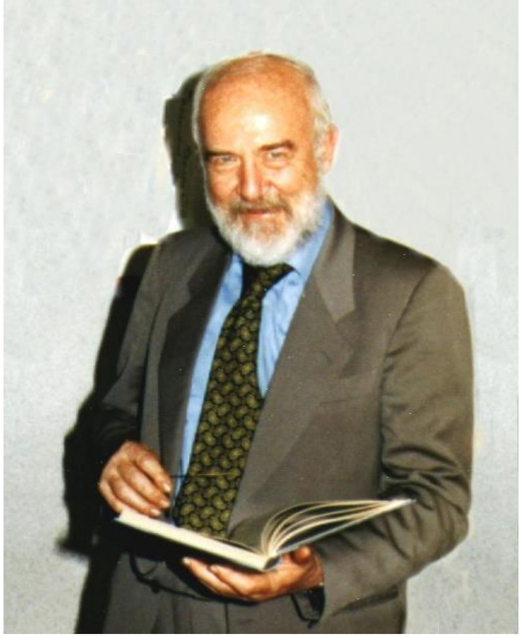
Obituary

Prof. Pietro Luigi Cavallotti (1938—2017)



Pietro Cavallotti was an accomplished scientist on surface treatments and coatings, especially those based on electrochemical treatments. His experience, which included magnetic electrodeposits of alloys, multilayers and nanostructures as diverse engineering coatings, integrated fundamental knowledge with industrial practice. Pietro's many PhD research students appreciated his ability and care as a supervisor; several went on to become established research leaders in coatings technology. I met up with maestro Cavallotti, an international traveller, many times in the 1980s to 2000s. Our last meeting in 2007 was in a picturesque, rustic restaurant near Ferrari in northern Italy, when we lectured to a short course on electrochemical engineering which Achille de Battisti had organised. Pietro kept a firm base in the Department of Chemistry, Materials and Chemical Engineering at the Politecnico (Polytechnic University) di Milano (a leading European engineering research and teaching institution) and took pride in Italy's history, culture and electrochemical science achievements and was happy to talk of the lives of Volta, Piontelli and others; however, he was much more applied and balanced in his outlook. A great conversationalist, he always took particular interest in cooking and eating food, with a fine glass of wine – hence our meeting place - together with catching up on news of other electrochemists he knew. Our conversations spanned the distractions of cold fusion to the practicalities of corrosion in ship's engines; we spent 20 minutes on coatings for frying pans, Cavallotti having studied several wear resistant, non-stick (now often termed 'self-cleaning' or 'superhydrophobic') finishes while I helped develop robust hydrophobic polymer-metal coatings by electrophoresis and electrodeposition, under the supervision of Kees Helle at AKZO's Arnhem research labs in 1974. Cavallotti held many awards as recognitions for his scientific output, which included hundreds of presented and published papers on applied electrochemistry, electroplating and coatings technology. We have lost a wonderful character, scientist and university research supervisor but his inspiration continues.

Frank C. Walsh.
Electrochemical Engineering Laboratory.
University of Southampton, UK.

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Awards – Castner Medal

Prof. Frank C. Walsh

Professor Frank C. Walsh from the Energy Technology Group of the Faculty of Engineering and the Environment at the University of Southampton was awarded the 2017 **Castner** Medal from the Society of Chemical Industry (SCI). The ceremony took place at the SCI headquarters at Belgrave Square, London on 31 October 2017 where Prof Walsh gave a lecture entitled: Development of Electrodes and Cell Design.

The prestigious **Castner** Medal award was established in honour of a Hamilton Castner (1859-1899) who revolutionised a number of industrial electrochemical processes, the most successful was the production of aqueous sodium hydroxide by electrolysis, patented in 1892.

Details of Prof Frank Walsh's lecture can be found at: Lecture

Information about the Hamilton Young Castner Medal award and the recipients can be found at the following links:

Hamilton Young Castner

Castner Medal

Dr Pauline Allen, chair of the SCI Electrochemical Technology Group and Prof Frank Walsh before been given the Castner Medal.

Colleagues from the Electrochemical Engineering Laboratory at the Castner Medal Lecture with Prof Frank Walsh (seated)

Castner Medal

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SCI Electrochemistry Postgraduate Conference 2017 in partnership with RSC and ISE

CONFERENCE REPORT

Friday 19th May 2017

Electrochemical Engineering Laboratory
Faculty of Engineering and the Environment
University of Southampton

Following the initiative of the Electrochemical Technology Group of the Society of Chemical Industry, this year's edition of SCI Electrochemistry Postgraduate Conference was hosted by the Electrochemical Engineering Laboratory of the Faculty of Engineering and the Environment of the University of Southampton. SCI-EPC 2017 was organised in partnership with Electrochemistry Interest Group of the Royal Society of Chemistry and the International Society of Electrochemistry. Additional support was provided by STFC Batteries Network and Clean Carbon USRG.

The event brought together more than 60 delegates from 9 British universities, including PhD students, postdoctoral researchers and renowned academics from many nationalities. The meeting aimed to promote discussions on the practical applications of electrochemistry and to celebrate the regional postgraduate community in the field. Participants from the Engineering and Chemistry faculties of the University of Southampton also found an opportunity to meet each other and discover links between their work.

Registered delegates and guests met from 10:00 to 18:00 at the Hartley Suite of the Staff Social Centre in Highfield Campus on Friday 19th May 2017. The programme featured one keynote, an invited lecture, 10 presentations from PhD students and postdoctoral researchers and 15 posters. There were two coffee breaks between the sessions, a working lunch and an informal networking reception.

SCI Electrochemistry Postgraduate Conference 2017 in partnership with RSC and ISE

The conference started with a welcome message to the delegates given by Luis F. Arenas in name of the SCI Electrochemical Technology Group Executive Committee. The word was then given to Professor Andy Cruden, who presented the research carried out at the Electrochemical Engineering Laboratory of the University of Southampton. After this, Dr. Guy Denuault from the Electrochemistry Group of the University of Southampton and UK Regional Representative of the International Society of Electrochemistry, talked about the activities and benefits of this society and invited the delegates to become members. Professor Phil Bartlett, current president of ISE was also present later during the event.

The stage was then handed over to the keynote speaker, Dr. Kathryn Toghill, who is an early career lecturer at Lancaster University and coordinator of the UK Redox Flow Battery Network. In her talk, she explained the exiting opportunities in the field of electrochemical energy storage and her work on new organic chemistries for redox flow batteries. The keynote was followed by Dr. Rachel McKerracher's (University of Southampton) invited lecture on catalysts and gas diffusion electrodes for metal-air batteries and on her new project on aluminium-ionic liquid batteries.

Dr. Kathryn Toghill (Lancaster University) giving a talk on the current challenges and opportunities in electrochemical energy storage.

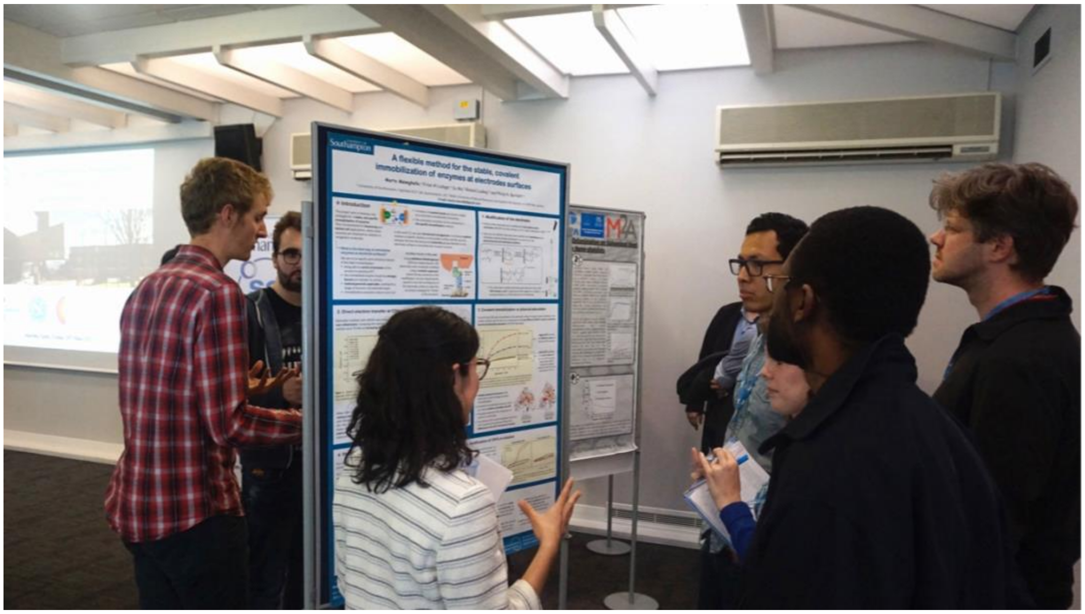
The second session began after a short coffee break, chaired by Alex Holland. Luis F. Arenas (University of Southampton) gave the first talk, which considered the scale-up of electrochemical flow reactors for cerium-based redox flow batteries. Next, Joshua Bates (University of Surrey) presented his work on modelling of lithium-air cells and its validations against charge-discharge curves. Stanislav V. Sokolov (University of Oxford) then explained the detection of silver nanoparticles at random assemblies of microelectrodes in a wall-jet cell and Catalina Pino (Imperial College London) talked about performance models for hydrogen-vanadium regenerative fuel cells.

Catalina Pino (Imperial College London) presenting her work on modelling of redox flow batteries.

Lunch ensued after the second session. This time was well spent by the delegates, who engaged in interesting conversations with colleagues. The menu choice was appreciated by all. The third session followed lunch and was chaired by Associate Professor Dmitry Babvykin. The first talk was delivered by Barak Aaronson (University of Bath), who talked about ionic diodes based on micro-holes containing membranes. Afterwards, Yuhua Xia (Imperial College London) presented his work on inexpensive alkaline polysulphide-air flow batteries and James T. Firth (University of Southampton) explained the role of redox mediator on the enhancement of sodium-air batteries.

Conference delegates having lunch at the Hartley Suite.

In the second poster session, students presented their work to other delegates and to several academics who joined the meeting. Emeritus Professor Derek Pletcher followed the work of students with interest. Some the topics treated by the displayed posters were photo-electrodes, catalysts, biosensors, aluminium-ion batteries, flow electrosynthesis, electrophoretic deposition, nanostructured materials, conductive coatings and corrosion protection. Tea and muffins made this time more agreeable.



Students discussing their work during the afternoon poster session and break.

The last session was chaired by Associate Professor Carlos Ponce de León. It began with the talk by Elena Madrid, (University of Bath) on the electroluminescence of a nanostructured polymer supported on tin-doped indium oxide. Afterwards, Alex Nielsen (Swansea University) presented his work on the analysis of brass corrosion via a scanning Kelving probe. Tammy Nimmo (University of Southampton) had the honour of delivering the last presentation of the day. She talked about the study of catalysts for the reduction of oxygen at platinum electrodes.

Alex Holland presenting the best poster award to Marta Meneghello (University of Southampton) and the best presentation award to Stanislav V. Sokolov (University of Oxford).

To finalize the event, Luis F. Arenas gave a summary of the meeting and acknowledged the contribution of all those involved in the organisation and sponsorship of the event. After this, Alex Holland presented the coveted best poster and presentation awards to Marta Meneghello (University of Southampton) and Stanislav V. Sokolov (University of Oxford), respectively. The prizes included £50 gift vouchers and the winner of the best presentation award also received a one-year SCI full membership.

Conference delegates networking reception with drinks and nibbles.

The event finalized with an informal networking reception, which lasted until 7:00 pm. Everyone enjoyed drinks and nibbles while discussing the day, interchanging emails, and making plans for the weekend. Some took the chance to have dinner in Southampton before taking the train back home and even to have a short vacation in this coastal city. We are sure that the delegates will look forward to SCI Electrochemistry Conference 2018.

Luis F. Arenas and Alex Holland
Organising Committee SCI-EPC 2017
University of Southampton
23th May 2017
https://sites.google.com/site/sciepc2017

Student volunteers from the Electrochemical Engineering Laboratory: Keletso Orapeleng, Christian Harito and Abdulaziz Abbahusain.

Acknowledgements. *The Organising Committee would like to thank Associate Professor Carlos Ponce de León for providing his full support to this event. We are also grateful to Professor Andy Cruden from the Energy Technology Group for backing up this meeting and to Associate Professor Guy Denuault from the Electrochemistry Group for providing his endorsement as Regional Representative of ISE. Thanks to Dr. Neil Rees and Professor Upul Wijayantha for approving this year's RSC Electrochemistry Group sponsorship and to Associate Professor Denis Kramer for obtaining sponsorship from the STFC Battery Network, which was approved by Dr. Paul Shearing of UCL. Additional funding from the Clean Carbon USRG was kindly offered by Dr. Lindsay Armstrong. We also thank Jacqui Colgate from SCI's conference department for helping with administration tasks. Special thanks to Professor Frank C. Walsh for offering useful advice and support to the event.*

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Meetings Reports (International):

231st Meeting of the Electrochemical Society
New Orleans, 25th May to 1st June, 2017

I had the opportunity to attend the 231st Meeting of The Electrochemical Society (ECS) held in New Orleans, USA from May 25th to June 1st. This was possible thanks to the support and grant given by the Electrochemistry group of the Royal Society of Chemistry to whom I am greatly thankful. The bursary scheme allows PhD students to attend major electrochemistry conferences abroad in order to present our work and to do networking with other groups. On this matter, my attendance to the ECS Conference was very useful to my career since I had the opportunity to discuss my work with leading electrochemists and to listen to what other groups are doing in the different areas of the Electrochemical sciences. From batteries to simulations, the conference covered a broad range of subjects. In my case, the topic called "Fuel cells, electrolyzers and energy conversion" was the most relevant to my project and as such I attended to almost all of the talks with few exceptions to attend some of the Nanotechnology sessions.

In this meeting, I had the opportunity to present both, a talk and a poster. The talk was titled "Transient study of adsorbed oxygen species arising from exposure to dissolved oxygen", where I presented results obtained recently during my PhD studies under the supervision of Dr. Guy Denuault and with the help of the undergraduate student assigned to the project, Felix Liew. The talk focused on the reduction of adsorbed oxygen species when Pt micro and sub-micron electrodes were used. During this session, I had the opportunity to discuss our work with the audience and receive valuable feedback and questions, especially concerning the construction of the sub-micron electrodes. I also had the opportunity to present a poster titled "Electrochemical investigation on the reduction of oxygen at a perovskite modified Au microelectrode" where I presented results obtained with our colleagues from the University of São Paulo, Dr. Mauro Bertotti, Dr. Alex Lima and Dr. Alan Lima. There were a lot of people interested in our work, especially on the construction of a perovskite microdisc electrode and the use of Sampled Current Voltammetry to study the oxygen reduction reaction at the millisecond scale and valuable input about the electrochemical characterisation of perovskites was given by Dr. David Fermin from the University of Bristol.

The plenary lecture given by Dr. Way Kuo titled "A risk look at energy development" was an eye opener. In it, he presented an overview of the different types of energies with their inherent risks. He listed many of the incidents that have recently occurred in the world as well as the number of casualties and the impact that each had on society. From traffic accidents (1.25 million casualties) to deaths due to air pollution (> 6 million), Dr. Kuo made sure we understood that the biggest problems that we face today come not from the use of technology itself, but from the daily decisions taken by our political leaders, especially when they do not have enough data available.

Dr. Kuo also mentioned during his lecture that out of the seven billion people living on this planet, five billion generates pollution and the other two billion is dying because of it. That statement was very powerful because it implied that we, scientists, are in the former. How is that possible? Some of us are trying to improve the knowledge available about clean energy, others are trying to make the technology affordable and others are trying to pass the laws so that this can be put into action. Still, that does not exempt us from the problem. Is it enough to be working on it? I recently realized that in my experiments I was generating a lot of waste. Am I excused because *I am working on it*? No. Should I stop doing it just *to calm my conscience*? No. This will always be in my mind.

Thanks to the ECS conference and especially to Dr. Kuo lecture, it is now clear to me that our role in society as a scientific community, is not only to generate knowledge and technology but also to dedicate part of our time to communicate our results to the general public, hoping that one day we can alleviate the pollution generated by ourselves. As Dr. Kuo said, nobody can leave alone, we are all together.

Oliver Rodríguez Martínez
PhD student, University of Southampton

The ideas expressed in this article are solely of the author.

Dr. Krishnan Rajeshwar welcoming the attendees.

Attendees during one of the breaks.

Winston Churchill statue on the British Plaza in New Orleans, just outside the Hilton Hotel where the ECS Conference was held.

The beautiful Jackson Square in New Orleans.

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Meetings Reports (International):

11th European Symposium on Electrochemical Engineering
"Today's research for tomorrow's technologies"
Prague, Czech Republic, 4 – 8 June, 2017

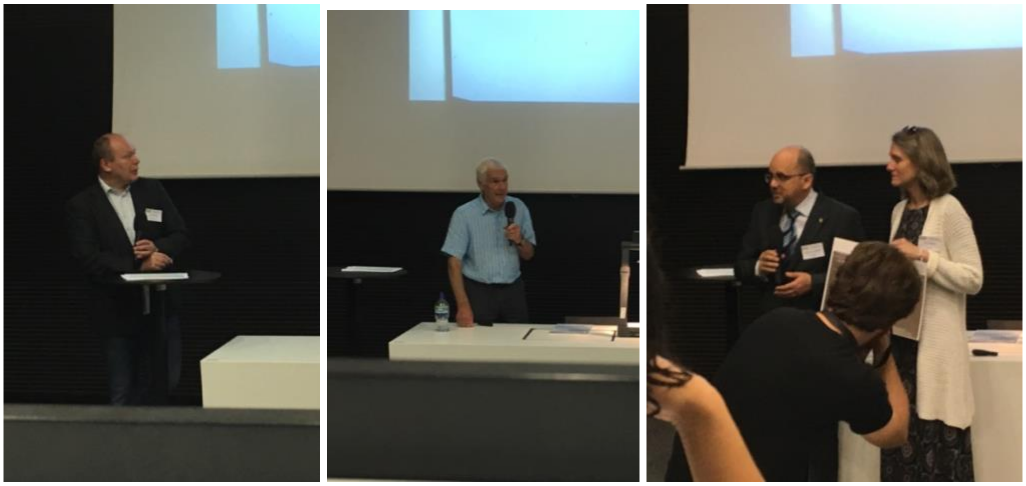
by Luis Fernando Arenas

The electrochemical engineering community met last summer in the beautiful city of Prague, Czech Republic, to hold the 11th European Symposium on Electrochemical Engineering. This conference has officially taken place since 1990 and with has roots in meetings in the UK in 1984. It takes place every three years and alternates with the European Summer School of Electrochemical Engineering. This year's edition was held at the National Library of Technology in the University of Chemistry and Technology Prague. Professor Karel Bouzek was chairman of the committee, which included other faculty members of this university.

Me at Legií Bridge, with a nice view of the iconic Karlův Bridge.

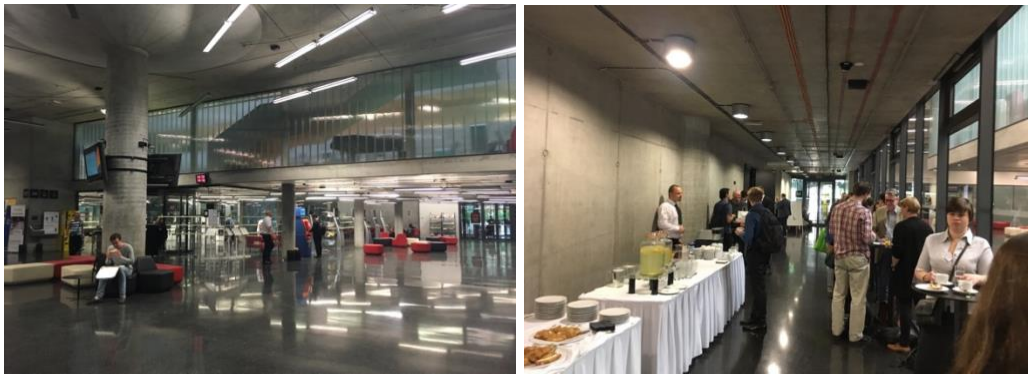
A welcome reception took place on Sunday at the university. Most attendees had just spent the day surveying the city, although some had just arrived from the airport. It is always good to find friends, collaborators and old colleagues at these meetings, especially when this happens unexpectedly. Most conversations revolved around the city of Prague itself, a place well known to electrochemists.

Early on the first day, Professor Karel Bouzek (University of Chemistry and Technology Prague) and Professor Manuel Rodrigo (Universidad de Castilla, La Mancha) delivered a welcome speech and introduced the lecture "Electrochemical Engineering Time Travel" by Emeritus Professor Anthony A. Wragg (University of Exeter). Tony gave a detailed account of the origins and history of ESEE meetings as well as insights into early concerns in the field of mass transport. He also took this opportunity to remind us that most British academics strongly opposed *Brexit*, and assured our community that research groups in British universities intended to remain fully European. As we all know, science respects no borders. We all agree that political changes will not be an obstacle to developments in electrochemical engineering and applied electrochemistry.



Professors Karel Bouzek (left), Manuel Rodrigo & Ann Cornell (right) presenting an award to Professor Tony Wragg (centre).

The same day, the Carl Wagner Medal was awarded to Carlo Santoro (University of Albuquerque) and João André da Costa Tedim (University of Aveiro). Afterwards, the conference was divided into two sessions. Each day there were plenary lectures delivered by recognised academics in the field. I presented the main contribution of my PhD project during the session chaired by Thomas Turek (TU Clausthal). As always, Geoff Kelsall (Imperial College London) had excellent questions during most of the presentations. During the lunch and break, I was happy to meet several professors whose publications I know well from my studies and to hear their opinion on our recent work. I also had to give regards to a number of people on behalf of my PhD supervisors, Carlos Ponce de León and Frank C. Walsh, since they couldn't join us this time in Prague. As well as delicious, the lunch was well organized.



National Library of Technology and lunch break.

During the second and third days, I followed several talks on redox flow batteries and electrochemical reactors. In special, I was interested in getting information about the most recent industrial developments, mostly on energy storage technologies, fuel cells and the chlor-alkali industry. There were also very interesting talks on environmental technologies, water treatment and even on the history of hydrogen technologies, which thought me a couple of things. The poster session took place on the same day. A benefit of poster sessions is that one can ask freely any number of questions to the presenter without time limit while accompanied by some appetisers and drinks. Universities from all over the world were represented in this session.

The fourth day of the conference was the most interesting from a social point of view. After the presentations in the morning we all went to an excursion to the Škoda car plant in Mladá Boleslav. This was the first time I visited one of these facilities and I really enjoyed the trip. In the afternoon, we went back to Prague for the conference dinner in the Strahov Monastery, in a hill that oversees the city. The elegant library offers a magnificent view and I liked one of the allegorical frescos in particular. It somehow reminded me of my PhD. The food was excellent and after almost exhausting conversations with old and new friends we went walking back towards the city centre. Some took a detour towards traditional Czech bars and pubs.

Scientia difficilis sed fructuosa. A fresco in the library of the Strahov Monastery.

During the last day, we attended to the last plenary and Carl Wagner lectures after the usual presentations. Professor Karel Bouzek then closed the conference, not before the committee delivered the student awards. I think we all were very thankful towards the organizers. Their hard work resulted in a truly memorable conference. After saying goodbye to our friends and colleagues, most of us then took a few days off to travel peacefully in this part of Europe. But not before one more walk in Prague.

The New Stage of the National Theatre and the Moldava River, Prague.

I thank RSC's Environment, Sustainability & Energy Division for granting me a travel bursary to participate in this event. (This time it wasn't the Electrochemistry Group!)

Luis F. Arenas, PhD, AMRSC
SCI Postgraduate Representative, lfam1g13@soton.ac.uk
Electrochemical Engineering Laboratory
University of Southampton, UK

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Meeting Memories:

11th European Symposium on Electrochemical Engineering
University of Chemistry and Technology Prague
4 - 8 June 2017

Schedule:

- Sunday 4th, Registration and welcome reception
- Monday 5th, Lectures and plenary talks.
- Tuesday 6th, Lectures and plenary talks. Poster session.
- Wednesday 7th, Excursion and conference dinner.
- *Thursday 8th, Lectures and closure ceremony.*

Group photo at University of Chemistry and Technology Prague.

Prof. Anthony Wragg receiving an award honouring his life achievements from the hands of Prof. Geoff Kellsal and Prof. Karel Bouzek.

Dr. Carlo Santoro, joint winner of Carl Wagner Medal of Excellence in Electrochemical Engineering 2017. Prof. Karel Bouzek to the right.

Excursion to the Skoda car plant.

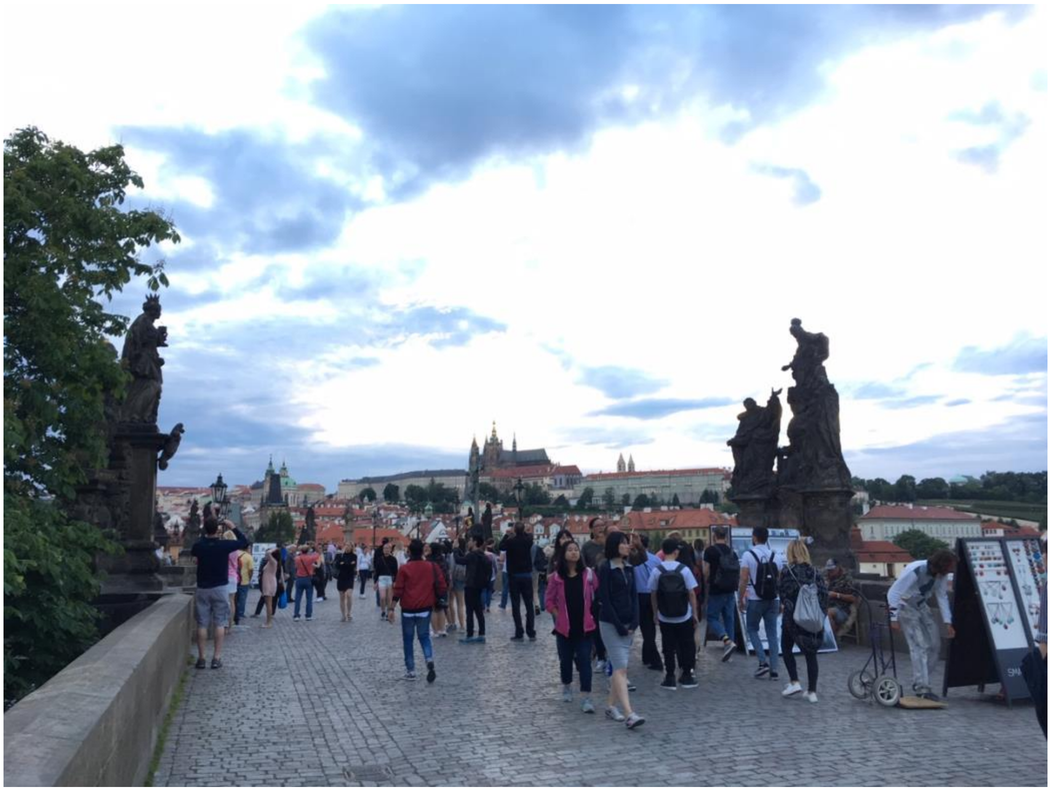
Perfect weather outside the Stratov *Monastery*.

Buffet and drinks at the Strahov Monastery.

The library in the Strahov Monastery.

Group photo at the Strahov Library.

Dr. *João André da Costa Tedim joint winner of Carl Wagner Medal of Excellence in Electrochemical Engineering 2017. Prof. Manuel Rodrigo and Prof. Ann Cornell next to him.*



The famous Karlův most in the afternoon.

Meetings Reports (International):

12th ECHEMS meeting
Milano Marittima, Italy, 6 – 9 June 2017

XII ECHEMS: Electrochemistry in…

Ingenious Molecules, Surfaces and Devices

The 12th ECHEMS meeting, held every two years, took place in the seaside town of Milano Marittima, Italy, situated east of Bologna; the first port of call for many of the 130+ attendees. Seeing as the meeting started on a Tuesday, we (the Marken group, University of Bath) managed to spend two days exploring Bologna prior to the meeting, sampling many of the gastronomical capital's delicacies including tagliatelle al ragù (Bolognese sauce), tortellini, and mortadella (cured pork). Not only is there fantastic food to indulge in, the city also beholds a wealth of museums and churches to visit, one of which being the 5th largest church in the world – Basilica di San Petronio.

Left to right: Photographs of Basilica di San Petronio; the aluminium can Atomium replica; and Ezio Bosso performing at the 'Concert for the Earth'.

Our visit to Bologna coincided with the start of the #All4TheGreen week of events occurring in the lead up to the G7 Environment Meetings in Bologna. Such events we managed to attend included a stunning, classical 'Concert for the Earth' in Bologna's Piazza Maggiore directed by Ezio Bosso, an incredibly talented pianist. Another form of art displayed during the #AllForTheGreen week was an Atomium replica (and so the chemistry begins) made from aluminium cans, representing the value of recycled aluminium. After an enjoyable start to our week, and with going 'green' on our minds, it was time to make our way to the conference venue, Hotel Gallia, in Milano Marittima – a short bus ride kindly organized by the ECHEMS committee.

The ECHEMS meeting was held over four days (6th-9th June) where, for the first time, talks were organized into parallel sessions. The sessions involved an amazing eleven distinct areas of electrochemistry including biological, luminescence, and sensor electrochemistry (to name a few). The conference started in the afternoon, opened by Patrizia Romana Mussini, a member of the organizing committee who, might I add, was well and truly the back-bone of the conference organization and delivery. All talk sessions were then opened with relevant plenaries to each field, such as the "Mechanism of Alzheimer Disease" (given by C. Amatore, ENS, Paris) and "Self-propelled Nanomachines" (by S. Sánchez, IBEC, Barcelona) for biological and nano electrochemistry sessions respectively. The wide range of talk topics enabled participants to learn about other aspects of electrochemistry, which for me were far from the corrosion research I conduct. I took great interest in the unfamiliar world of organic electrochemistry where, for example, I discovered the fascinating area of organic supercapacitors. I also delved into the battery parallel session, which gave me an in-depth overview on next-generation batteries and sustainable approaches to batteries. I feel that the extensive topics at hand made myself, and others too, realize just how diverse electrochemistry and its applications is.

Left to right: One of the 60 two-minute flash presentations (here given by Rose Brown, University of Bath); World map showing locations of research groups in attendance.

Posters and respective flash presentations were also given, as well as talks, by Ph.D. students, postdocs, and academics. Flash presentations and posters were given on consecutive days before and after gourmet four-course dinners, which were exceptional (both the posters and the food!). The overall friendly and relaxed atmosphere of the conference made the flash presentations (given on the first day) a lot of fun, and put me at ease during my first ever conference experience.

The flash presentations made a nice addition to the posters, where I had attendees approach me due to my flash presentation, which was very satisfying! More specifically, when presenting my poster on copper corrosion, I met Prof. Manfred Buck who explained his research in electrochemically controlled processes, where one of the processes of interest is copper deposition; seemingly contrary to my research in copper corrosion. It was fantastic to have Manfred take interest in my research, which enabled us to discuss copper chemistry from two different scientific points of view. All participants in fact were extremely approachable, and gave genuine interest in the posters and talks. That said, there was a real sense of collaboration amongst the electrochemists that attended.

Left to right: Photographs of Samuel Sánchez giving a plenary lecture entitled "Powering Tiny Particles with Catalysis: Self-propelled Nanomachines"; The poster session room; View from the dining table at the conference venue.

To conclude, ECHEMS 2017 was filled with intriguing electrochemistry which, together with the great company, food and wine, enabled the organizing committee to put together a thoroughly enjoyable and educational meeting. I would like to sincerely thank the Royal Society of Chemistry Electrochemistry Group, and the RSC Italy Local Section (from whom I gratefully received an abstract prize), for supporting my attendance at the XII ECHEMS Meeting, which has made my first conference, and first trip to Italy, unforgettable.

Amelia Rose Langley, University of Bath

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Meetings Reports (International):

XXIV International Symposium on Bioelectrochemistry and Bioenergetics of the Bioelectrochemical Society
Lyon, France, 3 – 7 July, 2017

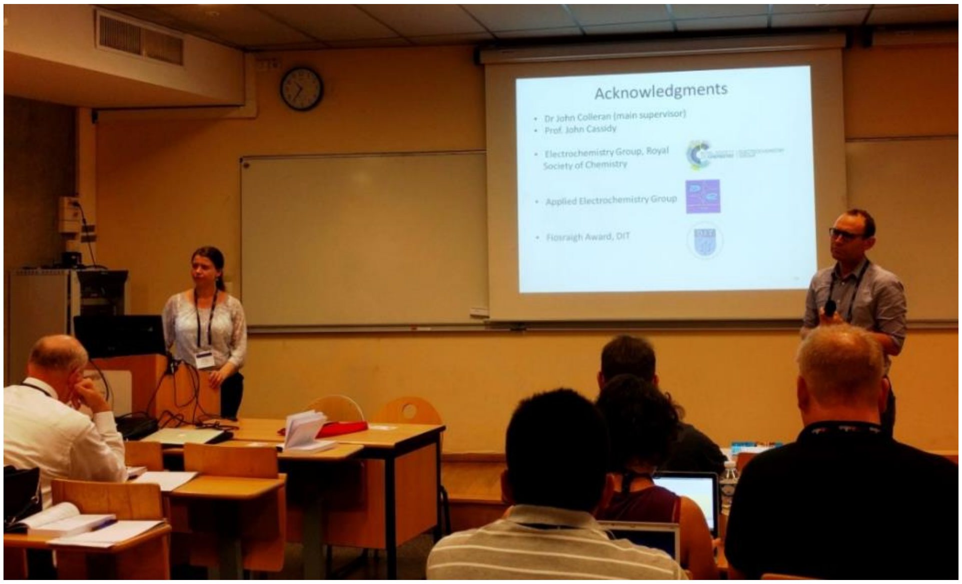
The Symposium organised by the Bioelectrochemical Society every two years is one of the biggest conferences in a bioelectrochemistry field. Thanks to the generous support of the Electrochemistry Group of the Royal Society of Chemistry, I was able to attend the Symposium this year and present my findings on an international forum. The Symposium was a great opportunity to get acquainted with different areas of electrochemistry; such as the electrochemistry of DNA, proteins, electroporation or microbial fuel cells. There were 161 presentations in three parallel sessions, over 80 posters and five plenary lectures given by the leading researchers in bioelectrochemistry.

My research includes a creation of a thiol-modified DNA self-assembled monolayer on gold electrodes, and looks at using it to investigate the interactions between DNA and potential anticancer compounds. Recently, I was able to develop a new, quantitative method to monitor the nuclease properties of some potential anticancer drugs. I presented my research findings in a talk entitled: ‘’Electrochemical Monitoring of the Interactions between DNA and Bioinorganic Compounds’’ on the second day of the Symposium. Previously, I had the opportunity to present my research at local Irish conferences; this was my first opportunity to give an oral presentation at the international conference. I was very happy to answer the audience questions, and have a few very inspiring conversations about my research during the break after the session.

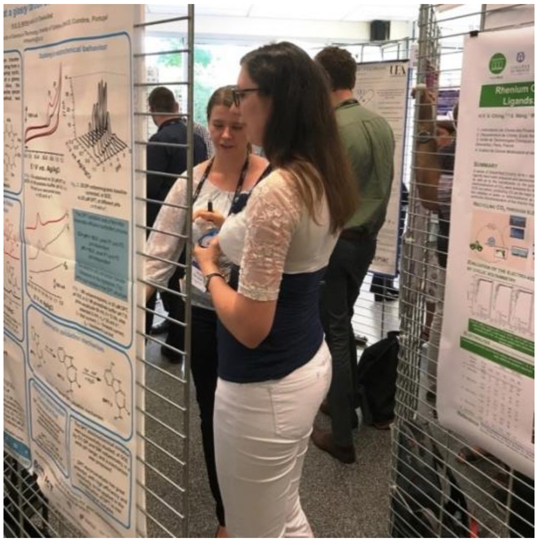
Several other young researchers presented their research about DNA-modified electrodes and their use in medicine during the Symposium as well. I was extremely happy to get to know the research work of other scientists. I feel that the exchange of experience with other researchers specialized in bioelectrochemistry can be extremely useful for my future work and ideas. The planar lecture about using high-frequency irreversible electroporation to treat brain cancer presented by Prof. R. Davalos made a lasting impression on me. The other planar lecture about creating stretchable and self-healing bioelectronic devices given by Prof. J. Wang was also very interesting. The poster session was organized on the second and third day of the Symposium. The session was another great opportunity for networking with PhD students from around the world.

During the Symposium, the awards were given to the member of Society who had made an important contribution to the field of bioelectrochemistry. The Giulio Milazzo Prize was granted to Prof. Frieder Scheller and the Luigi Galvani Prize was granted to Prof. Sergey Shleev this year. On the fourth day of the Symposium, I had a great opportunity to taste some of the French specialities and fantastic French wine during the banquet that took place in Brasserie Georges. The excursion organized just before the banquet allowed me to discover several secrets of Lyon- it is after all one of France's oldest cities.

Attending the XXIV International Symposium on Bioelectrochemistry and Bioenergetics was a fine chance for me to meet researchers interested in the same area of bioelectrochemistry and discuss with them the latest discoveries. I was especially interested in creating DNA sensors, and their medical application.
I would like to emphasize again how grateful I am for the financial support from the Electrochemistry Group of the Royal Society of Chemistry that helped me to attend this Symposium. I would like to also encourage all Bioelectrochemists to attend the next Symposium organized in Limerick (Ireland) in 2019.



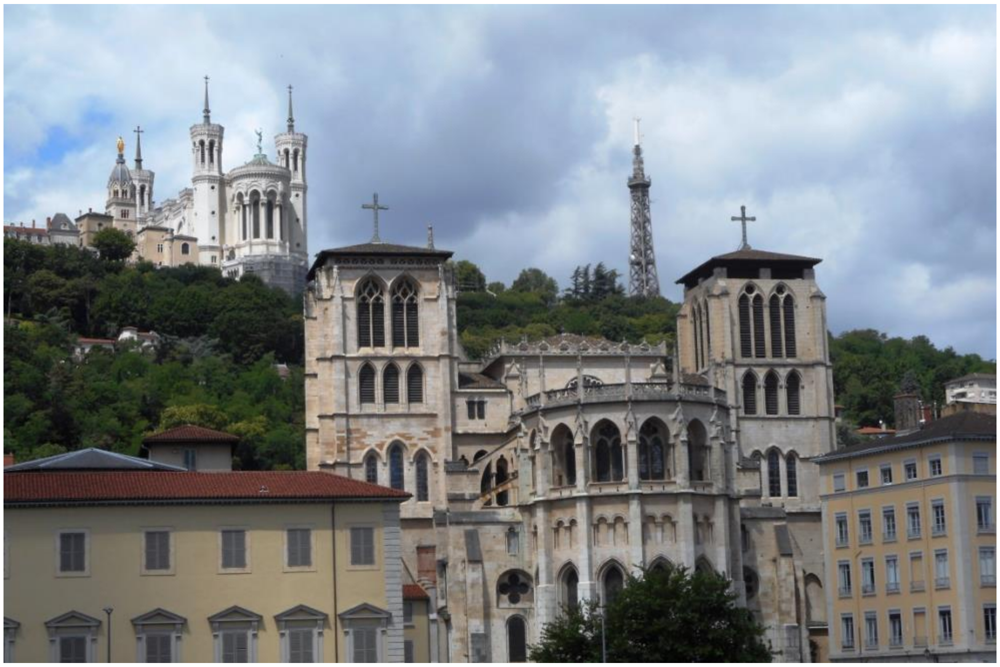
My presentation - answering the audience questions.



The poster session – next to Agata Krzak poster (Prof. Renata Bilewicz Group, University of Warsaw).

Left: Prof. Frieder Scheller receiving the Giulio Milazzo Prize. Right: Prof. Sergey Shleev receiving the Luigi Galvani Prize.

A view of Lyon from Fourvière Hill.



The three highlights of Lyon: on the left - Basilica of Notre-Dame de Fourvière, in the front -Cathedral of St. John, at the back on the right - Metallic tower of Fourvière – looks like Eiffel Tower.

Anna Banasiak, 3rd year PhD, Applied Electrochemistry Group, Dublin Institute of Technology

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Meetings Reports (International):

232nd Meeting of the Electrochemical Society
National Harbor, USA, 1 – 5 October, 2017

I was able to attend the 232rd meeting of The Electrochemical Society thanks to the generous support of a bursary from the RSC Electrochemistry Group. The conference was held at the Gaylord National Resort and Convention Center in National Harbor, MD and took place between the 1st and 5th October 2017. Squeezed into the five-day technical programme were a huge 49 symposia comprising over 2200 abstracts, within which 1800 were oral presentations and the remaining were posters. Given the size and breadth of the conference, I was spoilt for choice with regards to choosing sessions to attend. My PhD thesis involves the study of thin printed circuit board (PCB) metal films using a variety of electrochemical, morphological and reflectivity techniques, therefore for the most part I focussed on attending sessions within the 'Electrochemical/Electroless Deposition' section. During my time in these sessions, I learned of novel techniques which may be of use to me moving into the final year of my PhD. These included the use of a heated cell to carry out Electrochemical Quartz Crystal Microbalance (EQCM) experiments, which would prove useful for the deposition of certain metals in deep eutectic solvent (DES) media.

Figure 1. *View across the Potomac River from the Gaylord National Resort and Convention Centre, where the conference was held.*

In addition to attending many talks in my field, I attended some interesting talks in the 'The Brain and Electrochemistry' symposium, and a few of the battery-related symposia. A range of topics were covered in the former, including *in vivo* measurements of adrenaline and dopamine in mice for the detection of conditions such as Huntington’s and Parkinson’s disease. Battery research is not a field in which I am familiar, however the second poster session was almost entirely comprised of research into new battery technologies. I spoke to a number of authors about a variety of topics in this area, from the development of new cathode materials to the use of algae in sodium-ion batteries. The plenary talk took place on the second evening of the conference, and was given by Nobel Prize winning Physicist Steven Chu from Stanford University. His talk explored the role of electrochemistry in the development of sustainable energy.

I presented my poster entitled ‘A Novel Electrochemical Method for the Analysis of Thin Metal Films and Bilayers for Application in the PCB Industry’ during the General Poster Session on the evening of the 3rd October, and received much interest from a variety of delegates, including academics and industry members. Figure 2 includes a photograph of me with my poster during my designated session. My PhD supervisor, Professor Karl Ryder, was invited to speak in the ‘Electrodeposition’ symposium on the same day (*Characterisation of Metal Deposition and Metal Dissolution Processes in Deep Eutectic Solvents Using Electrochemical, Gravimetric and Neutron Scattering Methods*,) and presented a talk on similar work. I was pleasantly surprised by the amount of interest that both my supervisor and I received during the conference on the work that we presented. In addition to this, I was given lots of useful advice on careers looking towards the end of my PhD, with the offer of more support moving forward.

Overall, the conference provided me with a fantastic opportunity to not only present my own work and discuss it with a range of other delegates, but allowed me to explore a wide range of electrochemical research which would not otherwise have been accessible to me. This, coupled with a fantastic location, resulted in a very successful conference! I would like to thank the RSC Electrochemistry Group and my supervisor, Professor Karl Ryder, for allowing me to attend!

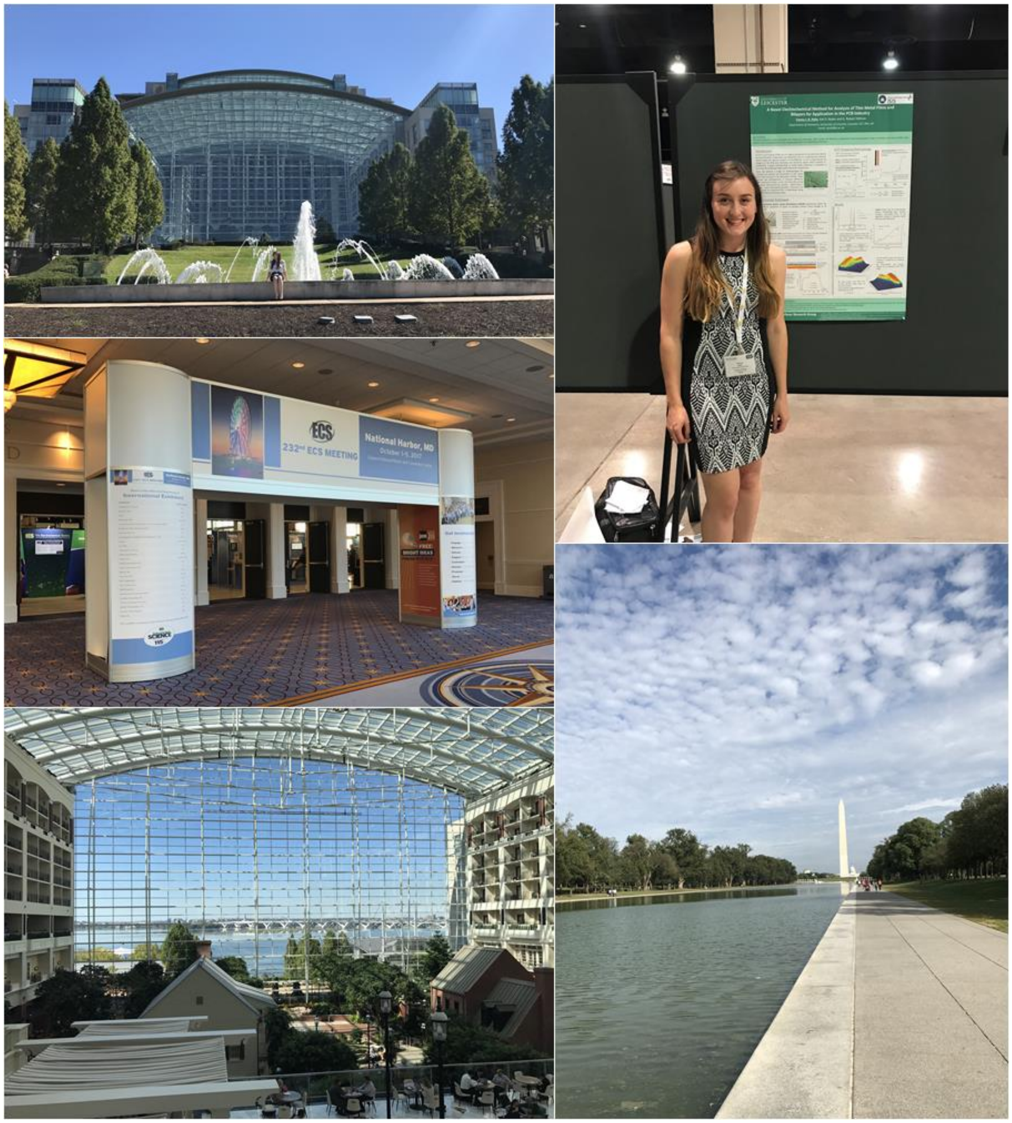

Figure 2. *From top-left clockwise: Fountain in front of the hotel and conference centre; photograph me in front of my poster presentation in the poster session on Tuesday 3rd October; view across the Lincoln Memorial Reflecting Pool in Washington D.C. to the Washington Monument; view from the hotel foyer across the Potomac River; entrance to the exhibitor hall and poster sessions.*

Emma J R Palin
Research Postgraduate
Materials Centre, Department of Chemistry
University of Leicester
University Road, Leicester, LE1 7RH

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Student Conference Bursaries

The Student Bursary Scheme provides financial support to promising postgraduate students to attend a major electrochemistry conference abroad. This includes UK based students travelling to a conference abroad and students based abroad wishing to attend a conference in the UK. The Bursary Scheme is open to all postgraduate student members of the RSC's Electrochemistry Group undertaking research in electrochemistry. Applications shall consist of:

(i) the application form (see **http://www.rsc.org/ScienceAndTechnology/Funding/TravelGrants/InterestGroups.asp**),
(ii) the abstract submitted to the conference organisers,
(iii) one A4 page *curriculum vitæ* stressing academic and scientific achievements (*e.g.*, research articles, oral and poster presentations ***made by the applicant***).

Applications may be made at any time of the year and shall be submitted to the Group Secretary in electronic form.

The selection committee of the Electrochemistry Group shall decide the sum awarded. Under normal circumstances this sum shall not exceed £300.

Successful applicants shall produce a conference report article for the Newsletter.

Candidates should submit their applications directly to the RSC Electrochemistry Group Secretary:

Dr. Upul Wijayantha (email: U.Wijayantha@lboro.ac.uk).

Related: also see RSC travel bursaries
http://www.rsc.org/Membership/Networking/InterestGroups/Electrochemistry/StudentBurs aryScheme.asp

Echem.NET

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SCI Electrochemistry Postgraduate Conference 2018
(SCI EPC 2018)

Thursday 31st May 2018

Strathclyde University, Scotland-UK

Organized by: Society of Chemical Industry (SCI) and the Electrochemistry and Corrosion Technology group of the University of Strathclyde.

Summary

The SCI EPC 2018 is a one-day conference for postgraduate students around the United Kingdom to showcase their research and advancements in the field of electrochemistry. This event is free of charge where students can present their work in two modalities, either oral presentation or poster exhibition.

The four key benefits for postgraduate students who will be attending to the conference are as follow:

1. Raise awareness of your research among the electrochemistry community.
2. Present your research in a friendly environment.
3. Receive feedback from appointed staff and peers.
4. Knowledge exchange and networking opportunities.

Call for abstract submission

PhD students and Postdoctoral researchers can submit their abstracts for oral and poster presentations after registration in the SCI platform. Successful applicants will be notified after the submission deadline expires. Oral paper (20 minutes) or poster modality (A0 portrait)

Registration

This event is opened to all postgraduate students. However, registration is compulsory. SCI registration website will go live soon. Please check regularly the SCI home website (https://www.soci.org/) for the SCI registration link update. The university website for the event is under construction and it will be available soon.

Awards and Prizes

Two prizes will be awarded during the conference. One prize will be for the best oral presentation and the other one for the best poster exhibition. Winning students will receive award certificates.

Program

The organizing committee is working currently in the event program and it will be available soon.

Venue

Strathclyde University
3rd floor, lecture theatre 301, McCance Building
16 Richmond Street
G1 1XQ
Glasgow - Scotland

How to get to the venue

https://www.strath.ac.uk/maps/?building=mccancebuilding

Organizing committee

Priscila Valverde (PhD student, Strathclyde University)
Xiaomeng Su (PhD student, Strathclyde University)
Jonathan Boualavong (MPhil student, Strathclyde University)

Sponsors

Society of Chemical Industry (SCI)
International Society of Chemistry (ISE). To be confirmed
Royal Society of Chemistry (RSC). To be confirmed

For additional information and enquiries please do not hesitate to contact
Priscila Valverde
e-mail: priscila.valverde-armas@strath.ac.uk

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Metrohm
Autolab U.K.

Free! NOVA Workshop

NOVA is Metrohm Autolab's software package, designed to control all the Autolab instruments with an USB interface. With NOVA you don't just use an electrochemical method; you can fully design all your electrochemical experiments.

NOVA workshops provide a general introduction to the software including:
- Guidelines for building basic Nova procedures
- Hints and tips for analysing and managing data
- An introduction to EIS measurements and equivalent circuit fitting
- Practical demonstrations.

At the workshop we will show the Optical bench, NOVA with Impedance and demonstrate theory and fitting.

We are running a workshop at the University of Strathclyde on 1st June 2018

Register your interest by emailing autolab@metrohm.co.uk or call us on 01928 579 600
Find out more at www.metrohm.co.uk

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More Meetings:

69th Annual Meeting
of the International Society of Electrochemistry

2 – 7 September, 2018
Bologna, Italy
Electrochemistry: from Knowledge to Innovation

Forthcoming Annual and ISE Topical Meetings:

2018
- 15 – 18 April, Tokyo, **Japan**. *22nd ISE Topical Meeting*. Materials Engineering and Process Optimization at Electrified Solid/Liquid Interfaces.
- 8 – 11 May, Vilnius, **Lithuania**. *23rd ISE Topical Meeting*. Electrochemistry for Investigation of Biological Objects: from Functional Nanomaterials to Micro/Nano-Electrodes.
- 2 – 7 September, Bologna, **Italy**. *69th Annual Meeting*. Electrochemistry from Knowledge to Innovation.

2019
- 7 – 10 April, Merida, **Mexico**. *24th ISE Topical Meeting*.
- 12 – 15 May, Toledo, **Spain**. *25th ISE Topical Meeting*.
- 4 – 9 August, Durban, **South Africa**. *70th Annual Meeting*.

2020
- 30 August – 4 September, Belgrade, **Serbia**. *71st Annual Meeting*.

Meetings Sponsored by
The International Society of Electrochemistry:

Conference on Electrochemistry in Advanced Materials, Corrosion and Radiopharmaceuticals
15-17 February 2018, Mumbai, **India**
Sponsored by: EC
Contact: Ashis Kumar

Challenges and Opportunities in Energy Research
5-9 March 2018, Crans-Montana, **Switzerland**
Sponsored by: Division 3
Contact: Raffaella Buonsanti

15th Symposium on Fuel Cell and Battery Modeling and Experimental Validation
12-13 April 2018, Aarau, **Switzerland**
Sponsored by: Division 3 and 5
Contact: Erik Berg

20th YUCORR International conference: "Meeting Point of the Science and Practice in the Fields of Corrosion, Materials and Environmental Protection"
21-24 May 2018, Tara mountain, **Serbia**
Sponsored by: Division 5
Contact: Marija Mihailovic

8th International Conference on Electrochemistry in Nanosciences: **Electrochemistry for Nano & Nano for Electrochemistry**
29-31 May 2018, Nancy, **France**
Sponsored by: Division 1
Contact: Alain Walcarius

International Fischer Symposium
27-31 May 2018, Kloster Seeon, **Germany**
Sponsored by: EC
Contact: Philippe Allongue

17th International Conference on Electroanalysis
03-07 June 2018, Rhodos, **Greece**
Sponsored by: Division 2
Contact: Anastasios Economou

5th International Symposium on Surface Imaging /Spectroscopy at the Solid/Liquid Interface
6-8 June 2018, Krakow, **Poland**
Contact: Michal Mosialek

Electrospinning for energy 2018
13-15 June 2018, Montpellier, **France**
Sponsored by: Division 1
Contact: Deborah Jones

The 16th International Symposium on Polymer Electrolytes
24-29 June 2018, Yokohama, **Japan**
Sponsored by: Division 3
Contact: Yoichi Tominaga

The World Conference on Carbon
1-6 July 2018, Madrid, **Spain**
Sponsored by: EC
Contact: Emilia Morallon

Electrochemical Methods in Corrosion Research 2018
22-27 July 2018, Cambridge, **UK**
Sponsored by: EC
Contact: Robert Cottis

Gordon Research Conference: Fuel Cells "Energizing the Future by Innovation in Fuel Cell Materials, Methods, Modeling, and Manufacture"
29 July - 3 August 2018, Smithfield, RI, **USA**
Sponsored by: EC
Contact: Deborah Jones

Summer Meeting on Bio-Electrochemistry 2018
22-24 August 2018, Antwerp, **Belgium**
Sponsored by: Division 2
Contact: Karolien De Wael

Advanced Batteries, Accumulators and Fuel Cells
26-28 August 2018, Brno, **Czech Republic**
Sponsored by: Division 3
Contact: Jiři Vondrak

Symposium of the French Group of Bioelectrochemistry
24-27 September 2018, Sète, **France**
Sponsored by: Division 2
Contact: Christophe Innocent

7th Baltic Electrochemistry Conference: Finding New Inspiration
4-7 November 2018, Tartu, **Estonia**
Sponsored by: EC
Contact: Enn Lust

5th Ertl Symposium on Catalytic and Adsorption Reactions in chemical ProcessEs
25-28 November 2018, Gwangju, **Korea**
Contact: Jaeyoung Lee

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The Electrochemical Society
Advancing solid state & electrochemical science & technology

Biannual Meetings

- **233rd ECS Spring Meeting**, 13 – 17 May, 2018, Seattle, **USA**
- **AiMES**, 30 September – 4 October, 2018, Cancun, **Mexico**
- **235th ECS Spring Meeting**, 26 – 31 May,2019, Dallas, **USA**
- **236th ECS Fall Meeting**, 13 – 17 October, 2019, Atlanta, **USA**
- **237th ECS Meeting with the 18th International Meeting on Chemical Sensors (IMCS 2020)**, 10 – 15 May, Montreal, **Canada**
- **PRiME 2020**, 4 – 9 October, 2020, Honolulu, **USA**
- **239th ECS Spring Meeting**, 30 May – 3 June, 2021, Chicago, **USA**
- **PRiME 2024**, 6 – 11 October, 2024, Honolulu, **USA**

Sponsored Meetings

- **First International Conference on 4D Materials and Systems**, Yamagata University, 26 – 30 August, 2018, Yonezawa, **Japan**
- **International Conference on Solid State Devices and Materials (SSDM),** 9 – 13 September, 2018, Tokyo, **Japan**
- **III Colombian Congress of Electrochemistry**, 2 – 5 October, 2018, Cali, **Colombia**
- **7th Baltic Electrochemistry Conference: Finding New Inspiration (BEChem 2018)**, 4 – 7 November, 2018, Tartu, **Estonia**

2019 Satellite Meetings

- **Electrochemical Conference on Energy and the Environment: Bioelectrochemistry and Energy Storage (ECEE 2019)**,
  21 – 26 July, Glasgow, **Scotland**

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INTERNATIONAL SOCIETY
OF ELECTROCHEMISTRY

ISE REGIONAL STUDENT MEETINGS

Graduate Students who are members of ISE and intend to organize a **Regional Student Meeting** can apply for ISE financial support. **Regional Student Meetings** are typically one-day meetings involving graduate students active in the geographic area where the meeting takes place.

The format of the meeting (oral presentations, posters, discussion sessions, other) is autonomously decided by the organizers who will be responsible for securing a venue and collecting registrations. No registration fee should be requested. No later than one month after the meeting, the organizer(s) will send to the ISE Office a report on the event, including the names and the e-mail addresses of the participants. The participants will be encouraged to apply for ISE membership. An overview of the report accompanied by suitable pictures if available will be posted on the ISE website under Student Activities.

Applications for ISE support must be sent by e-mail to the **ISE Office (info@ise-online.org)**, with a copy to the Regional Representative of the country where the meeting is organized, 3-12 months before the meeting date, using the **application form**. The local ISE Regional Representative ***(Dr. Tim ALBRECHT of Imperial College London, for the United Kingdom)***, if requested, will assist the potential meeting organizer in the preparation of the application. Applications will be analyzed by a committee consisting of (i) ISE Secretary General, (ii) ISE Treasurer, (iii) ISE Vice President responsible for Educational Activity and (iv) ISE Vice President responsible for Regional Sections.

The response will be communicated to the applicant and to the relevant Regional Representative no later than 1 month after the application submission.

The maximum financial support will be **600 €**; the expected use of the funds must be specified in the application. Co-sponsoring by other Societies and/or institutions is possible.

Find out more:

http://www.ise-online.org

Product Information

ALVATEK

Electrochemistry Product News

EmStat3 blue

- 8 hours of batterylife
- USB or Bluetooth communication
- potential range of ±4V
- current ranges from 1 nA to 100 mA
- ideal for sensor applications

Optional:

- 8 or 16 channel multiplexer
- stirrer control
- Pt1000 temperature sensor
- differential electrometer amplifier

PalmSens

Compact Electrochemical Interfaces

ALVATEK

Electrochemistry Product News

BaSyTec
Battery Test Systems

BASYTEC Battery cyclers and capacity testing systems

We are delighted to announce that we have signed an exclusive UK distribution agreement with BaSyTec GmbH.

BaSyTec is a leading supplier of high quality battery test systems with installations worldwide. BaSyTec systems have proven, superior capabilities – such as 3-electrode measurements as standard – excellent accuracy, powerful software, and all at lower cost.

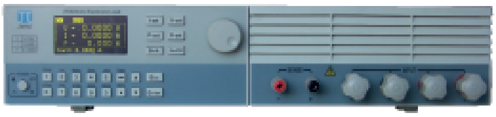
(Shown here, the 32 Channel Test System 32 x 5A channels. Parallel operation capability)

The BaSyTec range extends to high channel counts (to 480 channels) and also to high power systems to 1000V and 1000A in both stand-alone and networked configurations.

Finally, BaSyTec offers the portable, low cost Battery Capacity Test instruments (BCT) range which extends to 32A and 600W.. These provide an in-situ measurement of battery capacity and internal resistance using a defined discharge test. Please contact us for more information or to arrange a demonstration.

Nanjing Jartul Electronics Co., Ltd

Jartul Electronic Loads



Alvatek is now the exclusive distributor for Nanjing Jartul Electronics. Jartul offers a broad range of electronic loads from low power laboratory loads up to a powerful 500V/240A/6kW unit. These are surprising low-cost and range from around £500 for 30A/150V to around £6,000 for the most powerful unit. Please contact us for more information or to arrange a demonstration.

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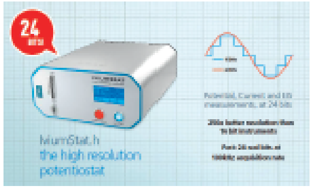
Ivium's new models with 24-bit measurement and 20-bit output resolution delivers:

- Ability to measure small signals on top of large background signals
- Faster speed (less switching and internal adjustments
- Reduced discontinuities / noise due to switched ranges
- Better linearity
- 20 bits output – 20uV resolution over a full 10V sweep.



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Network and protect your vital data in the event of a PC crash. Used with any Ivium potentiostat, this is a USB-connected data store with WiFi and LAN connection to the outside world. IviumSoft then runs on a PC networked to the instrument by WiFi or LAN. Should the pc connection be lost, or the PC crash, data will continue to be recorded onto the integral SD and, when the connection resumes, the data will be recovered and the system resynchronised.

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www.alvatek.co.uk

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Electrochemistry?

There's an app for that

PStouch

Use your PalmSens and EmStat with a tablet or smartphone

PalmSens

Compact Electrochemical Interfaces

New Product Information

PalmSens

Compact Electrochemical Interfaces

PalmSens3

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EmStat3 and 3+

Potentiostat

EmStat3 MUX8

EmStat3 with integrated
8 channel multiplexer (MUX8)

EmStat3 MUX16

EmStat3 with integrated
16 channel multiplexer (MUX16)

MultiEmStat3

4 channel multipotentiostat
with EmStat3 modules

MultiEmStat3 and 3+

4, 8 or 12 channel multipotentiostat
with EmStat3 or EmStat3+ modules

EmStat3 4WE

Polypotentiostat for use with up to 4 working electrodes.

Distributed in the UK by

ALVATEK

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www.alvatek.co.uk

New Product Information

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April 2013:
ALVATEK and BASi sign UK distribution contract

A Selection from the BASi range of electrochemistry accessories.
These can be found at www.basinc.com/products/ec.html

Electrochemical Cell Packages

- C-3 Cell Stand for Voltammetry
- Controlled Growth Mercury Electrode (CGME) for Polarography
- RDE-2 Rotating Disk Electrode
- Bulk Electrolysis Cell
- Thin-Layer Cross-Flow Cell
- Spectroelectrochemical Cell
- Glucose Sensor Interface

Electrodes

- Working Electrodes for Voltammetry
- Working Electrodes for Bulk Electrolysis
- Microelectrodes
- Reference Electrodes
- Auxiliary Electrodes
- Wired Enzyme Electrode
- Polishing Kit and Supplies

Cells

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- Cell Tops
- Gas Sparging & Magnetic Stirring
- VC-2 Voltammetry Cell
- Low Volume Cell

For more information on any of the above
products please contact Steve Fryatt at Alvatek

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New Product Information

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Whistonbrook Technologies design, manufacture and supply a full range of standard and custom potentiostats and other electrochemical instrumentation to meet all your needs.

Analogue Potentiostats

- Low noise analogue potentiostats
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- Current ranges from 1nA to 10mA

Prices from £1990

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- Instruments and software developed for medical diagnostic sensors

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- Amplifiers for Neuroscience
- Galvanostats
- High impedance buffer amplifiers
- Loads for fuel cells
- Analogue and Digital

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Digital Instrumentation with PC software packages

- EzeScan 4 – entry level potentiostat
- EzePG – potentiostat/galvanostat
- Quad potentiostat – four channel potentiostat
- EzeTouch – portable touch screen potentiostat

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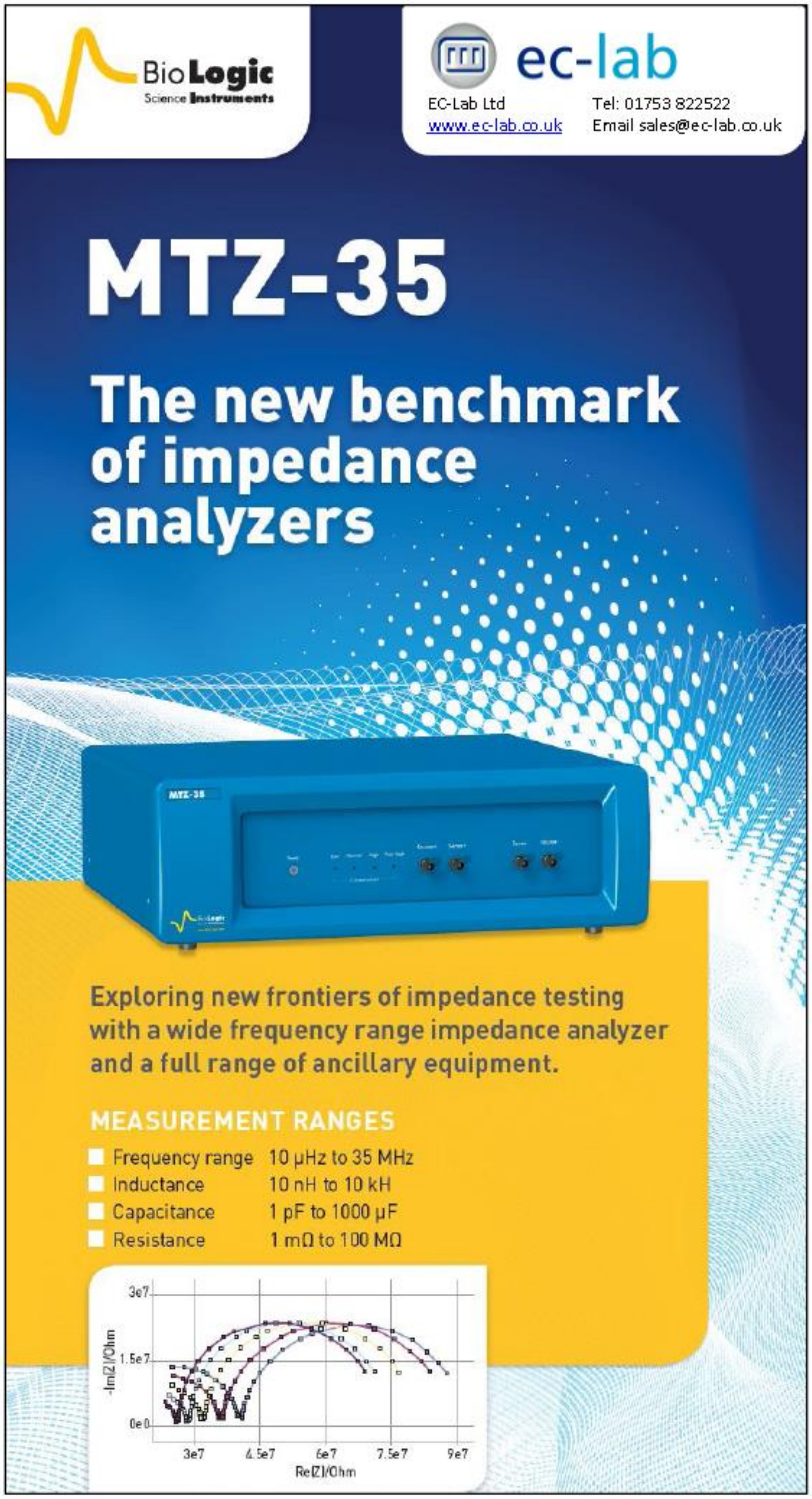
Website	www.whistonbrook.com
Telephone	01582 434252
Email	info@whistonbrook.com

Whistonbrook Technologies Limited, Unit C24, 110 Butterfield, Great Marlings, Luton, Beds, LU2 8DL

New Product Information



BioLogic
Science Instruments

ec-lab

EC-Lab Ltd
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Email sales@ec-lab.co.uk

MTZ-35

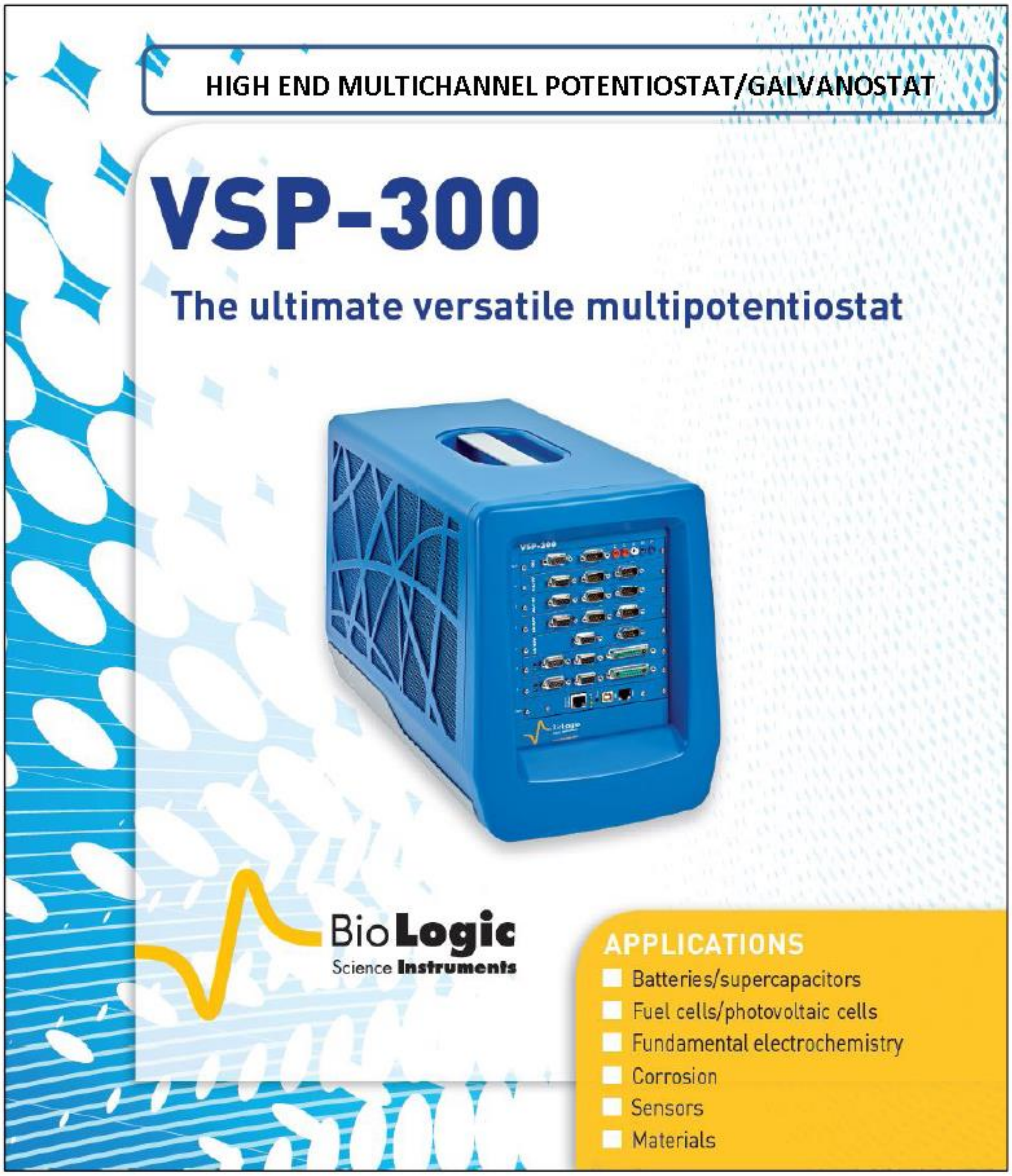
The new benchmark of impedance analyzers

Exploring new frontiers of impedance testing with a wide frequency range impedance analyzer and a full range of ancillary equipment.

MEASUREMENT RANGES

☐ Frequency range	10 µHz to 35 MHz
☐ Inductance	10 nH to 10 kH
☐ Capacitance	1 pF to 1000 µF
☐ Resistance	1 mΩ to 100 MΩ

New Product Information



HIGH END MULTICHANNEL POTENTIOSTAT/GALVANOSTAT

VSP-300

The ultimate versatile multipotentiostat

Bio**Logic**
Science **Instruments**

APPLICATIONS

- ☐ Batteries/supercapacitors
- ☐ Fuel cells/photovoltaic cells
- ☐ Fundamental electrochemistry
- ☐ Corrosion
- ☐ Sensors
- ☐ Materials

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New Product Information

Application areas:
bio-sensors,
biochemistry,
corrosion,
coatings,
catalysts...

M470

Introducing the 4th generation of scanning probe electrochemical workstations

- **9 available techniques**:
  SECM, LEIS, SVP,SDS, SKP, OSP, ic-SECM, ac-SECM, ac-SDS
- High performance scanning stage:
  0.09 nm ultimate z-resolution,
  20 nm resolution on all axes,
  100 mm scan range on all axes,
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  ac-SECM offering measurement of surface conductivity without a mediator.
- Fully integrated potentiostat/galvanostat/FRA:
  ±10 V potential range, current ranges from **1 A to 1 nA**,
  1 MHz to 1µHz EIS capability

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Product designed and manufactured by Uniscan Instruments Ltd,
a Bio-Logic SAS company

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ec-lab

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New Product Information

VMP-300

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POTENTIOSTAT/GALVANOSTAT

The ultimate multichannel electrochemical workstation

Modularity

- Multi-users
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- EIS capability (10 µHz to 7 MHz)
- Ultra Low Current (100 nA to 1 pA)
- Current boosters: 1A/48V, 2A/30V, 4A/14V, 10A/5V
- Current boosters in parallel
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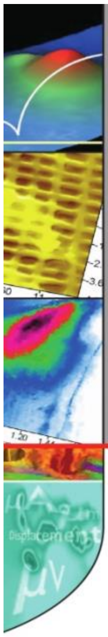
Unique features

- Up to 48 V control
- Up to 150 A (amplifiers in parallel)
- 1 pA min. current range
- 1 µs min. acquisition time

BioLogic
Science Instruments

ec-lab
EC-Lab Ltd.
www.ec-lab.co.uk
Tel: 01753 822522
E-mail: sales@ec-lab.co.uk

New Product Information



Metrohm Autolab

Metrohm Autolab has been a member of the Metrohm Group since 1999. Metrohm Autolab customers can look expect excellent sales and service support from a dedicated team of Electrochemists based at Metrohm's prestigious laboratories at Daresbury near Runcorn.

Metrohm Autolab produces four different potentiostat/galvanostat lines for a wide range of electrochemical applications, as well as modular extensions, software and accessories.

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Autolab U.K.

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Email: autolab@metrohm.co.uk

New Product Information

DROPSENS **Metrohm U.K. Ltd.**

µStat 8000P Multi Potentiostat

Ref. STAT8000P

DropSens is proud to announce the launch of the NEW portable Multi Potentiostat µStat 8000P.

Our brand new instrument, of only 22x20x7 cm, includes 8 channels that can act at the same time as 8 independent potentiostats; it also includes one multichannel that can act as a potentiostat where up to 8 working electrodes share an auxiliary and a reference electrode.

With µStat 8000P users can perform up to 8 different electrochemical techniques at the same time; or carry out the study of one technique's parameter in just one step by applying the same electrochemical technique in several channels but selecting different values for the parameter under study. These are just examples of the enormous capabilities that our new instrument offers.

µStat 8000P can be applied for Voltammetric or Amperometric measurements, including 11 electroanalytical techniques. In addition, µStat 8000P owners can later upgrade their instrument to a µStat 8000 by just purchasing an extension. This self-upgrade does not require any hardware modification, but it is implemented by means of a Galvanostat software update kit.

The NEW portable Multi Potentiostat is Li-ion Battery powered (DC charger adaptor also compatible), and can be easily connected to a PC via USB or Bluetooth®.

µStat 8000P is controlled by the powerful software "DropView 8400" which allows plotting of the measurements and performing the analysis of results. DropView software provides powerful functions such as experimental control, graphs or file handling, among others.

Available techniques:

POTENTIOSTAT

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LSV	Linear Sweep Voltammetry
CV	Cyclic Voltammetry
SWV	Square Wave Voltammetry
DPV	Differential Pulse Voltammetry
NPV	Normal Pulse Voltammetry
NDP	Differential Normal Pulse Voltammetry
ACV	AC Voltammetry

Amperometry

AD	Amperometric Detection
FA	Fast Amperometry ($t_{int} < 0.1$ s)
PAD	Pulsed Amperometric Detection
ZRA	Zero Resistance Amperometry

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New Product Information

DROPSENS

Metrohm
U.K. Ltd.

μStat 8000P Multi Potentiostat

Ref. STAT8000P

Instrument Specifications	
● Power	Li-ion Battery (3500 mAh) USB DC charger adaptor compatible (5 V, 15 W)
● PC interface	Bluetooth® USB
● Operating modes	8x 1 Channel Potentiostat 1x 8 Channel Potentiostat
● DC-Potential range	±4.096 V
● Current ranges (potentiostat)	±1 nA to ±100 mA (9 ranges)
● Maximum measurable current	±80 mA
● Rise time	20 μs
● Applied Potential Resolution:	1 mV
● Measured Current Resolution	0.025 % of current range (1 pA on lowest current range)
● Potential Accuracy	±0.2 %
● Current Accuracy	≤0.5 % (current range dependent)
● External inputs/outputs	· 5 Digital Input/Output pins [PIO 1, PIO 2, PIO 3, PIO 4, PIO 5] · 3 Analog Inputs multiplexing PIO 1, PIO 2, PIO 3 · 2 Analog Outputs (configurable I-out or E-out)
● Indicators	LCD display in front panel
● Dimensions	22.2 cm x 20.5 cm x 7.5 cm (L x W x H)
● Weight	1.6 kg

Control Specifications			
General Pretreatment	Conditioning stage duration:	0 – 1300 s	
	Deposition stage duration:	0 – 1300 s	
	Equilibration stage duration:	0 – 1300 s	
General Parameters	Begin, End, Base, Vertex potentials:	-4.096 V to +4.096 V	
	Step potential:	1 mV to 500 mV	
	Pulse potential:	1 mV to 250 mV	
	Scan rate:	1 ms up to 1.3 s per step	
Specific Parameters	SWV	Frequency:	1 Hz to 400 Hz
		Amplitude:	1 mV to 250 mV
	DPV, NPV, NDP	Modulation time:	1 ms to 1300 ms
		Pulse time:	1 ms to 1300 ms
	ACV	Frequency:	2 Hz to 250 Hz
		Amplitude:	5 mV to 250 mV (RMS)
	Chrono. Methods (AD, ZRA)	Interval time:	0.1 s to 1300 s
		Run time:	Hours (65000 points)
	Fast Chrono. Methods (FA)	Interval time:	1 ms to 1300 ms
		Run time:	Hours (65000 points)
	PAD	Pulse time:	1 ms to 1300 ms
		Interval time:	10 ms to 1300 ms
		Run time:	Hours (65000 points)

Specifications are subject to change without previous notice

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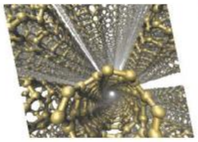


New Product Information

New Solartron EnergyLab XM for Energy Research

The Solartron EnergyLab XM is an electrochemical impedance workstation designed specifically for energy storage research:

- Batteries
- Supercapacitors
- Fuel cells

New Application-Focussed Product Line

The EnergyLab XM is the first of a new application-specific range of potentiostats from Solartron Analytical (Ametek), with small footprints and affordable pricing. There will be four systems in the range, which will be launched over the coming months.

Follow Blue Scientific on Linked In to receive details of the new instruments as they are announced.

EnergyLab XM

The first product in the series to launch is EnergyLab XM, for impedance testing of a variety of energy storage devices, including the testing of batteries, supercapacitors and fuel cells. The system includes all components required for this area of research, eliminating the need for costly hardware add-ons. The system includes:

- A reference grade potentiostat
- Frequency response analyser (FRA)
- 2A booster

The unit may be operated in boosted or unboosted mode (with automatic switching), providing optimum test conditions and accuracy for a wide range of devices.

EnergyLab XM's extreme sensitivity is ideal for complete characterisation of prototype low current or low impedance new generation cells. If high current is needed, external boosters can be connected and automatically controlled, allowing fully integrated high current tests at up to 100A.

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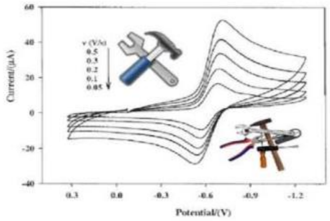
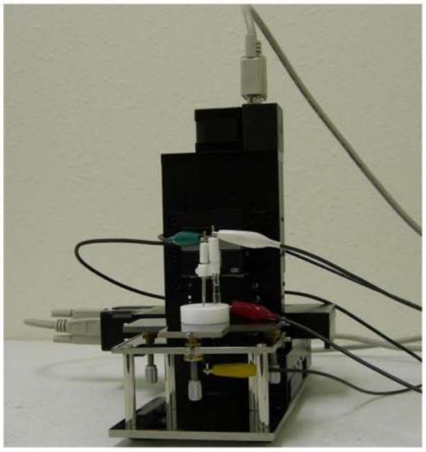

Current/(μA)
60
40
20
0
-20
-40
v (V/s)
0.5
0.3
0.2
0.1
0.05
0.3
0.0
-0.3
-0.6
-0.9
-1.2
Potential/(V)



New Product Information

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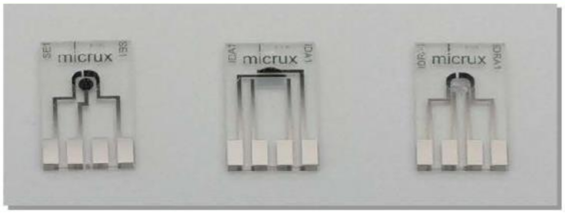

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The Electrochemical Technology Technical Interest Group is involved in all aspects of the application of electrochemical science and engineering. The Group's aim is to promote research and development of electrochemistry which leads to the production of appropriate technologies and industrial and consumer products. The Group provides an interface between academia and industry and is a forum for promoting research and collaboration between a range of scientific and engineering disciplines.

Industrial sectors

Electrochemical activities cut across all industrial sectors, including chemical, pharmaceutical, electrical, electronic and micro-electronic, information technology, mining and metallurgical, biotechnology, transportation, medical, water and wastewater. As such, the Group's interests include applications of electrochemistry in:

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- energy conversion and storage
- synthesis of chemicals, pharmaceuticals, biochemicals, polymers and electronic materials
- materials protection, processing and fabrication
- environmental protection and control

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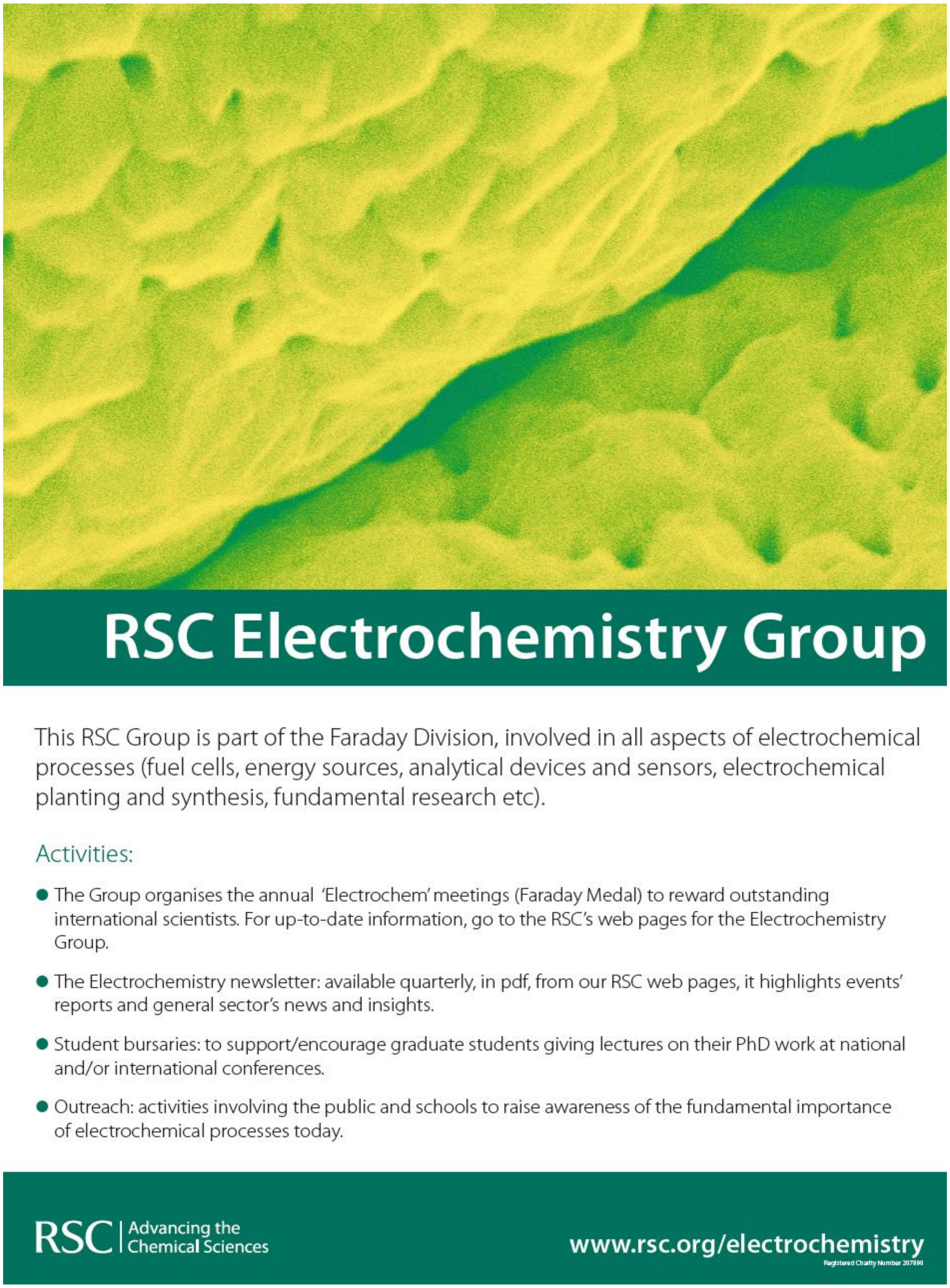
RSC Electrochemistry Group



RSC Electrochemistry Group

This RSC Group is part of the Faraday Division, involved in all aspects of electrochemical processes (fuel cells, energy sources, analytical devices and sensors, electrochemical planting and synthesis, fundamental research etc).

Activities:

- The Group organises the annual 'Electrochem' meetings (Faraday Medal) to reward outstanding international scientists. For up-to-date information, go to the RSC's web pages for the Electrochemistry Group.
- The Electrochemistry newsletter: available quarterly, in pdf, from our RSC web pages, it highlights events' reports and general sector's news and insights.
- Student bursaries: to support/encourage graduate students giving lectures on their PhD work at national and/or international conferences.
- Outreach: activities involving the public and schools to raise awareness of the fundamental importance of electrochemical processes today.

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Abstracts: Electrochem 2017

Welcome from the LOC

Welcome to Electrochem 17 at the University of Birmingham!

We are delighted to welcome you to our University and our city. Birmingham is known for many things: its canals, the Birmingham Royal Ballet, the Birmingham Philharmonic Orchestra, the balti, Cadbury's chocolate, Staffordshire hoard, Jewellery Quarter and the Bull Ring, to name a few. Within the University we also have the Lapworth Museum of Geology, the Barber Institute of Fine Arts, the recently opened Bramall Music Building and the Winterbourne Botanic Garden. Matthew Boulton and James Watt lived and worked here and Soho House, the home of Matthew Boulton and sometimes meeting place of the Lunar Society, is now a museum open for visitors. Whilst the industrial heritage of our region is widely recognised, what is perhaps less well-known is a strong local tradition in the metal finishing industry. There are many small plating shops around the city and wider region, as well as one or two larger companies developing products for metal finishing. One of us has fond memories of an interesting summer student work placement in a local company over some years, helping to make corrosion inhibitors for paints, electroplating customers' samples and helping to test additives for anodising baths.

We also have a strong academic tradition in electrochemistry. John Randles carried out his work in the School of Chemistry here, making varied and important contributions to our field of work, both in the development of theory and in careful, rigorous experimental Physical Chemistry. 70 years ago this year, he published work on the cathode ray polarograph, which soon led to his equation for the peak current, the Randles-Sevčik equation. In this year he also published his analysis of the impedance of an equivalent circuit to represent an electrochemical cell, the Randles Equivalent Circuit. A little later came his work on the liquid|liquid interface. We hope that he would be happy that we are meeting here this year to share our work and our interest in Electrochemistry.

We very much hope you enjoy the conference and would like to thank you all for coming and for participating. We would also like to thank Elizabeth Harrison, David Oram and George Merriman, the University’s Medical School Events Team, for their hard work in organising this meeting.

Dr Neil Rees, Dr Sarah Horswell, Dr Paramaconi Rodriguez, Professor Alison Davenport
University of Birmingham

Invited Speakers

Abstracts

Faraday Medal: Marc Koper

Proton-coupled electron transfer and electrocatalysis

Marc T.M. Koper

Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands
Email: m.koper@chem.leidenuniv.nl

This talk will outline a simple but general analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. It is shown that decoupling of proton and electron transfer leads to a strong pH dependence of the overall catalytic reaction, implying an optimal pH for high catalytic turnover, and an associated optimal catalyst at the optimal pH. When more than one catalytic intermediate is involved, scaling relationships between intermediates may dictate the optimal catalyst and limit the extent of reversibility that may be achievable for a multiple proton-electron-transfer reaction. These scaling relationships follow from a valence-bond-type binding of intermediates to the catalyst surface. The theory is discussed in relation to the oxygen evolution reaction and the electrocatalytic reduction of CO_2, focusing on the importance of charged intermediates, their pH dependence and structure sensitivity.

Evans Medal/Sword:

Dr Hugh Isaacs

Dr Hugh S Isaacs was named as this year's Evans Award winner shortly before his death in December 2016. Hugh's career in electrochemistry and corrosion spanned over 5 decades and he made significant contributions to our understanding of localized corrosion and of oxide film growth and passivity. He was an innovative experimentalist, and an early adopter and developer of new techniques including scanning electrode and synchrotron-based methodologies. He was also a great mentor to many electrochemists and an active member of the corrosion community.

The lecture will be given by Prof Mary Ryan and shall provide an overview of Hugh's career, work and his many contributions to corrosion science.

Fleischmann Lecture:

Stephen Fletcher

Martin Fleischmann's Epochal Contributions to the Kinetics of Phase Change, and Pathways to the Future.

Stephen Fletcher

The Fletcher Consultancy,
Loughborough
Leicestershire, LE11 3LU (UK)

Email: ProfSFletcher@Virginmedia.com

Martin Fleischmann FRS (29 March 1927- 03 August 2012) was a central figure in the post-war development of transient techniques in electrochemistry. He used these dynamic methods to study the kinetics of phase changes at electrode surfaces, and, in particular, he established the widespread occurrence of nucleation and growth kinetics in metal deposition reactions and in anodic film formation reactions. He also used his considerable mathematical prowess to model these phenomena. His work forms the bedrock of much present-day research in these important areas, and extends from quantum phenomena through to large scale corrosion.

In this lecture, I will attempt to summarize (briefly) Martin's work on the kinetics of phase change, which forms only a fraction of his total achievement. I will then describe the current status and outstanding problems of nucleation and growth theory in electrochemistry, which must be solved before further progress can be made. Finally, I will indicate some important directions for next-generation research.

Energy & Environmental

Oral Abstracts

EE1

Role of the adsorbed oxygen species in the selective electrochemical reduction of CO_2 to alcohols on copper single-crystal electrodes

Cecile S. Le Duff, Paramaconi Rodriguez

School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, UK
Email: P.B.Rodriguez@bham.ac.uk

To date, copper and copper oxide-derived surfaces are the only catalysts that could electrochemically convert CO_2 to high-value and energy-dense products such as methane ethylene, formic acid, methanol and ethanol, among others.[1-3] However, the efficiency and the selectivity of this process are far from optimal and the parameters controlling these factors are not-fully understood. Until now, such differences in reactivity and selectivity have been attributed to the surface area, surface structure, the oxidation state of the Cu, the oxygen content on the films and roughness as well as to the history of the electrode.[1,3-7]
We have recently used Cu(100) and Cu(111) electrodes and have pulsed voltammetry to control the surface structure and the oxygen content at the surface. The pulse sequence was programmed to guarantee reproducible initial conditions for the reaction (Figure 1A) at every fraction of time and at any given frequency without compromising the surface structure.

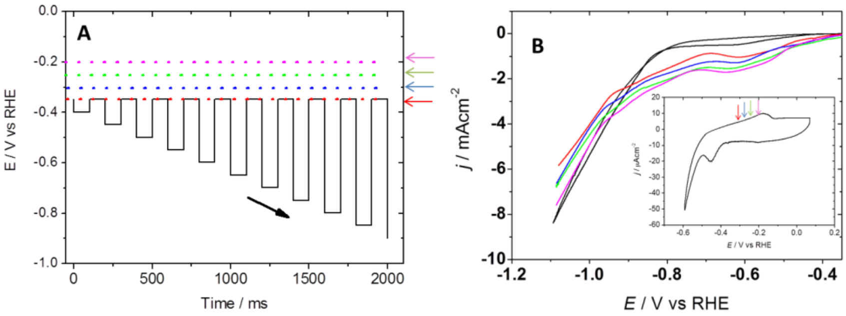

Figure 1: (A) Pulse program for the pulsed voltammetry. (B) Pulse voltammetries of Cu(111) electrodes in phosphate buffer solution in presence of CO_2. The black curves correspond to the cyclic voltammetry's at (υ=10 mV/s). Inset: cyclic voltammetry's in absence of CO_2 of the Cu(111) and Cu(100). The arrows indicate the e positive potential steps during the pulse voltammetry's.

We have found that oxygenated hydrocarbon species – formaldehyde, formate, methanol, ethanol, acetone and acetaldehyde – were only observed under pulse potential conditions. This may be associated to the adsorption of OH species to the surface when the potential is stepped up to the upper potential. The product selectivity would be associated to the OH coverage, which is surface structure and potential dependent.

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EE2

Scanning Electrochemical Cell Microscopy (SECCM): A Versatile Tool for Probing the Active Sites and Quantifying the Activity of Electrocatalysts

Cameron L. Bentleya, Minkyung Kanga, Faduma M. Maddara, Fengwang Lib, Marc Walkerc, Jie Zhangb and Patrick R. Unwina

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[b]*School of Chemistry, Monash University, Clayton, Vic 3800, Australia*
[c]*Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.*
Email: C.Bentley.1@warwick.ac.uk

The (electro)catalytic performance of (nano)materials is usually evaluated from the “total electrode activity”, measured with macroscopic (“bulk”) electrochemical techniques (*e.g.,* cyclic voltammetry) after immobilization on a supposedly inert, conducting substrate. Taking this approach, the intrinsic activity of each catalytic site can only be inferred from the total electrode activity if the number of active sites is known, which is generally challenging to measure for functional catalysts. In contrast, high resolution electrochemical imaging techniques, such as Scanning Electrochemical Cell Microscopy (SECCM) considered herein1, are able to investigate and map the electrochemical activity of complex (catalytic) materials at the nanoscale, and target particular characteristic features on a surface (*e.g.*, edge plane vs. basal plane).

In this work2, we report the first spatially-resolved measurements of hydrogen evolution reaction (HER) activity on natural crystals of molybdenum disulfide (MoS2), which has shown promise as an abundant and low-cost alternative electrocatalyst to platinum in this application. This is achieved using voltammetric SECCM, whereby pixel-resolved linear-sweep voltammogram (LSV) measurements have allowed the HER to visualized at multiple different potentials to construct electrochemical flux movies with nanoscale resolution. Through correlation of the local voltammetric response with information from scanning electron microscopy (SEM) and atomic force microscopy (AFM) in a *multi-microscopy approach*, it is demonstrated unequivocally that the basal plane of MoS2 is much more active than previously considered, and that the HER is greatly facilitated at surface defects (*e.g.*, steps, edges or crevices), with important implications for the design of MoS2 electrocatalysts. Semi-quantitative treatment of the voltammetric data reveals that the HER at the basal plane of MoS2 has a Tafel slope and exchange current density (*J*0) of ~120 mV/decade and 2.5 × 10−6 A cm−2 (*i.e.*, comparable to polycrystalline Co, Ni, Cu and Au), respectively, while the edge plane has a comparable Tafel slope and a *J*0 that is estimated to be more than an order-of-magnitude larger than that of the basal plane (~1 × 10−4 A cm−2).

[1] Ebejer, N.; Güell, A. G.; Lai, S. C. S.; McKelvey, K.; Snowden, M. E.; Unwin, P. R. In *Annual Review of Analytical Chemistry, Vol 6*; Cooks, R. G., Pemberton, J. E., Eds.; Annual Reviews: Palo Alto, **2013**; Vol. 6, p 329

[2] Bentley, C. L.; Kang, M.; Maddar, F. M.; Li, F.; Walker, M.; Zhang, J.; Unwin, P. R., Electrochemical Maps and Movies of the Hydrogen Evolution Reaction on Natural Crystals of Molybdenite: Basal vs. Edge Plane Activity. *Submitted,* **2017**

EE3

Poly-amine Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide

Sunyhik Ahn,[a,b] Konstantin Klykin,[c] Russell J. Wakeham,[b] Francesco Carla,[d] Vitaly Alexandrov[c], and Enrico Andreoli[b]
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b) Energy Safety Research Institute, Swansea University, Bay Campus, Swansea, SA1 8EN, UK
c) Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, Lincoln, USA
d) European Synchrotron Radiation Facility, CS 40220, 38043, Grenoble Cedex 9, France
Email: sunyhik.ahn@gmail.com

Electrochemical reduction of CO_2 into hydrocarbons and alcohols is a particularly attractive prospect given the tremendous infrastructure in place for the storage, transport and utilisation of such fuels and industrial feedstock. In this study, large surface area metallic copper foam electrodes are modified with polyamine groups for electrochemical reduction of CO_2. It is shown that the activity of copper towards CO_2 reduction can be enhanced or completely switched off depending on the chemical nature of the modifying polymer groups, with poly(acrylamide) leading to record levels of (geometric) partial current for hydrocarbons. Well reported effects from oxide derived copper and distribution of crystalline phases are ruled out as the source of enhancement by correlating changes in selectivity with material properties probed with XPS and in-situ XRD. Supporting density functional theory calculations suggest that the poly(acrylamide) stabilise the CO-CO* intermediate which enhances selectivity for ethylene and ethanol as observed in the experimental data. Tethering functional groups on copper that affect catalysis kinetics offers an additional tuneable parameter that can synergize with the conventional approach of modifying catalyst-intermediate binding strength, this demonstrates a new approach to the optimization and design of CO_2 reduction catalysts.

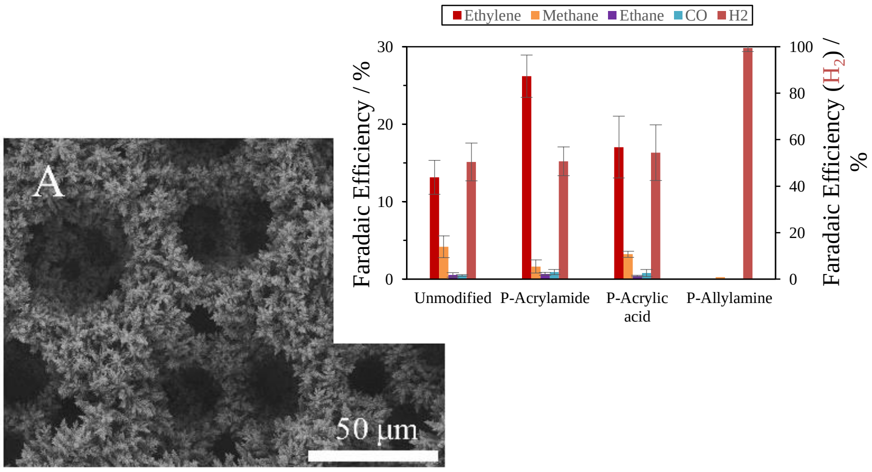


Figure. SEM image of copper foam electrode, with a bar chart of faradaic efficiencies for gaseous CO_2 electrolysis products.

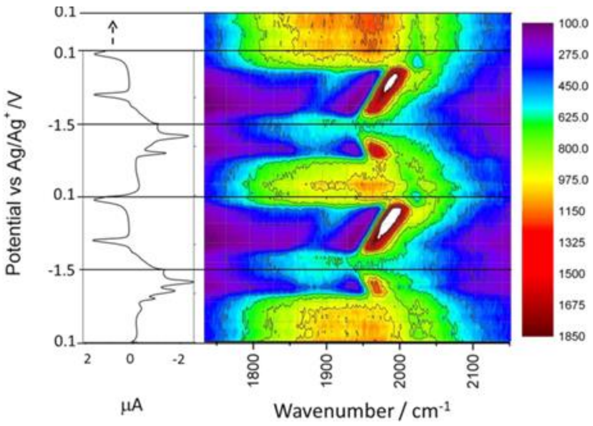
EE4

Studying electrocatalytic CO_2 reduction mechanisms with IR-Vis SFG spectroscopy

Gaia Neri,[a] Paul Donaldson[b], Alexander Cowan[a]
a) Department of Chemistry and Stephenson Institute for Renewable Energy, University of Liverpool, L69 7ZD, Liverpool, UK
b) Central Laser Facility, STFC Rutherford Appleton Laboratory, Harwell, Didcot, Oxfordshire, OX11 0QX, UK
Email: acowan@liverpool.ac.uk

The electrochemical reduction of CO_2 to fuels ($CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$) and feedstock's ($CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$) is an attractive goal with potentially enormous environmental and economic impacts. However to make such a process economically viable new more efficient electrocatalytic materials and molecules are required. A key issue is that the exact mechanism of many of the state-of-the-art catalysts are unproven experimentally, making rational development difficult.

IR-Vis Sum-Frequency Generation (SFG) spectroscopy specifically probes molecules at interfaces offering a sensitive probe of only the catalytically relevant species at the electrode surface. SFG has been widely used to study heterogeneous electrocatalysis but rarely to explore the mechanisms of molecular electrocatalysts. Here we will present our latest studies exploring the mechanisms of group 6 and 7 transition metal complex mediated CO_2 reduction and demonstrate how this powerful spectroscopic probe can provide unique insights into the factors controlling efficiency.



IR-VIS SFG spectra of $Mn(bpy)(CO)_3Br$ in CH_3CN/Ar recorded at 50 mV s^{-1} on Au electrode. The full data set recorded in <150 s

Benchmarking the activity, stability and inherent electrochemistry of amorphous MoS_x thin films for the hydrogen evolution reaction

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Transition metal dichalcogenides (TMDs), and in particular molybdenum disulfide (MoS_2), have been found to be earth-abundant candidates to replace platinum group metal catalysts for the hydrogen evolution reaction (HER) in PEM Electrolyzers. As only the Mo-edge sites are catalytically active,[1] strategies to obtain edge-abundant MoS_2 nanostructures are in high demand.[2–5] Recent studies reported a one-step, substrate insensitive electrodeposition method to obtain amorphous MoS_x thin films with tunable stoichiometry from a $(NH_4)_2MoS_4$ aqueous solution.[6] While initial investigations have focused on the elucidation of the MoS_x electrodeposition mechanism and stoichiometry, critical aspects in catalysts benchmarking such as durability and long-term stability remain unexplored. Several reports not only have confirmed the influence of pH in the inherent electrochemical activity of TMDs[7] but also its effect in the long-term stability under operating conditions.[8] Herein we present a comprehensive study of MoS_x thin films deposited on Au substrates for the HER across the 0.6-13 pH range. Plotting of the MoS_x redox peak potentials and peak heights vs. operating pH demonstrates a correlation between the inherent MoS_x redox mechanisms and the final HER activity. Accelerated durability tests on several voltage windows monitored with ex-situ X-ray photoelectron and Raman spectroscopies inform of the electrochemically induced morphology and stoichiometry changes in the MoS_x films. Finally, stability tests (3000 cyclic voltammograms, maximum current density output= 10mA cm^{-2}) benchmark the optimum pH operation range for the prepared MoS_x films.

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EEK1

Keynote: Nuria Garcia-Araez

Using redox mediators for Li-O_2 and Li-S batteries and Li recycling

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Email: n.garcia-araez@soton.ac.uk

Lithium-oxygen and lithium-sulfur batteries have the potential to revolutionize the energy storage market, since they can in principle store >5 times more energy than the current lithium-ion battery technologies. However, the performance of Li-O_2 and Li-S batteries is currently limited by several fundamental issues.

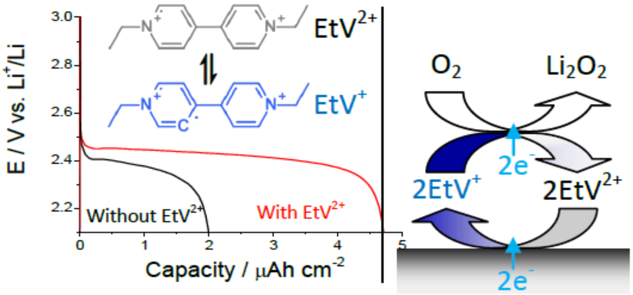
We have recently shown that redox mediators can solve the two more important issues associated to Li-O_2 batteries, i.e. electrode passivation and degradation reactions.[1] Degradation reactions are initiated by superoxide radical species that are formed as intermediates in the pathway of the reduction of oxygen:

$O_2 + e^- + Li^+ \rightarrow LiO_2$
$LiO_2 + e^- + Li^+ \rightarrow Li_2O_2$

On the example of ethyl viologen, EtV^{2+}, we demonstrated that redox mediators can be used to decrease the lifetime of superoxide species by promoting the fast reduction of superoxide to peroxide:

$EtV^{2+} + e^- \rightarrow EtV^+$
$LiO_2 + EtV^+ + Li^+ \rightarrow Li_2O_2 + EtV^{2+}$

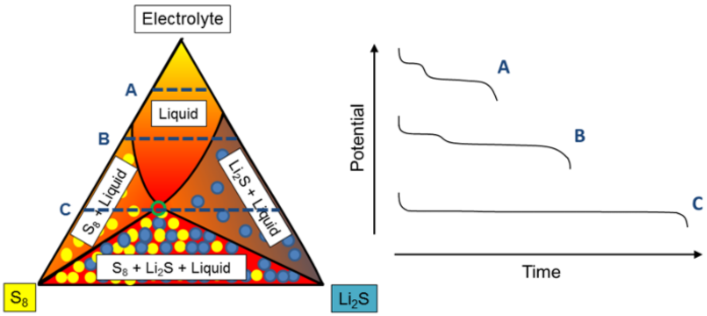
where EtV^{2+} acts as homogeneous catalyst and it is not consumed in the reaction. Furthermore, EtV^{2+} also acts as an electron shuttle, preventing electrode passivation by displacing the location of the reduction of oxygen from the electrode surface to the solution. Indeed, a major increase in capacity is obtained upon addition of EtV^{2+} to a Li-O_2 cell.



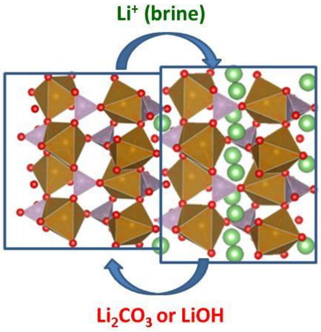
In Li-S batteries, a variety of polysulfides, Li_2S_n, are formed in the pathway of the reduction of S to Li_2S:

$n S + 2e^- + 2Li^+ \rightarrow Li_2S_n$
$Li_2S_n + (2n-2) e^- + (2n-2) Li^+ \rightarrow n Li_2S$

We hypothesize that polysulfides can act as redox mediators and shuttles in Li-S batteries, and their action can be optimized via a selection of suitable electrolytes. We have recently developed a new method that allows predicting the equilibrium concentration of polysulfides in Li-S cells, as well as the theoretical electrochemical response of the cell as a function of the amount of electrolyte.[2] This new approach, based on the construction of an experimental phase diagram, will be used for the rational screening of electrolytes for Li-S batteries.



Redox mediators are also a promising tool for Li recycling. We have shown that the reaction of battery materials (e.g. $LiFePO_4$) with redox agents is a fast, selective and efficient new method to extract lithium from natural brines and for recycling spent batteries.[3]



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EE6

Electrochemical Exfoliation and Functionalisation of 2D-materials for Energy Storage Devices

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Electrochemical exfoliation of graphite is considered to be a fast, scalable and eco-friendly way to produce graphene.[1, 2] Cathodic exfoliation in organic electrolyte, unlike anodic exfoliation, produces high quality graphene as it avoids the formation of oxygen containing functional groups.[2] However, development of applications of graphene is currently hampered by its poor dispersion in common, low-boiling point, solvents. In this contribution, we describe the single step simultaneous electrochemical exfoliation and functionalisation of graphene using diazonium compounds.[3] Using caesium salt (dissolved in dimethyl sulfoxide) the intercalating ions, functionalisation was achieved in combination with diazonium salt (either 4-nitrobenzenediazoniumtetrafluoroborate, 4 bromobenzenediazonium tetrafluoroborate or anthraquinone-1-diazonium chloride) as functionalisation moieties. We found that the presence of diazonium compounds in solution not only acts to functionalise the graphene but also aids the exfoliation through the generation of N_2 gas which assists the separation of the functionalised graphene layers. The functionalisation also enhanced the dispersibility of graphene in aqueous solution by two orders of magnitude and increased the charge storage capacity of graphene by three times because of the introduction of surface active redox reactions (Figure 1). Finally, we will introduce a simple electrochemical route for the synthesis of metallic phase trilayer MoS_2 nanosheets.

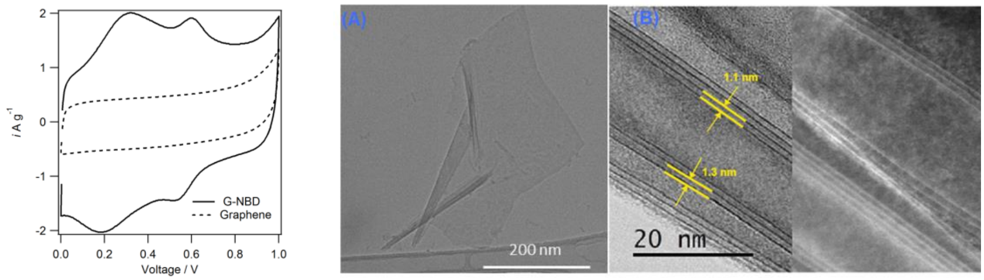

Figure 1: Cyclic voltammograms recorded at 100 mV s^{-1} in 6.0 M KOH (aq) using symmetrical coin cells constructed from electrochemical exfoliated restacked graphene and graphene functionalised insitu with 4-nitrobenzenediazoniumtetrafluoroborate (G-NBD) and high resolution TEM image of electrochemically exfoliated MoS_2 (A and B)

Refernces (1) K. Parvez, R. J. Li, S. R. Puniredd, Y. Hernandez, F. Hinkel, S. H. Wang, X. L. Feng and K. Mullen, *ACS Nano*, 2013, **7**, 3598-3606. (2) A. J. Cooper, N. R. Wilson, I. A. Kinloch and R. A. W. Dryfe, *Carbon*, 2014, **66**, 340-350 and (3) D. W. Johnson, B. P. Dobson and K. S. Coleman, *Current Opinion in Colloid & Interface Science*, 2015, **20**, 367-382.

EE7

Complexes with Tuneable Ligands as Redox Flow Battery Mediators

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Redox flow batteries are a fast emerging class of electrochemical energy storage system, aimed primarily at large grid scale storage. They are unique in the electrochemical energy genre, in that their design inherently decouples power and storage capacity, providing a flexible system ideal for an increasingly complex energy network. Commercialised systems comprise electrolytes of vanadium, dissolved to high concentrations in sulphuric acid. Whilst efficient and low maintenance, these systems are not viable for long term scale up and roll out, due to the crippling cost of vanadium. Alternative chemistry is being sought to provide a redox flow battery that retains the attributes of the all vanadium flow battery, whilst offering sustainability, lower costs, and long-term viability.

Metal-organic compounds are a potential source of redox mediators that may be molecularly engineered to deliver properties desirable in a flow battery, whilst comprising earth abundant elements. They also offer the prospect of working in non-aqueous solvents, to attain higher cell voltages, and to engage in multielectron transitions, thus introducing a much higher energy density system than the VRB.

Recently we have explored a new class of cobalt(II) complexes with ‘tuneable’ tridentate azole-pyridine type ligands. Four structures were synthesised and their electrochemical, physical and battery characteristics were investigated as a function of successive substitution of the ligand terminal pyridyl donors. Modification of the ligand demonstrated tuneable redox potentials in which the cobalt potential difference was increased from 1.07 to 1.91 V via pyridine substitution. The charge-discharge properties of the system were evaluated using static and flow systems, the results of which will be discussed. Modification of the ligands also improved solubility from 0.18 M to 0.50 M via pyridyl substitution with 3,5-dimethylpyrazole, though the low solubility of the complexes limits the overall energy capacity to between 2.58 to 12.80 Wh L^{-1}.

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Armstrong, Craig G.; Toghill, Kathryn E., Journal of Power Sources, Vol. 349, p. 121-129.

EE8

Cyclable All-Iron Membraneless Redox Flow Battery Based on Multiphase Immiscible Liquid Electrolytes

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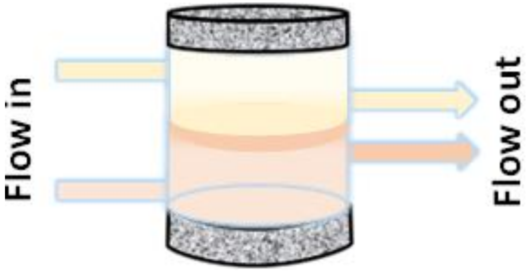
Introduction

Previous attempts at true membraneless redox flow batteries (RFB) have not been able to demonstrate multiple cycling due to reactant crossover (which limit capacity retention) and difficulty of separation of the mixed electrolyte after charging for a recharging pass[1]. Even the notable higher power density hydrogen-bromine[2] and vanadium species[3] based membraneless RFBs did not demonstrate capacity retention from multiple cycling of recirculated electrolyte. In response, we pioneer a membraneless (non-hybrid) RFB capable of recharge/recirculation of the same electrolyte for multiple cycles by applying immiscible aqueous - organic anolyte - catholyte liquid streams respectively.

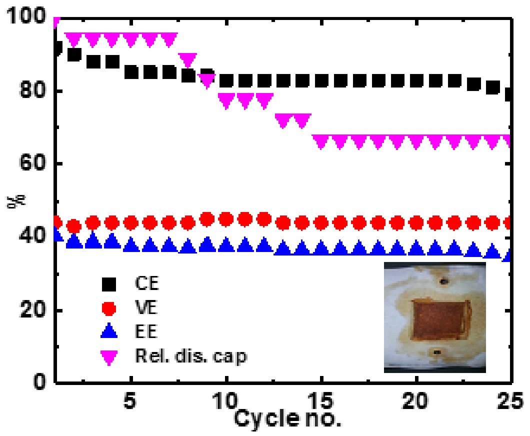
Preliminary results

Based on environmentally benign materials, an all iron chemistry was setup with; iron(II) sulfate ($FeSO_4$) as active species on the aqueous side (anolyte), and our recently investigated iron(III) acetylacetonate ($Fe(acac)_3$)[4] as active species dissolved in hydrophobic ionic liquid (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) supported ethyl acetate in the immiscible organic phase (catholyte).



Organic $[\mathrm{Fe(acac)_3}]^0 + \mathrm{e}^- \leftrightarrow [\mathrm{Fe(acac)_3}]^-$ ~ -0.4 V vs. SHE (1)

Aqueous $\mathrm{Fe}^{2+} - \mathrm{e}^- \leftrightarrow \mathrm{Fe}^{3+}$ ~ 0.8 V vs. SHE (2)



At the present work stage, over 65% of first discharge capacity can be retained even after 25 cycles, where columbic and energy efficiencies averaged at 85 and 38% respectively on a test flow cell utilizing 0.1 M $FeSO_4$ + 0.5 M sodium chloride in the aqueous anolyte and 0.1 M $Fe(acac)_3$ in 60/40 volume percentage ethyl acetate/ionic liquid catholyte.

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EE9

Two-step electrochemical intercalation and oxidation for mass production of graphene oxide

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Graphene oxide (GO), a single layer graphene sheet functionalized with oxygen groups, has numerous applications in both functional and structural areas, such as printed electronics, energy storage, polymer composites, etc. Conventional chemical oxidation to produce GO suffers from environmental and safety issues due to the use of hazardous and explosive chemicals. To mitigate such problems, electrochemical oxidation of graphite is a very promising alternative route to GO although it faces challenges associated with low yield (inhomogeneous oxidation) and complicated cell configuration (scalability). Here we report a two-step electrochemical intercalation and oxidation approach to produce GO on a large scale (tens of grams): (1) forming stage 1 graphite intercalation compound (GIC) in concentrated sulfuric acid; (2) oxidizing and exfoliating the stage 1 GIC in aqueous ammonium sulfate solution. This two-step approach leads to GO with high yield (>70 wt.%), good quality (>90%, monolayer), and oxygen content that is lower than that typically obtained from chemical routes (17.5 at.%). Moreover, the as-produced GO could be deeply reduced (3.25 at.% oxygen; C/O ratio 29.8) to highly conductive (54600 S m^{-1}) graphene. Use of the resultant reduced material as an electrochemical capacitor shows ultra-high rate capability up to 10 V s^{-1}. The two-step method is expected to advance research in electrochemical production of GO and extend its application to various areas.

EE10

Modification of Ti Surface as a Way to Reduce Excessive Surface Passivation During PEM Water Electrolysis Operation

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PEM water electrolysis represents important technology in hydrogen economy scheme. It is given mainly by the fact that it allows flexible operation even at very high intensity. PEM water electrolysis suffers, however, from several issues. The most critical one is stability of the materials on the anode side of the cell. This is given by a combination of acidic environment and high positive potential. Under these conditions the majority of electron conducting materials undergo dissolution which greatly limits list of materials available for anode catalyst and gas diffusion layer. For this reason the practically only useful anode catalyst material is based on Ir and gas diffusion layer is commonly made of Ti (or Ta). These metals are under such conditions stable only due to the presence of protecting passivation layer on their surface. However, the passivation layer itself is electrically insulating. The passivation layer of excessive thickness is therefore causing substantial surface contact resistance and leads to substantial energy loss, especially when the electrolysis process is operated at high current density. A common way of solving this issue is to cover the Ti surface with protecting layer based on Pt metal. This approach, however, leads to substantial increase in precious metal loading and further raises already very high investment cost of the PEM water electrolyser .

Aim of this work was to test an alternative approach based on appropriate modification of the Ti surface with acid. Results showed that etching of the Ti with hydrochloric acid leads, first of all, to a removal of the existing surface passivation layer, which decreases surface contact resistance. Additionally, a hydrogen generated during Ti metal dissolution in acid penetrates into bulk of Ti metal and forms subsurface layer of Ti hydrides slowing down growth of the newly forming passivation layer. The hydride layer formation was investigated using various electrochemical techniques, focused ionic beam in combination with secondary ion mass spectrometry, X-ray photoelectron spectroscopy and X-ray diffraction. The positive effect of Ti etching was confirmed during PEM water electrolysis operation.

Financial support by the Czech Science Foundation within the framework of the project No. 15-02407J, is gratefully acknowledged.

EE11

Platinum Decorated Manganese Oxide – Graphene Oxide sheets for Methanol Oxidation Reaction in Direct Methanol Fuel Cells

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Manganese Oxide – reduced Graphene Oxide (MnOx-GO) hybrid catalyst supports have promise for improving the performance of direct methanol fuel cells (DMFCs)[1], by improving the durability and stability of the expensive precious metal catalyst currently used in such devices.

MnOx – GO hybrid materials are highly tuneable, due to the numerous possible oxidation states of manganese, and different morphologies that can be produced.

In this instance, manganese oxide has been grown on graphene oxide via a rapid microwave assisted one pot wet chemical method[2]. This relatively 'green' synthesis route uses low energy microwaves and aqueous solvent and also promises facile scale up as it is fast and relatively simple. These hybrid MnOx-GO materials have subsequently been decorated with platinum nanoparticles via a further one pot microwave assisted polyol process[2], in order to test them for use in DMFCs.

These Pt/MnOx-GO materials have been thoroughly characterised via: thermo-gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), showing that the MnOx content in the support affects the growth of platinum nanoparticles.

Ex-situ electrochemical testing has been carried out to determine the material's suitability for use in DMFCs. The Pt/MnOx-GO produced shows promise in improving the tolerance of the platinum catalyst to methanol intermediates.

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EE12

Low Energy Intensive Electrochemical Reduction of Chromium contaminated wastewater and soil matrices

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Hexavalent chromium (Cr^{+6}), a human carcinogen is widely distributed heavy metal in surface, groundwater and soil matrices and is categorized one amongst the national priority pollutant (USEPA). The discharge of Cr^{+6} is prima facie from tannery, textile dyeing or electroplating industries. Though they exist in several oxidation states (from -2 to +6), the most potent forms are +3 (non toxic, insoluble) and +6 (highly toxic, soluble). Various *in-situ* and *ex-situ* treatment technologies such as physical, chemical and biological is well established for remediating Cr^{+6} contaminated wastewater and soil; but several of them have limitations such as generation of secondary wastes, high capital cost, low reliability and efficiency. Electrochemical technologies (ET) on the other hand, offer advantages of clean energy system operable at ambient conditions without the generation of any residual contamination. Though ET is widely accepted, the critical barrier that exists with this technology is the energy expended and the stability of the electrodes at high voltage applications.

Thus our present study investigated the reduction of Cr^{+6} at cathode by assessing the synergistic effect of a suitable electrolyte additive at the anode compartment. Several waste materials were explored to curtail the input energy to our system (from 10V to 5V), and amongst all alkaline urea (a nitrogenous waste) served the best to enhance the reduction of acidic Cr^{+6}. Furthermore, tailoring bare Ti substrate to nanoporous materials, a best performance of 97.7 % reduction of aqueous Cr^{+6} was obtained in 15 mins at 5V. As we were successful with aqueous systems, the study was further extrapolated to clayey soil matrices to mimic a natural environment. Hence, we could simultaneously achieve the dual benefit of remediating Cr contaminated wastewater and soil with oxidation of a nitrogenous waste as an anolyte fuel. The present study aimed in enhancing the energy and treatment efficiency of existing ET, and thus can find its application on field scale on par with several *in-situ* techniques.

Keywords: Chromium removal, electrochemical reduction, low energy intensive system.

EE13

Development of a self-cleaning wall-jet flow cell for continuous quality monitoring in drinking water distribution systems

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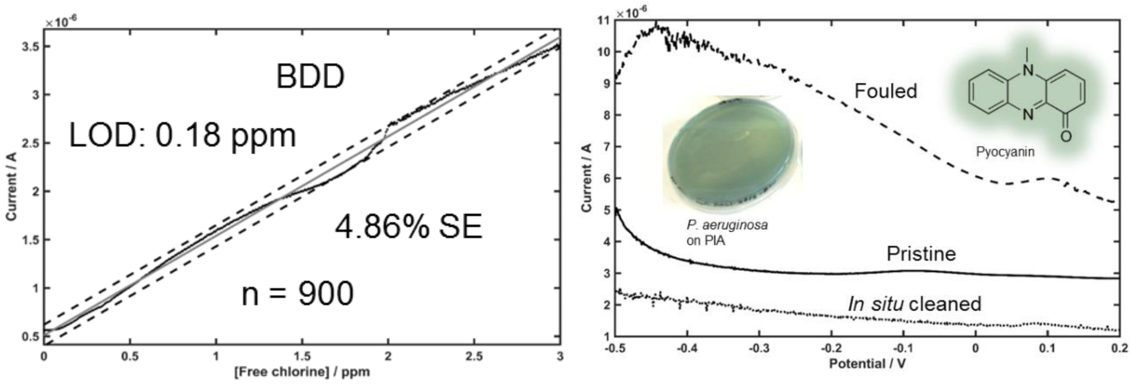
Long-term, continuous monitoring with electrochemical sensors in complex media is challenging due to the effects of biofouling. Drinking water biofilms reduce the performance of sensors by inhibiting mass transport to the sensor surface. Boron-doped diamond (BDD) electrodes are more resistant to biofouling than conventional electrodes, and remain inert at high potentials. These properties can be exploited to produce a sensor that can resist biofouling, and electrochemically remove biofilm on sensor surfaces, without disassembly or disconnection. Incorporating BDD into a wall-jet flow cell, a geometry that is highly scalable with minimal dead volume, has resulted in the production of prototype self-cleaning sensors which have been tested in both the laboratory and in a drinking water treatment works.

We have demonstrated that a BDD, wall-jet flow cell is both able to detect free chlorine accurately, with a standard error of 4.86%, and with a limit of detection which is less than the accepted minimum required concentration of 0.2 ppm. Additionally, the prototype sensor was capable of detecting the presence of a drinking water biofilm indicator organism, *P. aeruginosa*. The *in situ* cleaning process also compares very favourably to manual sensor surface cleaning methods. The next generation of prototype sensors based on this technology, and the results of laboratory and field trials, is currently under development. These sensors will be installed in drinking water systems to assess long-term performance of free chlorine detection in a challenging environmental medium.



Left: A calibration curve for the amperometric detection of free chlorine in solutions of sodium hypochlorite in deionised water using a prototype BDD sensor. Right: Detection by square wave voltammetry of electroactive Pyocyanin on biofouled sensors, produced by P. aeruginosa in drinking water biofilms, before and after both in situ cleaning and chemical cleaning.

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EE14

Desalination and Nanofiltration through Functionalised Laminar MoS_2 Membranes

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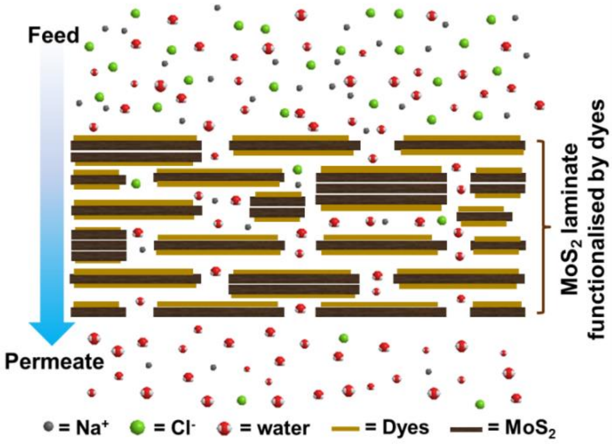
Laminar membranes consisting of two-dimensional materials are excellent candidates for efficient water filtration applications. The restacking of individual crystal layers leads to the formation of a network of nanocapillaries that can exhibit a molecular and ionic sieving effect, while allowing high water flux. This approach has been exemplified recently with graphene oxide but these membranes suffer from swelling when exposed to liquid water, leading to low salt rejection which is critical for desalination applications. Here we demonstrate that by producing laminar membranes of exfoliated molybdenum disulphide (MoS_2), followed by a simple chemical functionalisation step, we can efficiently filter out the ions commonly found in sea water, while maintaining excellent water flux. These functionalised MoS_2 membranes, which can be produced in a simple and scalable process, are shown to be highly stable in a range of liquid solvents, indicating that they are ideal for a variety of technologically important filtration applications.



NaCl Separation Mechanism

EE15

The influence of anions on the release of Ag(I) from silver nanoparticles (AgNPs).

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Silver nanoparticles (AgNPs) are widely being incorporated into products such as socks [1], sportswear and wound dressings [2] to serve as antibacterials. As these products are washed, the silver nanoparticles are leached and disperse in water where they may release Ag(I) ions. Ag(I) is very toxic to aquatic organisms [3] that make up the base of a series of food chains. In this study, AgNPs were prepared in the presence of various anions and in pure water in order to examine the effect of the medium on the release of Ag(I). The mean hydrodynamic diameters of AgNPs as measured by DLS ranged from 100 nm in the 10 mM chloride before dialysis to 890 nm in the 50 mM sample after dialysis. In general, the increase was due to aggregation. Individual particle sizes as measured by AFM decreased after dialysis; this suggests corrosion of the AgNPs. The release of Ag(I) was monitored by anodic stripping voltammetry at glassy carbon electrodes. We find that: (i) substantial (90 μM) Ag(I) is present in the initial preparation and (ii) the concentration of Ag(I) after 73 h dialysis was about 4 μM irrespective of the concentration of chloride present.

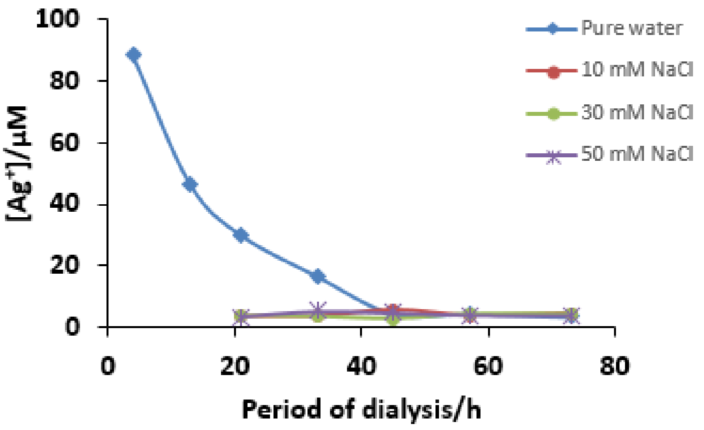

Figure 1. Variation of silver ion concentration in the dialysate with time of dialysis. Four different experiments are shown indicating the composition of the medium against which the sample was dialysed.

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Study of model carbon materials with graphitic-N sites for oxygen reduction reaction

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Functionalization of carbon materials, especially by nitrogen substitution, can be used to modulate the electronic properties, the morphology and the surface chemistry of carbon materials. Nitrogen-doped carbons materials have showed catalytic activity for the oxygen reduction reaction (ORR), resulting in a potential alternative for the substitution of precious metal catalysts in energy applications, such as metal-air batteries and fuel cells [1, 2]. Nitrogenated carbons typically contain a mix of nitrogen species thus making it difficult to relate an electrochemical response to individual active sites. Pyridinic- and graphitic-N have been attributed as the nitrogen species responsible of the catalytic activity for the ORR [3], however, model electrodes with exclusively pyridinic-N or exclusively graphitic-N remain elusive so far.

Herein, we present the study of amorphous nitrogenated carbon films with only graphitic nitrogen. We report the synthesis, characterization and electrochemical testing of this model nitrogenated carbon materials. Amorphous nitrogenated carbon films were prepared using a combination of physical deposition and thermally-driven reactions yielding nitrogenated carbon materials with smooth topography, excellent electrical contact and homogeneous graphitic-N site presentation. These materials were used to study the effect of these specific sites on the ORR activity. Graphitic-N sites were found to improve the onset potential with respect to the pristine materials. Also, a mixed $2e^-/4e^-$ mechanism was evident from rotating ring disk electrode (RRDE) measurements. Despite the activity observed, graphitic-N sites were found to undergo extremely fast degradation under ORR conditions. We will discuss in-situ electrochemical and ex-situ spectroscopic methods that probe the degradation process.

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N-Doped Carbon Aerogel Supported Cobalt Catalysts by Supercritical Deposition for Oxygen Reduction Reaction

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Hydrogen fuel cells are promising devices for electricity generation due their higher efficiencies and lower emissions than internal combustion engines. The oxygen reduction reaction (ORR) which occurs at the cathode of a PEM fuel cell has sluggish kinetics and necessitates the usage of expensive catalysts at high loadings for satisfactory fuel cell performance. Although carbon supported Pt catalysts are considered as the best ORR catalysts, high cost of Pt severely hinders the widespread commercialization of fuel cells. To overcome this obstacle, development of low-Pt, Pt-free and even metal free carbon based nanomaterials for ORR has been attracting increased attention. Among these, transition metal containing (usually Co, Fe) N-doped carbon materials are the most promising candidates. N-doped carbon aerogels (CAs) are attractive alternatives to conventional N-doped carbons in preparation of non-noble metal based ORR catalysts due to their unique properties such as high surface are, high porosity, high electrical conductivity and tunable morphological architecture. Conventional techniques to prepare supported metal catalysts are not quite suitable for aerogels because of the high surface tension of the liquids which can cause the collapse of the nano-sized pores of the aerogels. An alternative route for the preparation of aerogel supported metal nanoparticles is supercritical deposition (SCD). The use of $scCO_2$ for the preparation of aerogel catalysts is advantageous since the low surface tension prevents the collapse of nano-sized pores. SCD consists of the dissolution of a metal complex in a supercritical fluid with subsequent adsorption on the interior surface of porous support followed by the conversion of the metal complex to its metal form. In this study, we prepared highly active N-doped CA supported Co catalysts using SCD combined with ammonia treatment. Firstly, resorcinol formaldehyde aerogels were contacted with a solution of cobalt acetylacetonate ($Co(acac)_3$) in $scCO_2$ at 20 MPa and 353 K. The cobalt precursor was found to adsorb and react on the surface of the organic aerogel. Subsequently, the resulting sample was subjected to pyrolysis performed under NH_3 flow resulting in N-doped CA supported Co catalysts. The effects of cobalt loading and pyrolysis temperatures ranging from 700 °C to 900 °C on the properties of the electrocatalysts were investigated. Nitrogen content decreased with increasing pyrolysis temperature and different types of C-N sites, as well as Co-N and metallic Co were detected on the samples by XPS. The electrochemical characterization of the catalysts was performed using cyclic voltammetry (CV) and Rotating Disk Electrode (RDE) measurements. The electrocatalyst pyrolyzed at 800 °C had the highest ORR activity which was 11.03 $mA/mg_{catalyst}$ as determined from the current density at 0.8 V vs RHE in 0.1 M KOH solution. To the best of our knowledge, this is the highest value reported in the literature so far. It also had an onset potential of 1.01 V vs RHE where the cathodic current reached 0.1 mA/cm^2 compared to 1.04 V for Pt/CA.

EE18

Graphene doped with boron, nitrogen, phosphorus and sulfur as metal-free electrocatalysts for the oxygen reduction

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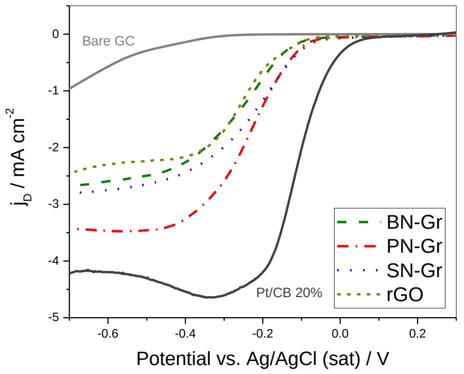
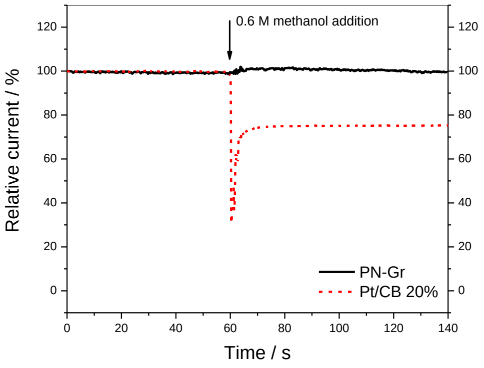
Doping graphene with heteroatoms, such as B, N, P or S, can tailor the properties of the 2D structure of graphene[1] and increase the catalytic activity towards the oxygen reduction reaction (ORR) with respect to pristine graphene.[2] Here we present a new study in which we compare the performance of single, dual, ternary and quaternary-doped graphene electrocatalysts in terms of physical characterisation and electrochemical performance. The doping-precursor agents are boric acid, melamine, orto-phosphoric acid and benzyl disulfide. These are mixed with a commercial graphene oxide (GO) and subjected to a thermal treatment at 900 °C during 2 hours under a protective N_2 atmosphere. The resulting catalysts are physically characterised using HR-TEM, XRD, Raman and XPS, while the electrochemical ORR performance is evaluated by CV measurements and the number of electrons transferred during the reaction are obtained *via* direct determination of peroxide intermediate by rotating-ring disk electrode measurements. The results demonstrate that the single, ternary and quaternary-doped catalysts do not improve significantly the performance with respect to thermally reduced GO without doping. Nevertheless, dual-doped graphene shows a significant improvement with respect to the other catalysts, especially in the case of PN-Gr (Fig. left). The better performance of the dual-doped graphene catalysts is attributed to a synergistic effect between the two different elements incorporated into the active 2D graphene structure.[3] In addition, comparative tests of methanol tolerance conclude that the doped-graphene catalysts are not affected by the presence of methanol, whereas a commercial Pt/C catalyst suffers a 25% of performance decrease in presence of a 0.6 M methanol concentration (Fig. right).





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EE19

Elucidating the Mechanism of High-Rate and High-capacity Lithium-ion Intercalation in Bulk Complex Oxides

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Energy storage materials with both high capacity and high charge/discharge rate enable applications that require long life, high power, and rapid recharge. Electric double-layer capacitors offer high power and battery electrodes offer relatively high capacity but the combined properties require advanced materials. While nanostructures have dominated this emerging field, there are well-known issues regarding cost, stability, scalability, and safety of nanoparticles for battery applications. Recently, we have demonstrated and characterised complex oxide structures from facile solid-state synthetic methods with promising rate, capacity, and stability for reversible lithium intercalation.[1] Dense particles with high packing density of non-nanostructured T-Nb_2O_5 were shown to intercalate lithium at high rates with capacity performance and retention similar to the best nanostructured analogues; a mechanistic investigation was undertaken to explain this novel behaviour.

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EE20

Effect of different ionomers on the performance of alkaline exchange membrane (AEM) fuel cells

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The current AEM fuel cells can be operated only up to 50 °C which limits the performance of the system and requires the use of expensive cooling system and balance of plant. However in order to commercialize the system and operate up to 70 °C at par with proton exchange membrane (PEM) fuel cells, the membranes and ionomers which are stable at higher temperatures needs to be developed. The cost of the systems can be further reduced in comparison to PEM fuel cells by the use of non-noble metal catalyst. This presentation will highlight the results obtained using different ionomers i.e. PVBC-TMA (polyvinyl benzyl chloride - trimethyl amine), SEBS (Styrene-Ethylene Butylene-Styrene) and commercial ionomer with an aim to increase the performance and operating temperature of the fuel cell to 70 °C.

EE21

The Relationship Between Synthesis, Formulation and Performance of Low Cost Non Platinum PEM Fuel Cell Catalysts

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A collaborative research project between Amalyst and The University of Birmingham is seeking to evaluate synthesis and formulation alternatives to Amalyst's current process for making platinum replacement fuel cell catalysts.

Although the sluggish cathode catalyst reaction attracts far more research, there is still scope to improve the much faster hydrogen oxidation reaction at the anode. By moving away from pure Pt catalysts in PEM fuel cells, not only can cost savings be made but CO poisoning can be reduced as well as possible augmented activity and stability.

In addition to characterising synthesised catalysts for their polarisation performance, accelerated stress testing is being used as a proxy for in-service transients that are often the cause of significant damage to Pt based materials. Results are presented to show current progress in this collaborative study.

Effects of Sn anode-infiltration on direct-biogas SOFC's electrochemical performance

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This work presents a novel method of Sn-infiltration on SOFC anodes for direct-biogas operation and the effects of Sn-infiltration on the SOFCs' electrochemical performance. Operating an SOFC directly with hydrocarbon fuel poses risks of low efficiency and formation of deleterious carbon. This work shows that Sn infiltration on NiYSZ anode improves the SOFC's efficiency with very low formation of carbon. Sn-infiltrated NiYSZ SOFCs containing varied amounts of Sn were manufactured. Operating in simulated biogas of 1:2 volume ratio of CO_2:CH_4, these SOFCs were tested for their electrochemical performance and quantity of deposited carbon. At 750 ^{o}C with H_2 as fuel, non-infiltrated NiYSZ SOFCs were able to generate 350 mA cm^{-2} current at 0.7 V; however, when simulated biogas was introduced, current dropped significantly to 90-200 mA cm^{-2}. On the contrary, a series of Sn-infiltrated cells under the same operating conditions performed well both in H_2 and biogas fuels producing 310 to 450 mA cm^{-2} depending on the Sn content. The cells showed stable electrochemical performance over 150 hours of operation both in H_2 and biogas without significant carbon formation. Significant supporting data were generated from mass and electrochemical impedance spectra. Mass spectra of the fuel cell outlet gas show Sn-infiltrated SOFCs produced much more H_2 and CO than the non-infiltrated SOFCs did. Impedance spectra show much lower polarisation resistance observed on Sn-infiltrated cells than those observed on non-infiltrated ones. Several possible mechanisms are proposed to explain the phenomena. These include (i) Sn forms surface Sn-Ni alloy on NiYSZ anode which alters Ni catalytic activity [1], (ii) Sn breaks Ni atoms ensemble in the surface structure associated with carbon formation [1,2] (iii) Sn changes the Ni surface electronic structure associated with critical shifts in the Ni d-band electronic centre which in turns change Ni chemical activities and catalytic performance [2]. More work is required to further evaluate the electrochemical performance in relation to the anode surface and electronic characteristics. So far the results of this work are promising in that Sn-infiltrated NiYSZ-based SOFC can be operated on simulated direct-biogas under dry reforming mode with high electrochemical performance and low carbon deposition.

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EEK2

Keynote: Kylie Vincent

Hydrogen energy in biology: learning from nature’s electrocatalysts

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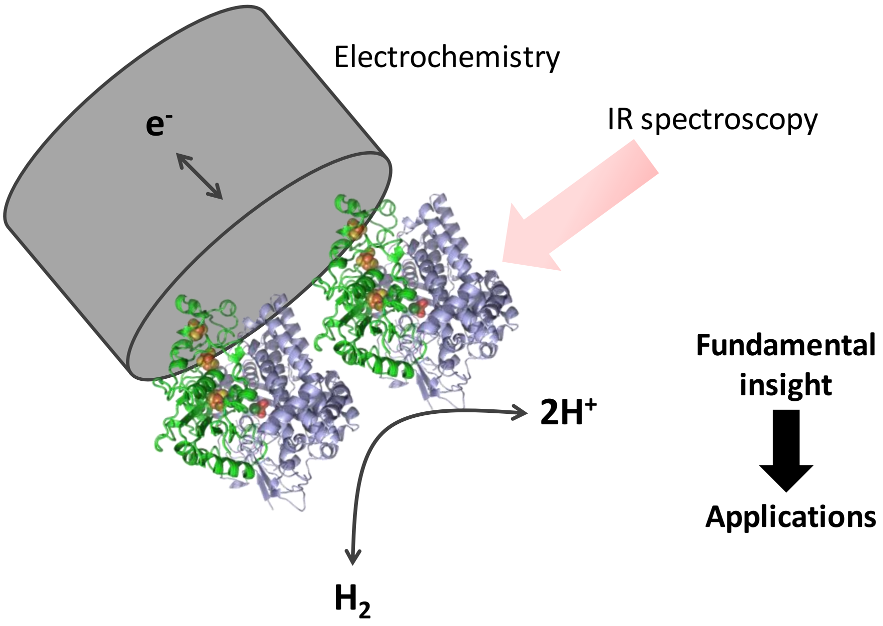
Hydrogen is widely used in the microbial world as an energy source or sink, and nature has a specially tailored array of catalysts (enzymes) for redox reactions to manage hydrogen utilisation, storage and production. In our research, we are interested in studying the mechanisms of these enzymes to see how we might learn from nature’s finely tuned catalysts. To do this, we separate individual enzymes from their biological redox circuits and interface them with electrodes. In this way, we interpret the current response as the enzyme engages in electrocatalysis on an electrode, alongside spectral information from in situ infrared spectroscopy probing the enzyme at the electrode interface.[1] What we have learnt about hydrogen in biology has inspired development of a technology for hydrogen-driven synthesis of fine chemicals, relying on cascades of redox enzymes ‘plugged in’ to conductive carbon beads.[2] This talk will cover some of our fundamental studies of hydrogenases as electrocatalysts, through to development of applications in clean chemical synthesis.



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Living electrodes: using microbes as electrocatalysts for a sustainable future.

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A class of microbes, known as ‘electrogens’, are capable of directly exchanging electrons with an adequately polarised solid electrode (1). Naturally, such microbes, which are mainly anaerobic, use electron acceptors / donators, such as iron oxide, present in their environment as oxidising / reducing equivalents for respiration. Bio-corrosion is a common example of this process. In the last twenty years intensive research has focused of using this class of microbes as catalysts for electrochemical reactions. *Geobacter* and *Shewanella* species are two of the most widely studied ‘electrogenic’ bacteria which form thick electron conducting biofilms on electrodes. Such biofilms oxidise complex organic molecules down to CO2 and transfer liberated electrons to the electrode leading to applications in wastewater treatment and bioremediation (2). Although the ability of these biofilms to conduct electrons is well established, the mechanism by which electrons are transferred from within the cell cytoplasm, across a double membrane, through the biofilm, and to the solid electrode is still unclear. In this presentation, we present insights into this mechanism using a combination of voltammetric and proteomic analysis of biofilms (3,4). We also present how ‘electrogenic’ biofilms immobilised at electrodes may be utilised in emerging electrochemical carbon capture and utilisation technologies.

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EE24

Biopower and biosensors: aspects of enzymatic electrodes

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Applications of biomedical devices as implantable and semi-implantable systems such as sensors, valves and pumps is of increased importance. These devices rely heavily on battery power which are reliant on re-charging or sufficient reagents contained within. An alternative strategy is fuel cell technology, using readily available in-vivo substrates (glucose and oxygen) as fuel and oxidant. This is difficult to achieve using chemical catalysts as they are non-selective and operate under harsh conditions (pH and temperature). Enzymes as catalysts offer an alternative route towards powering of such devices. Enzymatic active sites are selective and operate under mild conditions thus offering a potential solution for semi-implantable devices.
Here we report on co-immobilisation of osmium based redox complexes and support polymers with specific enzymes on electrode surfaces. These enzymes are capable of substrate catalysis (glucose oxidation and oxygen reduction) [1]. Tailoring of the osmium redox potential to the enzyme active site improves electron transfer to electrode surface. Combining enzyme and redox centre with nano supports such as carbon nanotubes achieves higher current densities and greater power outputs. This is achieved through refinement of the immobilisation procedures as well as optimisation of the enzyme electrode components.

Our research compares the electropolymerisation of L-dopa with the dropcoating of polymer supports as a route towards immobilisation. Current densities of 0.25 mA cm-2 have been achieved to date. A design of experiment approach to component optimisation has been used to improve anodic current density using glucose dehydrogenase. Previous work improved current density by 32% over traditional approaches [2].

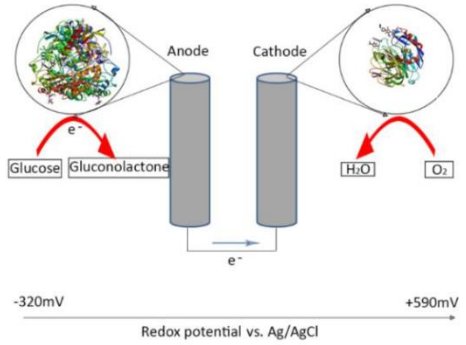

Figure 1: Schematic representation showing the principle of an enzymatic fuel cell with the immobilisation of a glucose oxidising enzyme on the anode and an oxygen reducing enzyme on the cathode.

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Solution-Processed Cascaded-Junction Quantum Dot Solar Cells

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The infinitesimal semiconducting nanocrystals, which are called 'quantum dot' (QD) have been shining the light to the next generation solar cells. The advantage of employing the photoactive semiconductor in the state of QD is due to the band gap (ε_{gap}) tuning accessibility and solution-processed reproducibility. Due to the size-dependent quantum confinement effect, the QD ε_{gap} can be easily adjusted by tuning the size. Lead sulphide (PbS) QDs is considered as one of the most promising candidates for QDs solar cell due to wide ε_{gap} adjustability from NIR to visible emission spectrum.[1] PbS QDs have been deployed into different types of solar cell system, such as DSSC type solar cell, Schottky junction solar cells, p-n junction solar cells and organic dye hybrids solar cells. PbS QDs solar cell (QDSC) has been improved their light harvest efficiency dramatically in recently years. Up to now, the lab scale cell efficiency has been achieved by around 10%. Recently, we elucidate an efficient and reliable synthesis protocol for fabricating high-quality PbS QDs. Through adjusting the precursor concentration systematically, in a fixed reaction time, a wide range of different sizes of colloidal PbS QDs is produced with a narrow size distribution and high reproducibility.[2] Typically, in QDSC, the PbS QD films are ligand exchanged from pristine oleic acid to tetrabutylammonium iodide or 1, 2-ethanedithiol for efficient charge depletions. ZnO nanoparticles which spin coated on top of ITO play a role as electron depletion layer and also forming a quasi 'p-n' junction with the QDs. In the end, gold films are deposited by thermal evaporator on the QD films as an anode electrode. Based this structure, we have achieved a lab-scale device power conversion efficiency (PCE) above 8%. In the end, based on the understanding of optical-electrical properties of as-prepared PbS QDs and QDSCs, three distinct sizes PbS QDs are selected and tentatively fabricated into Cascaded-Junction solar cells. The elaborately designed devices show impressive high PCE (9.05%) and short circuit current density (32.51mAcm^{-2}) compared with previously reported devices.[2]

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EE26

Photo-Induced Electron Transfer at Porphyrin Sensitised Water-Oil Interfaces for Solar Energy Conversion

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A photoactive assembly of photosensitiser aggregates at an electrified immiscible water-oil interface, often termed the *i*nterface between *t*wo *i*mmiscible *e*lectrolyte *s*olutions (ITIES), may achieve **incident-photon-to-current conversion without using solid electrodes to effect charge separation** by a process known as photo-induced heterogeneous electron transfer [1], as detailed in ***Fig. 1***.

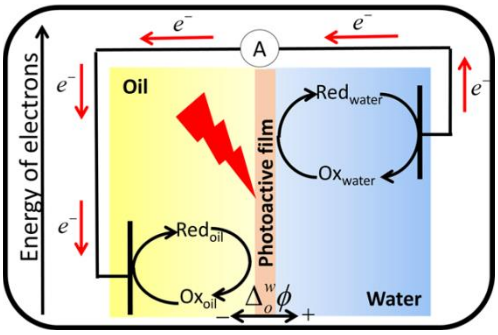

Fig. 1: *Scheme illustrating the concept that photoactive films trap solar energy, generating high-energy electrons. In theory this allows electron transfer across the interface between redox couples that thermodynamically are incapable of heterogeneous electron transfer in the dark due to their respective redox potentials in each phase.*

The basic design of all solar energy conversion devices necessitates **the efficient harvesting of light energy combined with an embedded asymmetry in the charge separation process**. The ITIES possess attributes to fulfil this remit including: (i) their ease of functionalisation with light harvesting photosensitizer molecules; and (ii) the separation of photoproducts on either side of the interface by local hydrophobicity gradients beneficially limiting unwanted recombination pathways to improve charge separation.

In this presentation, the dynamics of the different charge transfer reactions (rates of electron transfer, photoproduct separation; *etc*.) during the photo-induced heterogeneous electron transfer process at an ITIES functionalized with interfacial supramolecular assemblies of zinc tetrakis(4-carboxyphenyl) porphyrin (ZnTPPC) were studied by **photocurrent transient** and **intensity modulated photoelectron spectroscopy (IMPS)** measurements [2-3], commonly applied to DSSCs. These photoelectrochemical experiments allow us to identify the precise experimental conditions required (in terms of interfacial aggregate surface coverage, aqueous phase pH, magnitude of the interfacial electrical polarization, etc.) to **maximise the photoconversion efficiencies possible at the ITIES** (currently unsatisfactorily < 1 %).

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EE27

Tuning the size and shape of novel nanoscale metal oxide photocatalysts using the cathodic corrosion method

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Growing energetic demands, in conjunction with the ever-growing consensus surrounding the increasing adverse effects of climate change and global warming, have led to much research dedication to the development of renewable energy technologies. A hydrogen economy has long been sought after, but with most the earth's hydrogen stored in water and the main source of hydrogen production involving the burning of fossil fuels, a widely applicable alternative is required.

Transition metal oxide semiconductors were first shown to be active towards hydrogen evolution from water under UV-irradiation by Fujishima and Honda.[1] Nanoscale photocatalysts are desired to overcome the limitations surrounding the low natural abundance of solar UV light by modifying the semiconductor band gaps to harness more of the visible spectrum and minimize ion carrier migration distances. Current state-of-the-art photocatalysts include TiO_2, $FeTiO_3$, H_2WO_4, $BiVO_4$ and their metal-doped analogues.

Cathodic corrosion[2–4] is a powerful tool for the electrochemical synthesis of nanomaterials with enhanced electrochemical properties. Here we demonstrate that the particle size and shape of mixed transition metal oxide semiconductor nanoparticles can be tuned by changing the synthesis conditions. This has resulted in an effective way to change the photocatalytic properties of the nanomaterials. The structure-reactivity relationship for the photocatalytic water oxidation will be presented.

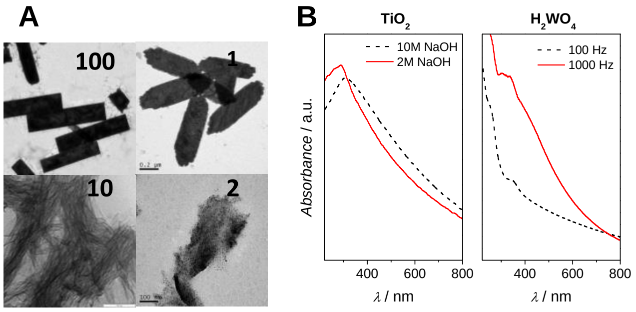

Figure 1. (A) TEM images of H_2WO_4 (top) and TiO_2 (bottom) nanoparticles synthesized by cathodic corrosion using varying conditions as indicated in the figure; frequency of the square wave form and concentrations of NaOH (B) UV-vis absorption spectrum of the H_2WO_4 and TiO_2 nanoparticles.

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Effect of water on Cu electrodeposition from a water-containing deep eutectic solvent

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Ionic Liquids (ILs) have been proposed as alternatives electrolytes for metal electrodeposition. Deep Eutectic Solvents (DESs) are a novel type of ILs tolerant to water. Moreover, DESs formulated from quaternary ammonium salts and hydrogen bond donors are promising electrolytes since they are water tolerant and they are available at a reasonable cost. Although DESs are hygroscopic and absorb water from the atmosphere, earlier studies to plate Cu have concentrated on low-water containing DESs (<0.5 wt% H_2O). However, for DESs to become exploitable, metal deposition from water-containing electrolytes requires to be investigated.

In this work, we have endeavoured to establish a quantitative correlation that might explain the effect of water content on the electrolyte and on Cu deposition process. The intrinsic concentration of water in the electrolyte was measured using Karl Fischer titration. Thereafter, to quantify the electrolyte uptake of water a time-dependant test was conducted. After adding various concentration of water to the electrolyte determined from the time-dependant experiment (3 to 15 wt%), the influence of water content was examined with polarisation experiments collected using a rotating disc electrode. Finally, Cu deposition was carried on steel substrata from electrolytes containing different weight percentages of water. Cu deposits were characterised with Scanning Electron Microscopy (SEM) (Figure 1) and Energy Dispersive X-ray Spectroscopy (EDS).

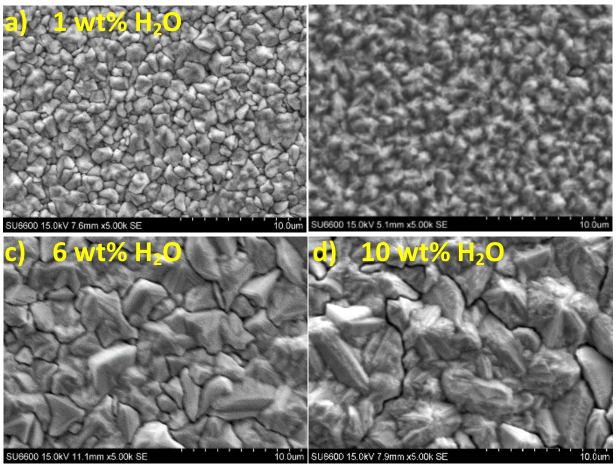

Figure 1. Micrographs of Cu deposits electroplated using an inert anode at 25 °C, rotation speed of 700 rpm from water-containing electrolytes (a) 1 wt%, (b) 3wt%, (c) 6wt% and (d) 10 wt% total H_2O.

Different water contents in the electrolyte reduced the viscosity of the liquid which promotes the diffusivity of Cu^{2+} ions in the liquid. As a result, the limiting currents of the process increased. Higher water content changed the morphology of Cu films. Even at low water content (~3 wt%), the current distribution on the deposits is non-uniform. Furthermore, adding H_2O worsens the already uneven current distribution leading to less uniform Cu deposits.

EE29

A New Procedure for the Template Synthesis of Metal Nanowires

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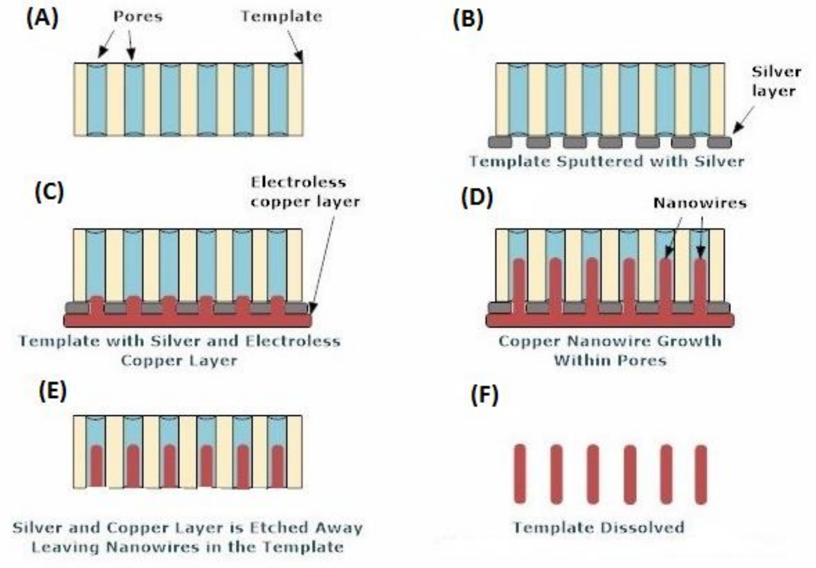
Metal nanowires fabricated by electrochemical template deposition have been investigated in a wide variety of applications for energy generation[1,2]. This work describes a new procedure for the fabrication of metal nanowires by template assisted electrodeposition. Porous polycarbonate membranes were chosen as templates, (A). A thin silver sputtered film, typically < 15 nm in thickness, was deposited on one side of the template (B). The layer was used to catalyse electroless copper deposition and a copper layer was grown to a thickness of 500 nm in less than 10 mins (C). The deposited layer ensured the pores on one side were completely covered and the electrode layer had a high electrical conductivity for good uniform growth of the nanowires by electroplating (D). Furthermore, the copper layer could be easily removed, using a chemical etchant (E), to aid the release of the nanowires from the template (F). To demonstrate the process, copper nanowires were prepared by controlled potential deposition and characterised by SEM and TEM. This new procedure has the potential to be applied to the preparation of a wide range of metallic nanostructures over a wide range of scale; it avoids the need for an extended vacuum deposition step and has the advantage of using inexpensive metals in a combined vacuum / wet chemical process to form the important electrode layer for nanowire growth.



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EE30

Copper turmeric electrochemically deposited composite coatings

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Composite coatings can be used to change the surface properties of a material whilst leaving the underlying material unchanged. As such they have been used in corrosion resistance, wear resistance, thermal resistance and even antibacterial applications. Composite coatings can be produced by several methods including electrochemical deposition [1-8]. Electrochemical deposition factors such as current density, type of particle (also concentration), and bath composition can all effect the morphology and characteristics of the coating, making it of great academic interest [8]. Unfortunately, composite materials are notoriously difficult to recycle and particles that are used in them are often expensive requiring energy intensive production, making them unsustainable in the long term [9]. The Aim of this research was to produce composite coatings by electrochemical deposition, using a more sustainable source of particles that had not previously been electrochemically deposited.

Turmeric is a common kitchen spice which is often used in Indian cuisine; it has been shown to have strong antibacterial activity [10]. A known amount of turmeric was placed in an acid copper electrolyte with 10 ml/l of Tween 20, and deposited onto a substrate. The concentration of turmeric and the current density used to deposit it were varied. The morphology of the coatings was then examined and the coatings further characterised in terms of hardness, contact angle and antibacterial activity.

Results have shown that the addition of just a small amount of turmeric to the plating bath had a significant effect on the morphology of the deposit and increased both the hardness and the contact angle of the composite coating. Although the composite coating did show strong antibacterial activity, pure copper showed stronger antibacterial activity.

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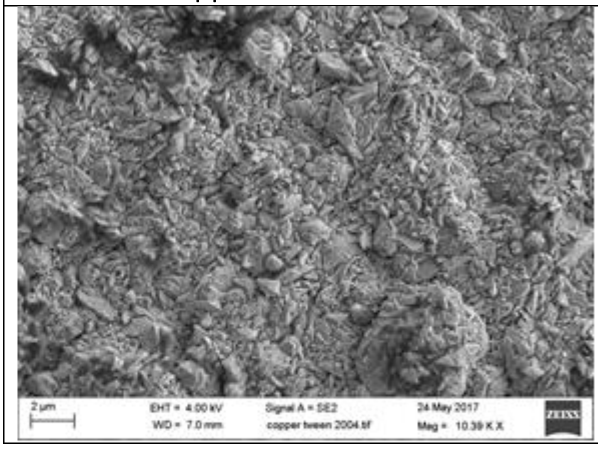
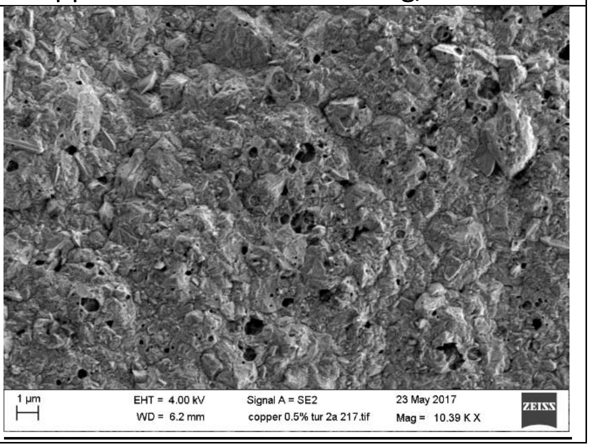
<tr><th>Copper with Tween 20</th><th>Copper with Tween 20 and 5 g/l turmeric</th></tr>
<tr><td>
</td><td>
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Sensors & Analytical

Oral Abstracts

SA1

Sensor using Molecular Dynamics of Drugs in Carbon Nanotubes Under External Uniform Electric Field

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We present an analysis on molecular dynamics between hallucinogenic drugs molecules (cocaine, heroin, morphine, etc) interacting with one carbon nanotube section at low initial-temperature of simulation, corresponding to 10−3 K, and under uniform electric field, in order to verify the performance of this system like as drugs sensor. During simulations, each drug was relaxed for 50 *ps* inside and outside of carbon nanotube, describing each possible arrangement for the capture of each drug, and an constant electric field was applied over the system, longitudinally to the carbon nanotube length, promoting an evanescent effect, able to trap each drug orbiting the carbon nanotube. Simulations for electric fields intensities in a range of 10^{-6} au up to 10^{-1} a.u. were performed, and mean orbit radius are estimated, as well as, some physical quantities of the system. The quantities calculated were: kinetic energy, potential energy, total energy and temperature *in situ*, among molar entropy variation. Our results indicates that a combination of uniform electric field and van der Walls interactions derivatives of carbon nanotube is enough to create an evanescent field with attractive potential, showing it system as a good drugs sensor.

Keywords: Drugs, Carbon Nanotube, Electric Field, Evanescence Effect, Molecular Dynamics.

SA2

Electrochemical stability of thiols and disulfides assembled on gold in physiological medium

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The importance of thiol-modified gold surfaces has been continuously investigated by the development of sensors[1], immobilised catalysts[2] and drug delivery strategies[3], with a substantial effort being focused on biomedical applications.

Electrochemistry has been widely applied in the field of sensors because its high sensitivity[4] and recently the electrochemically-controlled delivery of drugs have also attracted the attention of researchers around the globe.[5] Therefore, electrochemical desorption of thiols is of interest since it determines the operational limits for the reliable sensor performance. On the other hand, it provides the conditions of a platform for a systematic drug delivery. While the electrochemical desorption of thiols from gold surfaces has been mainly studied in alkaline media using a range of techniques, only a few attempts have been conducted in neutral medium; and none of them in an electrolyte that mimics physiological conditions.[6]

In this work, we explore the electrochemical stability of thiol-modified electrodes in physiological medium. First, we investigate the stability of 4 different thiols: 3-mercaptopropionic acid, 2-mercaptoethanol, 1,4-dithiothreitol and thioctic acid on polycrystalline bead-electrodes using cyclic voltammetry (CV) and newly introduced progressive potential-step chronoamperometry. Subsequently, we study the impact of the crystalline structure of gold on the electrochemical desorption of thiols.

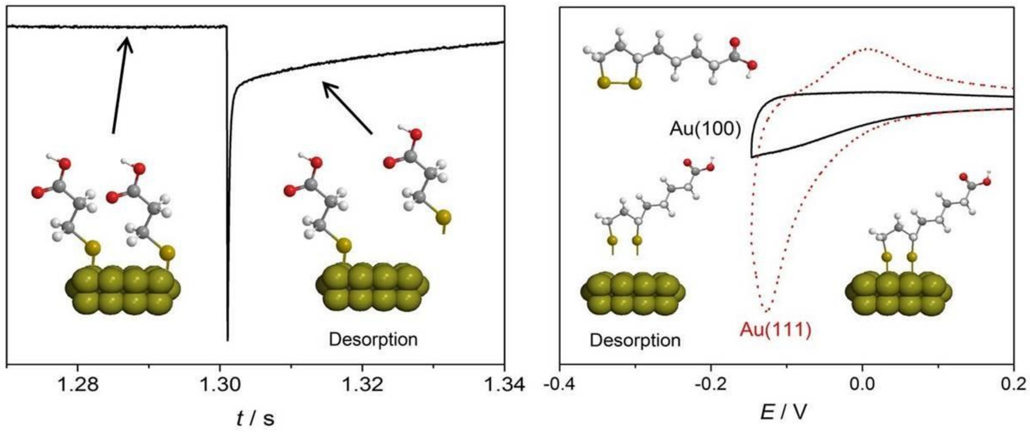

Figure 1: Chronoamperometric profile showing desorption of 2-mercaptoethanol from polycrystalline gold electrode (left panel). Voltammetric profiles showing desorption of thioctic acid from Au (111) (dotted line) and Au (100) (solid line) (right panel).

Our results indicate that SAMs of disulfides on gold electrodes are more stable than SAMs formed by thiols. We also report on the superior stability of the SAM on the Au(100) in comparison with the monolayers adsorbed on the Au(111) electrode.

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SA3

Electrochemical Detection of DNA Methylation: A possible method for detecting changes to health

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An increase in DNA methylation has been shown to correlate with around 80% of all cancers, where a large proportion of carcinogenic gene silencing is the result of altered levels of methylation at cytosine residues [1]. In addition to cancer, aberrant DNA methylation has an emerging role to play in many age-related diseases, including cardiovascular disease (CVD), Alzheimer's disease, osteoporosis/osteoarthritis and ageing [2]. A number of electrochemical methods have been developed to detect the relative amounts of methylation in real and synthetic DNA/genes. Of particular interest is the elegant and low cost eMethylsorb technique, which exploits the strong affinity of adenine groups to gold [3]. In this technique, a gene of specific interest is selectively extracted from a patient's DNA, multiplied and then treated via a process that produces adenine enriched samples. The higher the methylation level of the gene, the lower the amount of adenine in the test sample. A gold electrode is then exposed to the sample and the relative amount of DNA/gene adsorption, which is indicative of the relative amount of methylation, is determined via a voltammetric method that monitors the deactivation of the electrode surface.

This work reports a thorough investigation of the key parameters in the eMethylsorb technique. Using a methylated and the analogous unmethylated synthetic gene sequence, differential pulse voltammetry, cyclic voltammetry and electrochemical impedance spectroscopy are compared to find the optimum electrochemical technique to assess the different levels of electrode deactivation. The effect of solution flow during the adsorption stage is shown to be of critical importance in producing repeatable results with significant differences between methylated and unmethylated DNA samples. Once optimised, the improved method is used to measure methylation levels in real DNA samples. The results offer a considerable improvement on the repeatability of the eMethylsorb technique and demonstrate the potential value of this approach as a complimentary tool for the early diagnosis of cancer and age-related diseases.

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Fabricating Cellular Bioelectronic Systems by Combining Inkjet Printing with Bipolar Electrochemistry

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In order to seamlessly integrate electronics with cells there is a pressing need to develop new methods that advance our ability to construct 3D multi-material conductive systems. Moreover, to ease the transition of building cellular electronic systems an in-situ remote approach to merging electrical components with cells is desirable. We present a method that combines inkjet printing with bipolar electrochemistry to fabricate conductive wires of silver with key diameters of up to 200 nm. Wires were formed by self-assembly of silver nanoparticles, generated by applying a potential difference to inkjet printed electrodes. Conductive wires were grown via bipolar electrochemistry in a 3D coordinated manner to connect electrical components and importantly, forming such connections between elements in different z-planes. We then use the same approach to grow and interface conductive conduits in-situ with mammalian cells. This subsequently allowed for sensing of cell redox events. This technological approach provides a platform to fabricate and advance the development of 3D multifunctional bioelectronic systems.[2]

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SA5

Electrochemical characterisation and regeneration of sulfur poisoned Pt catalysts

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Catalytic hydrogenation processes are widely employed in chemical industry for the synthesis of organic compounds. Typically, the catalysts in these processes consist of Pt and Pt-group nanoparticles supported on carbon.1,2 Additionally, sulfuric acid is frequently added, for operational reasons, to protonate the products and prevent product binding or over-reactions. However, it is found that the presence of sulfuric acid may lead to a poisoning of Pt catalysts,1,3 and it is unclear what species causes this effect, *i.e.* is it due to the presence of bisulfate, or due to sulfide owing to sulfuric acid reduction? Little is known about the sulfate/sulfide redox chemistry at Pt surfaces, nor is there a diagnostic measurement to identify and quantify the process.

In this work, we have studied the electro-oxidation of sulfur-containing species adsorbed at various types of Pt electrodes, namely polycrystalline, single-crystal and Pt nanoparticles on a glassy carbon support. A number of sulfur compounds were considered, with the oxidation states of sulfur ranging from 2- to 6+. We demonstrate that almost all sulfur-containing compounds investigated lead to poisoning of the Pt surfaces. Furthermore, we show that the poisoned Pt electrodes can be regenerated by repeated CV cycling, in the range of 0.05 ⍰ 1.2 V (versus palladium-hydrogen electrode). Importantly, the recovery kinetics are strongly related to the initial sulfur sources. Additionally, single-crystal studies allow decoupling the effect of steps and terraces. Finally, XPS analysis is also employed, to elucidate the chemical state of sulfur species during recovery process.

This approach introduces electrochemical processing for the regeneration of catalysts, and we believe it will offer new ways for understanding and discover new catalysts in hydrogenation reactions.

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SAK1

Keynote: Darren Walsh

How Ionic are Ionic Liquids? Measuring the Ionicity of Protic Ionic Liquids using Electroanalytical Chemistry

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Due to their wide electrochemical windows, thermal stabilities, and inherent conductivities, room temperature ionic liquids (RTILs, salts that are liquid at room temperature) are being proposed for use in devices such as electrochemical sensors, batteries, fuel cells, and supercapacitors. Of particular importance when designing and synthesising RTILs for such applications is determining their degree of "ionicity." Some RTILs exhibit relatively high vapour pressures, poor thermal stabilities, and low conductivities, due to the presence of neutral molecules and stable ion pairs and clusters in the liquids. These effects are particularly acute for protic ionic liquids (PILs), which can comprise a mixture of the salt and parent neutral acid and base, depending on the extent of proton transfer during synthesis. The formation of non-stoichiometric mixtures of acids and bases in PILs also yields neutral parent molecules. The only methods available for determining the degree of ionicity of PILs are indirect methods, such as conductimetry. However, conductimetry cannot differentiate between the presence of neutral molecules, and neutral ion pairs or clusters, none of which contribute to a PIL's conductivity.

In this presentation, I will show that residual parent species can be quantified in PILs *in situ* using ultramicroelectrode voltammetry and scanning electrochemical microscopy. Electroanalysis shows that PILs based on acids such as triflic acid and trifluoroacetic acid, when synthesised using common literature methods, can contain significant concentrations of acids (up to 100s of mM), due to loss of thermally-unstable bases from the liquids during synthesis. The excess acids are extremely stable in PILs, even at 10^{-7} mbar. I will also describe a method for analysing the concentration of bases in PILs, which is based on the electrochemical behaviour of H_2 in PILs. Finally, I will discuss some of the electrochemical effects of residual precursors on the electrochemical reactivity of PILs. For example, Figure 1 shows that the onset potential, E_{onset}, for O_2 electroreduction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) in diethylmethylammonium triflate shifts positive by almost 1 V when the PIL contains 0.1 M of the parent acid, demonstrating that the acid plays a key role during O_2 electroreduction in the liquid.

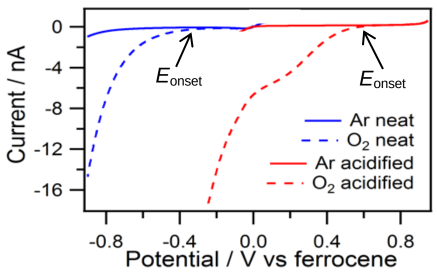

Figure 1. Voltammograms recorded in diethylmethylammonium triflate in the presence (dashed) and absence (solid) of O_2. The blue curves were recorded using PILs containing no detectable acid and the red curves were recorded in the presence of 0.1 M triflic acid.

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SA6

Investigating Bacterial ROS with Tailored Carbon Nanotube Sensors

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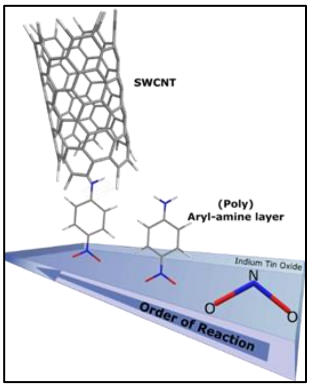
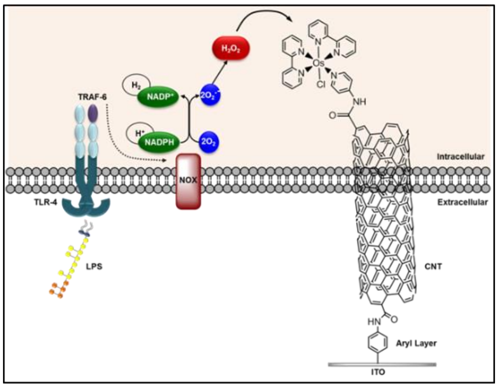
Nano sensors are emerging as a key technology for intracellular sensing. With their small size, they can penetrate cell membranes and have proven to be highly sensitive to minor changes in analyte. In this work, we present our ability to tailor the properties of single walled carbon nanotube (SWCNT) based sensors for superior sensing of reactive oxygen species (ROS). The sensors are based on the immobilisation of SWCNTs onto an indium tin oxide (ITO) surface via in situ grafting of aryl diazonium which results in an aryl-amine tether layer between the ITO and the CNTs. By restricting the aryl-amine layer to ~3nm instead of the regular 20nm electron transfer kinetics of the sensors were improved by more than a factor of ten[1]. These sensors were then modified as described previously by Rawson et al[2] with an osmium complex for hydrogen peroxide selectivity. Various surface analysis techniques were used including AFM, ToF-SIMS and ellipsometry in conjugation with electrochemical techniques to analyse the surfaces. A murine macrophage line (RAW264.7) was used in conjugation with the sensors to examine ROS production in response to bacterial infection. With these improved sensors, we have been able to reduce the lower limit of detection of hydrogen peroxide and apply them to numerous bacterial strains of lipopolysaccharides for investigation.





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SA7

SECM Study of Metals Extraction at the ITIES

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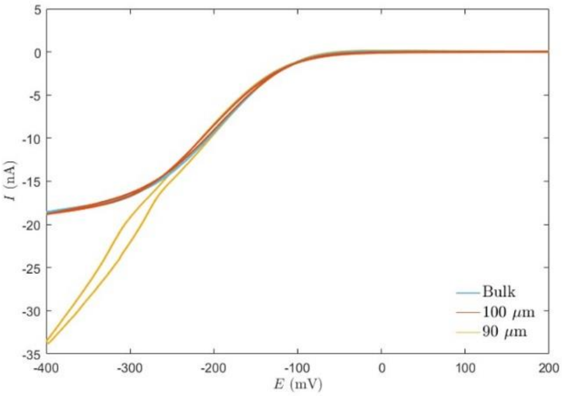
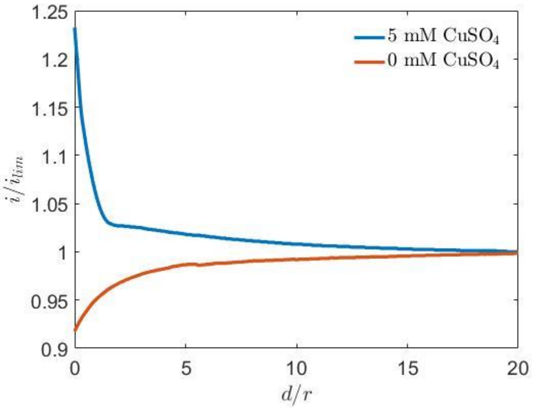
Solvent extraction is the elementary process in hydrometallurgy but the solvents used in industry (e.g. kerosene) do not allow conventional electrochemical study because of their very low relative permittivity that impedes dissolution or dissociation of electrolytes. Immiscible liquid-liquid interfaces (ITIES) have now been studied for ca. 40 years but have mainly remained as an analytical tool. Here, we study the transfer of metals across the ITIES, driven by the Galvani potential difference created by a common ion TB^- in the aqueous and organic phases. In addition to shake-flask experiments, SECM measurements are done to elucidate the effect of the Galvani potential difference on the transfer process. An industrially relevant solvent, methyl isobutyl ketone (MIBK) is used as the organic solvent. The target is to find novel means to separate precious and rare earth metals in recycling processes.



Cyclic voltammograms (SECM tip currents) at varying distance from the liquid-liquid interface. $[Cu^{2+}]^w = 5.0$ mM; $[BATB]^o = [LiTB]^w = 0.1$ mM. Without the potential determining ion TB^-, current does not increase in the linear fashion. Redox mediator TCNQ is reduced on the tip. [1*]



Approach curves in absence and presence of Cu^{2+} in the aqueous phase. $[BATB]^o = [LiTB]^w = 0.1$ mM. d is the tip-interface distance and $r = 12.5$ μm, the tip radius. The positive feedback comes from the reduction of Cu^{2+} by $TCNQ^-$ that is oxidised back to TCNQ.

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[*] BA^+ = Bis(triphenylphosporanylidene), TB^- = Ammonium tetrakis(pentafluorophenyl) borate; TCNQ = Tetracyanoquinodimethane

SA8

MRI of electrochemical systems: batteries, corrosion and electroplating

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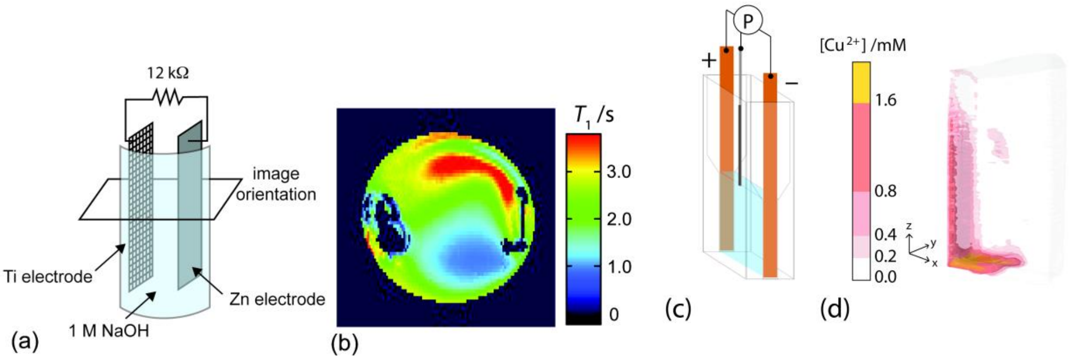
The design and development of improved energy storage devices, and other electrochemical technologies, requires detailed understanding of the electrochemical reactions, ion transport and concentration gradients within these systems. However, there are few methods that are able to visualise and quantify these non-invasively, spatially, in situ and in real time. Magnetic resonance imaging (MRI) has proved to be an excellent tool for non-invasively studying complex, spatially heterogeneous chemical systems in materials, engineering and chemical research[1]. While, MRI has enormous potential for in situ investigation of the spatial distribution, speciation, and mobility of molecules and ions in electrochemical devices, there are currently very few examples of MRI being used to probe such systems. This is largely due to the experimental challenges associated with setting up an electrochemical cell inside a strong magnetic field and the imaging artefacts caused by the presence of metals that lead to undesirable variations in the radiofrequency (RF) and magnetic fields across the sample[2]. However, it has been found recently that such technical issues can be overcome and that it is possible to collect viable, quantitative, in situ data[3-6]. This paper will discuss the challenges of studying electrochemical systems by MRI and demonstrate how they can be overcome to enable the collection of unique, viable, quantitative, in situ data during the operation of batteries, as well as other electrochemical systems, including corrosion[3,7] and metal electroplating in ionic liquids.



(a) Model Zn-air cell (b) MRI of Zn dissolution in Zn-air cell[6] (c) Cu corrosion cell (d) Cu^{2+} concentration map[7] during electrodissolution of Cu^{2+}.

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SA9

The development of electrochemical online monitoring in nuclear pyroprocessing using in-house microelectrodes.

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Electrochemical techniques are being extensively developed for molten salt pyroprocessing of spent nuclear fuel. For online monitoring, data obtained from macroelectrodes often requires involved analysis to gain key information, particularly due to the contribution and complexity of convection. Microelectrodes have significant advantages that change the measured signal, which improves the quality of collected data and simplifies the analysis required to extract key information. Photolithograhpically defined and patterned in-house microelectrodes have been developed that we have shown to be capable of withstanding the harsh environment in LiCl-KCl eutectic (LKE) molten salt[1-3] at temperatures up to 500 °C, which is often highly corrosive. This talk will detail our work studying nuclear relevant redox species with macro and microelectrodes (Figure 1), highlighting the significant advantages of the microelectrodes due to the differences in data collected and analysis required.

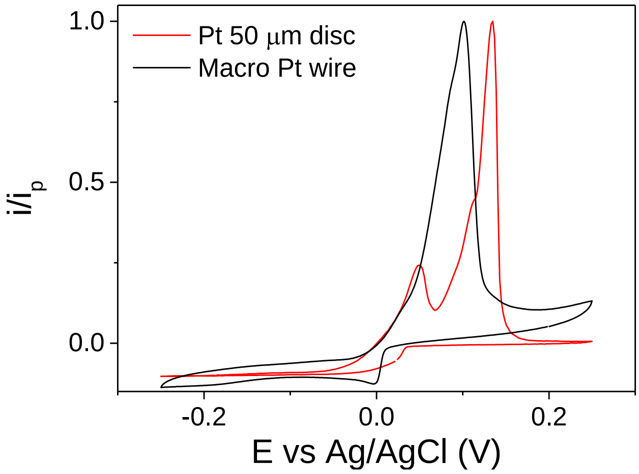

Figure 1: Comparison of CVs of $BiCl_3$ in LKE on a Pt macroelectrode and microelectrode.

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Keynote: Tim Albrecht

Nanopore sensing for DNA fingerprinting and profiling applications

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Nanopore devices are still a relatively new class of stochastic single-molecule sensors, which nevertheless have reached a certain degree of maturity. The fundamental concept is based on small biological channels on one hand and their micrometer-scale, solid-state analogue, the famous Coulter counter on the other. Initially driven by prospects of fast and label-free DNA sequencing, a feat that has now been achieved,[1] new applications are now coming into focus, especially for chip-based nanopore sensors and nanopipettes. In comparison to biological channels, those pores tend to be somewhat larger and less reproducible (at the low-nm scale), but they offer more design flexibility and are more readily be adapted to different and larger analytes, such as protein/DNA complexes.[2-4] To this end, mapping of structural features along a double-stranded DNA (dsDNA) carrier strand has emerged as an area of particular interest and the detection of DNA knots, bound PNA and proteins been demonstrated.[2,4-6] Using electric detection, It is now possible to resolve those features individually in a label-free manner and locate them along the DNA strand.

Building on our recent work on high-speed sensing in nanopipettes with time resolutions in the low microsecond range (and 10s of pA amplitude) and in particular the direct detection of dsDNA fragments as short as 100 bp,[7,8] we have now developed a new sensor concept akin to a DNA assay 'on a string'. Here, we first build a DNA architecture based on molecular self-assembly ('DNA Origami'): it consists of a 7.2 kbp dsDNA carrier with ~100 nt single-stranded (ss) DNA overhangs in known locations along the carrier (currently up to 3). Those can be detected by electric readout in a nanopipette, as spikes superimposed on the translocation event itself ('sub-events'). However, just as in a DNA assay, the ssDNA overhangs can also hybridize with a specific target sequence, e.g. a disease marker, to form dsDNA overhangs. Since the latter are bulkier and presumably more rigid, the sub-events change in comparison to their ssDNA analogues, which can in turn be used to differentiate between hybridized and non-hybridized 'arms'. At present, the effect is not large, but we are confident that optimisation of the carrier and the sensor design can further improve the performance.

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SA10

Performance characteristics of New NO_2 and O_3 Low Cost Air Quality Gas Sensors.

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A new generation of air quality NO_2 and O_3 gas sensors have recently been developed at Alphasense. The use of electrochemical sensors for monitoring air quality provides a low cost alternative to the existing methods [1]. These sensors show improvements over standard sensors, especially in air quality monitoring applications. Main criteria include stabilisation time, signal noise, zero temperature dependence, transient humidity performance, linearity at low concentrations, limit of detection, long term sensitivity stability and gas specificity [2]. In particular, these sensors are less sensitive to environmental conditions such as temperature and humidity transients. Limits of detection as low as a few ppbs were obtained in a laboratory environment. The new sensors are now being deployed commercially and corresponding field data will be shown.

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SA11

Electrodeposition of Tin Nanowires into an Anodic Alumina Template from a dichloromethane electrolyte.

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Nanowires of various materials have a myriad of potential uses in electrical devices such as transistors[1], thermoelectric materials[1] and solar energy devices[2] due to their semiconducting properties that occur at smaller nanowire diameters[2]. One method of forming nanowires is to electrodeposit the material inside a porous template such as an anodic alumina membrane[3], for control of the nanowire diameter.

Tin was electrodeposited from a dichloromethane solution onto flat substrates at various temperatures. Tin was also electrodeposited into anodic alumina membranes of various pore sizes. The effect of grafting the alumina pore wall with various functional groups was also studied. It was found that decreasing the electrodeposition temperature decreased the crystallite size of the deposited tin and causes the onset of the reduction potential to become more positive. Nanowires of tin were successfully deposited into anodic alumina membranes with 55 and 13 nm pore diameters. It was found that the tin preferentially deposited into the anodic alumina membrane is <200> aligned. Grafting the anodic alumina pore walls with tin had little effect on the tin alignment and deposition.

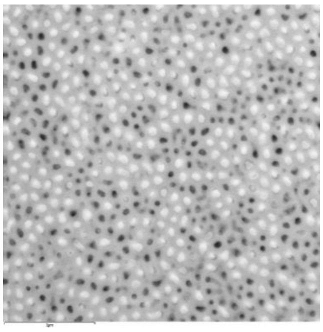

Figure 2: A TEM image showing tin (white spots) deposited in an anodic alumina membrane with 55 nm diameter pores.

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SA12

Development of a Boron doped diamond pH sensor for unbuffered media: The effect of Quinone surface coverage on pH response.

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High power laser micromachining systems are used to cut diamond and have previously been used to manufacture all diamond electrochemical devices, including disk electrodes, band electrodes and ring disk electrodes[1]. The machining process also leaves non-diamond (sp^2) carbon behind which has been found to have a significant effect on the electrochemistry observed. Recently, we have shown how we can use this approach to functionalise the BDD surface with sp^2 sites, which are more catalytically active than the surrounding sp^3 BDD surface. The nature of this sp^2 carbon is still not completely understood, but has been shown to contain quinone-like moieties (QLM's) which demonstrate a quantitative pH response[2] and can be used as a measure of the surface sp^2 content[3].

Previous carbon pH sensors based on the electrochemical reduction/oxidation of surface bound quinone groups have been shown to have significant limitations, often struggling at high pH[4] and in unbuffered solutions. The latter is due to the fact that by making the measurement protons are removed from solution resulting in a changing proton concentration at the surface of the electrode. The surface attachment of these molecules has also been shown to fail in extreme environments[4,5].

QLM's produced on the surface of BDD by laser micromachining (figure 1.) have a significant advantage over previous approaches. The QLM's are incredibly stable, being resistant to mechanical abrasion, extremely high temperatures and extreme environments. In this talk we will discuss methods for optimizing the sensor design to provide a linear pH response in unbuffered solutions.

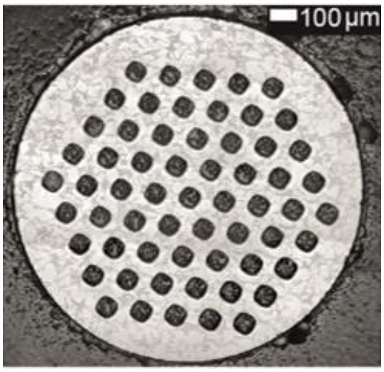

Figure 3: Laser micromachined pH array in a BDD electrode

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Physical & Fundamental

Oral Abstracts

PF1

Electrochemical Processes Leading to Ionic Diode Phenomena

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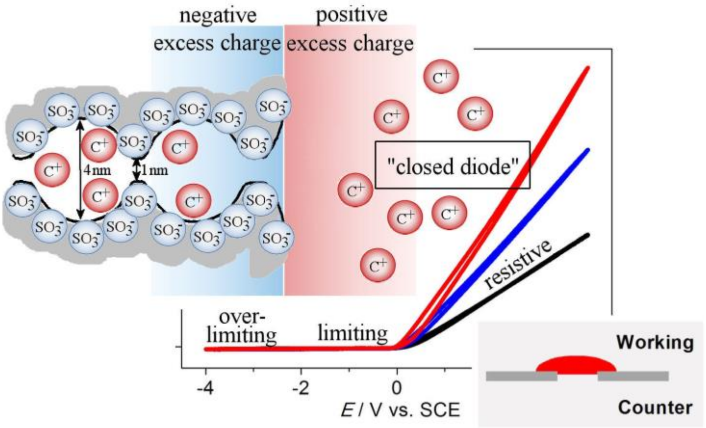
Ionic rectifiers (or ionic diodes) work like electronic diodes, but allow ion flow to be controlled. We have developed [1-4] novel ionic diode devices based on ionomer and polymer materials coated onto microholes to typically 5 μm to 40 μm diameter. When a potential is applied across the membrane an open (or "resistive") state is observed and at the opposite potential a closed (or "limiting") state occurs. Ionic diodes can respond to pH and external parameters or "invert" polarity, but the underlying mechanisms can be diverse.



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PF2

The Influence of Acetonitrile on Cu Under-Potential Deposition in presence of adsorbing anions

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The presence of specifically adsorbed anions and/or small organic molecules can significantly affect the electrochemical reactivity of a metal electrode and the formation of metal adlayer on a foreign metal substrate at potentials more positive than the Nernst potential, the under-potential deposition (UPD). [1] Furthermore, a prominent effect of the interaction between metal ions and anion is the influence on the kinetics of the metal layer formation. [2]

Acetonitrile (AcN) is an organic molecule which solvates noble metal ions by receiving electrons into the cyanide group of the molecule, an important process in the organometallic complex formation of transition metals. Moreover, it has been presented that AcN molecules compete for adsorption sites on metal electrodes. [3] For the investigation of the influence of organic molecules on the process of metal deposition it is vital to comprehend their mechanism.

The presentation will demonstrate that different Acetonitrile concentrations show a systematic change in the Cu UPD formation in the presence of sulphate (Figure 1) and perchlorate anions through initial characterisation by cyclic voltammetry, the alteration of the kinetics of the systems by modelling chronoamperometry transients and structural changes between potentials by the use of Surface X-Ray Diffraction.

The increase of Acetonitrile concentration from 10 mM up to 4 M enhanced Cu deposition (positive shift of the cathodic peak) and moreover, chronoamperometry analysis showed that the final Cu coverage in sulphuric increased in the presence of Acetonitrile.

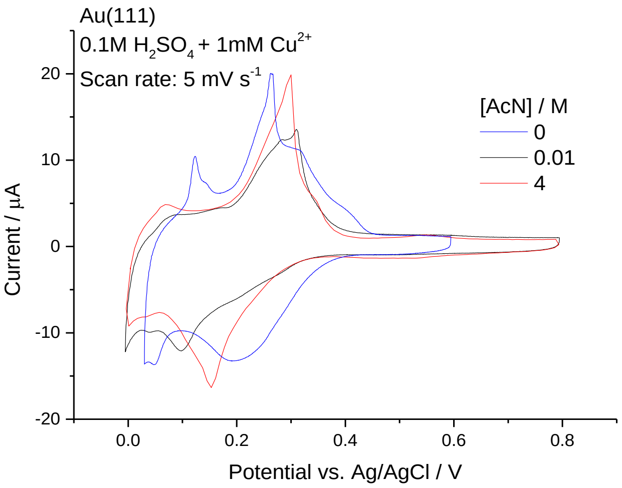

Figure 1. *Cyclic voltammogram of Au(111) in 1 mM $CuSO_4$ / 0.1 M H_2SO_4 in different concentrations of Acetonitrile*
Scan rate: 5 mV s^{-1}

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PF3

Spectroscopic Evidence of Size-Dependent Buffering of Interfacial pH by Cation Hydrolysis during CO_2 Electroreduction

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The nature of the electrolyte cation is known to affect the Faradaic efficiency and selectivity of CO_2 electroreduction. Singh et al. (J. Am. Chem. Soc. 2016, 138, 13006–13012) recently attributed this effect to the buffering ability of cation hydrolysis at the electrical double layer. According to them, the pKa of hydrolysis decreases close to the cathode due to the polarization of the solvation water molecules between the cation's positive charge and the negative charge on the electrode surface. We have tested this hypothesis experimentally, by probing the pH at the gold-electrolyte interface in situ using ATR-SEIRAS. The ratio between the integrated intensity of the CO_2 and HCO_3^- bands, which has to be inversely proportional to the pH, provided a means to determining the pH change in-situ during the electroreduction of CO_2. Our results confirm that the magnitude of the pH increase at the interface follows the trend Li+ > Na+ > K+ > Cs+, adding strong experimental support to Singh's et al.'s hypothesis. We show, however, that the pH buffering effect was overestimated by Singh et al., their overestimation being larger the larger the cation.

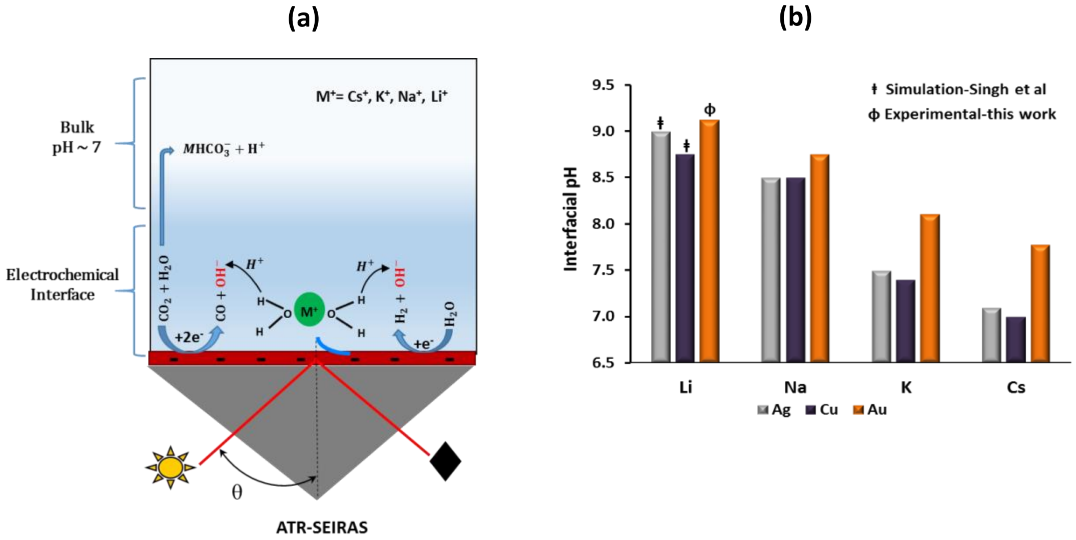

Figure 1: (a) Illustration of cation hydrolysis buffering the interfacial pH during electroreduction of CO_2 (b) Steady-state pH at the metal-electrolyte interface during the electroreduction of CO_2 at -1 V vs. RHE in CO_2-saturated 0.05 M M_2CO_3 solutions (M=Li, Na, K, Cs). pH values for Ag and Cu correspond to those resulting from Singh's at al.'s calculations, while in the case of Au they correspond to our experimental determination using ATR-SEIRAS.

PF4

Combined Optoelectronic and Electrochemical Study of Nitrogenated Carbon Electrodes

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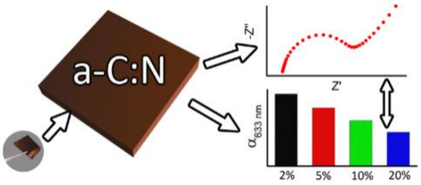
The incorporation of Nitrogen into carbon-based materials has been suggested as a route towards new electrode materials with properties amenable to applications in electrocatalysis[1] and biosensing[2]. Materials based on nitrogen-incorporated carbons have also been suggested for use as support materials in fuel cells due to their corrosion resistance and metal-free ORR activity[3].

The realisation of these proposed applications requires a fundamental understanding of the effects of nitrogen incorporation on both the bulk physical properties and the surface chemistry of carbon materials. To this end we have prepared nitrogen-incorporated amorphous carbon thin films with varying N-content via DC magnetron sputtering and characterised them using a combination of optical and electrochemical techniques including X-ray photoelectron spectroscopy, ellipsometry, voltammetry and impedance spectroscopy. Here we present results indicating that low-levels of nitrogenation produce films with lower optical gaps and faster electron transfer kinetics to outer-sphere redox couples compared to unmodified amorphous carbon; higher levels of nitrogen-incorporation decrease the metallic character of the films, ultimately yielding materials with optical and electrochemical properties consistent with disordered cluster aggregates rather than amorphous solids[4].

In addition to the physical properties of the bulk, surface chemistry is also important for understanding how structural changes induced in carbon materials by nitrogen incorporation may be best controlled to allow for the synthesis of new materials tailored for specific electrochemical applications. We therefore present studies on the electrochemistry of a-C:N electrodes with the surface-sensitive redox probe dopamine as a function of nitrogen content.



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PF5

Electrowetting without Dielectrics

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Electrowetting (EW) is a powerful method to achieve external wetting control, with many applications ranging from variable focal-length liquid lenses, electronic paper and the actuation of droplets in lab-on-a-chip devices. Recent work from Manchester has shown that EW can be observed on graphite: unprecedented changes in contact angle are seen for voltages below the electrolysis threshold (50° with 1 V for a water in air, and 100° with 1.5 V for water immersed in hexadecane) that are highly reproducible, stable over hundreds of cycles and free of hysteresis [1]. This enables one to realize EW on a conductor (EWOC), thus enabling the use of voltages that are one or two orders of magnitude lower than EW usually performed in device applications, with a dielectric layer ("EW on a dielectric", EWOD). Current developments, including the extension of this work to aged/functionalised surfaces and other materials will be discussed [2].

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Keynote: Gary Attard

The slowly-evolving picture of the Pt{110} electrode surface: Is there still something new to learn from single crystal platinum voltammetry?

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It is crucial for a proper understanding of electrocatalysis that reactions at well-defined electrodes are pursued since such studies will inform how structure/activity relationships at 'real' supported electrocatalysts may be elucidated and optimised [1]. However, even a cursory inspection of the published literature pertaining to Pt{110} will highlight the fact that full understanding of the surface structure of "well-defined" Pt{110} is far from complete [2 - 5]. In this presentation, it will be demonstrated that depending on the cooling environment following flame-annealing, several different surface structural phases may be identified corresponding to (1x1) and variously disordered (1x1) and (1x2) reconstructed phases. Each of these phases in turn afford quite different activity in relation to the oxygen reduction reaction (ORR). Furthermore, by utilising stepped Pt{110} electrodes together with CO charge-displacement measurements (and also electrolyte pH/ionic strength studies) it is suggested that one may assign "local" values of the potential of zero charge to the voltammetric peaks observed. The consequences of this assertion for the interpretation of **all** of the complex voltammetric behaviour displayed by clean Pt{hkl} electrodes in aqueous media will be discussed [6].

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PF6

Polymer of Intrinsic Microporosity (PIM) Film Coating Dampens Chaotic Copper Corrosion

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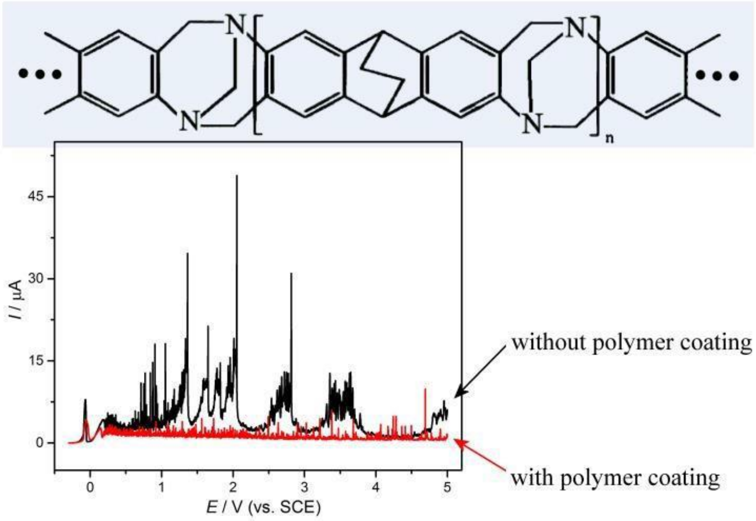
Copper surfaces are known to exhibit oscillatory/chaotic behavior [1,2] under anodic conditions when immersed in salt water. The process can be dissected into the formation of insoluble Cu(I)Cl at the electrode surface followed by re-dissolution as Cu(II)Cl3- with complex/chaotic dynamics.



Here, the effect of an intrinsically microporous polymer (PIM-EA-TB, see Figure [3,4]) with micropores of typically 1-2 nm diameter coated over the copper surface is investigated. With voltammetry experiments at copper microelectrodes, it is demonstrated that the intrinsically microporous polymer can dampen the oscillatory behaviour depending on the thickness of the polymer coating. A mechanism is proposed.

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PF7

STM Studies of Electrochemical Single Molecule Transistors and Molecular Wires

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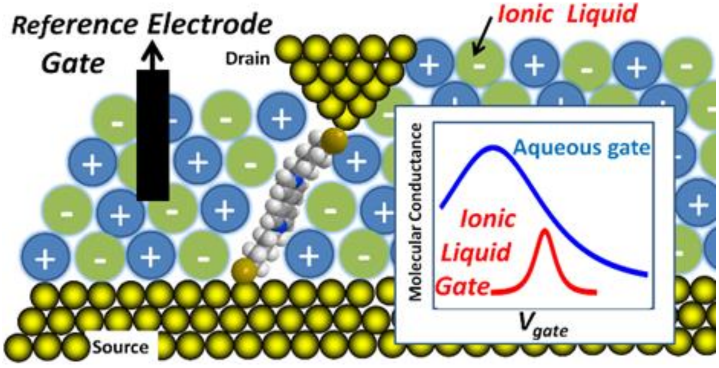
We have exploited STM based methods for making single molecule measurements under electrochemical potential control in ionic liquid electrolytes.1-4 The electrochemical potential can be used to control the redox state of single molecule bridges and switch the electrical conductance from low to higher values. This has been referred to as the "single molecule electrochemical transistor" configuration, with the electrochemical potential "gating" the molecular conductance in the STM nano-gap configuration. Recent results from our group on gating the conductance of single molecules in ionic liquid electrolytes will be discussed including studies of viologens, redox active metal terpyridine molecular wires and pyrrolo-tetrathiafulvalene (pTTF) molecular bridges. Mechanisms of charge transport in the STM nano-gap setup are discussed alongside the advantages of undertaking such single molecule electrochemical measurements in ionic liquids. **Very recent results with semiconductor contacts will also be presented, with potential future applications in semiconductor electrochemistry.**



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PF8

Using X-ray and neutron reflectometry to monitor corrosion mechanisms at the angstrom-level

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The corrosion of ferritic steel in salt solutions remains a major problem across a range of industries and is a massive drain on the economies of developed nations (coming in around 3-4 % of their GDP)[1,2]. Although great effort has been expended into researching its causes and prevention, this has mainly focused on bulk electrochemical or physical methods. X-ray and neutron reflectometry (XRR and NR) are both extremely powerful techniques that allow angstrom-level quantification of the thickness, composition and roughnesses of surface films and hence offer unique opportunities to increase understanding concerning the fundamental surface chemistry underlying corrosion and inhibition mechanisms[3].

In this work, XRR and NR were used with complementary techniques such as XPS to study iron films (as a model for ferritic steel) under a range of different corrosive environments and with the addition of potential corrosion inhibitors. NR in particular was used to elucidate the structure of organic species at the interface *in situ*, whereas XRR was more powerful in terms of characterising the changing metal surface. This allowed a detailed breakdown of the time-dependent structural changes caused by corrosion (for example, as shown in Figure 4, the growth of a void under the film surface followed by complete dissolution of the iron layer) as well as a direct comparison of several potential corrosion inhibitors. Some surprising methods for protecting the surface that didn't involve addition of inhibitors but that proved extraordinarily effective were also revealed.

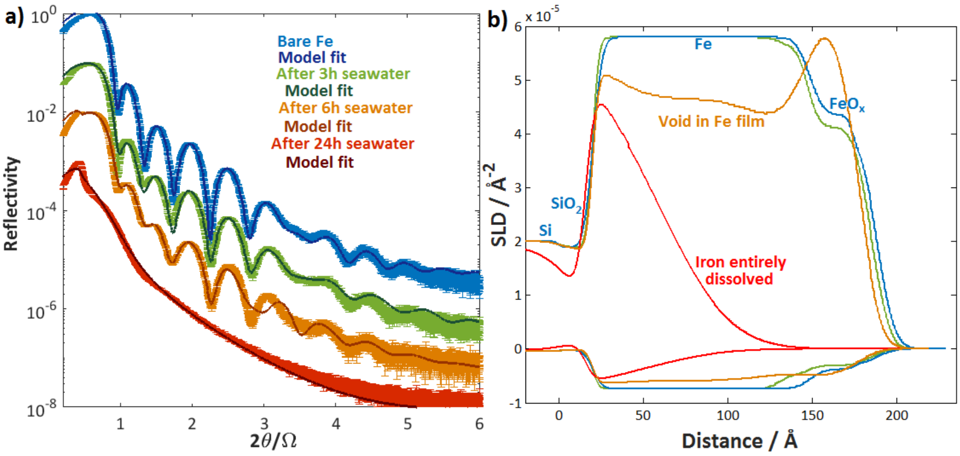

Figure 4a) Example of XRR data for a 20 nm Fe film after various amounts of time soaked in seawater (fits shown as solid lines). b) Scattering length density (SLD) profiles of the fitted models, showing evolution of the iron structure with increasing corrosion.

With thanks to Shell for project funding and to the ISIS neutron source for instrument time.

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PF9

Electroless Ni-B plating in a gradient magnetic field.

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Electroless deposited Ni-B is a promising material for the automotive and aerospace industries due to its exceptional hardness. The morphology, grain size and roughness affect the properties of the material. The introduction of a magnetic field during the alloy deposition process has been reported to have effects on the layer formation and therefore the properties of the deposit [1]. The magnetohydrodynamic effect arises when the magnetic field is applied and improves the mass transport in solution during electrochemical deposition, affecting the morphology and crystal structure of the deposit [2]. In addition, patterning has also been observed during electrochemical deposition in a gradient magnetic field [3].

The current work was conducted at the University of Mons, Belgium and Coventry University, UK as a short term scientific mission sponsored by e-MINDS COST MP1407. The Ni-B electroless deposition was performed on a stainless steel substrate in baths of various compositions and using a magnet of 0.2 T strength and 10x10x5 mm size attached behind the test piece.

The deposit showed the distinctive patterning effect (Figure 1 (a)) as well as more uniform layer morphology (Figure 1 (b and c)). This paper will propose the theory underlying these findings and discuss potential industrial applications.

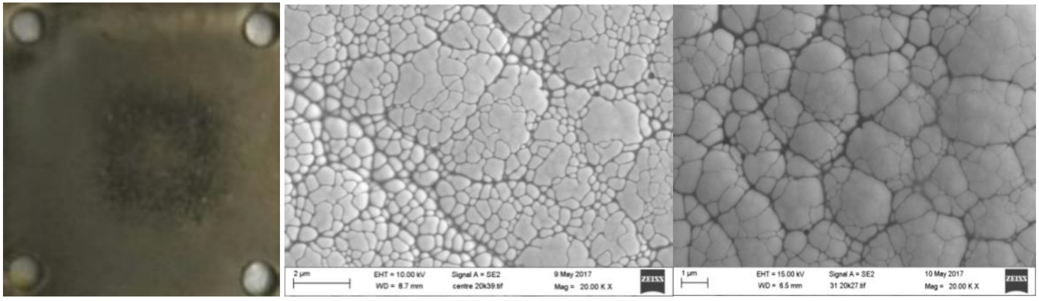

Figure 1. Electroless Ni-B deposition under gradient magnetic field. (a) Optical image of substrate with distinctive pattern effect, (b) SEM image of layer deposited under magnetic field, (c) SEM image of layer deposited without magnetic field.

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Proton conduction pathways in porous organic cage networks and functionalised silica ionogels

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Organic molecular cage salts containing protonated secondary amine groups show promise as proton conducting electrolytes due to their high water uptake, intrinsic porosity and appreciable ionic conductivity. Herein we report the proton conductivity of reduced amine cage salts with conductivities in the range 10^{-3}-10^{-2} S cm^{-1} [1], at temperatures up to 80°C. These cages are formed from reversible imine bond formation and packing of discrete, rigid cage molecules results in a defined microporous structure [2]. Proton conductivity was investigated using the 2-probe AC method of impedance spectroscopy under varying humidity and temperature for various cage systems. The determined activation energies of ca. 0.3 eV indicate a mixed Grotthuss and vehicular method of proton transport and suggest high intrinsic proton transport for some cage materials[1]. Comprehensive simulation studies and structural characterisation using powder XRD, and water uptake measurements suggests that water molecules form clusters within the voids of the charged cage cations and as a result, become polarised which facilitates proton transport. Both molecular dynamic simulation and transference number studies imply that the anionic moieties investigated (for example Cl^- and SO_4^{2-}) are too large to be mobile and remain fixed around each cage cation.

Inorganic silica gels can be readily synthesised via sol-gel processing of tetraalkyl-orthosilicates in a suitable solvent under acidic or basic conditions [3]. The resulting porous aerogels can be used as a matrix to entrap small molecules and ions to increase the functionality of these gels for applications such as solid electrolytes, sensors, ion exchange resins and as supercapacitors and are thermally stable [3]. We have optimised the sol-gel process to create porous ionogels incorporating low concentrations (<10% wt.) of [4+6] porous proton conducting amine cage salts, which have previously demonstrated appreciable proton conductivity. A series of water-stable ionogels were investigated using electrochemical impedance spectroscopy and the confinement of the cage salts was probed using short angle X-ray scattering (SAXS). Synthesised ionogels exhibited proton conductivity of 10^{-6}-10^{-4} S cm^{-1} from room temperature to 150°C.

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PF11

Trends in oxygen reduction on a Pt-alloy single crystal: acidic versus alkaline media

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Electrochemists have made huge progress in understanding how to tune the reactivity of the electrode-electrolyte interface. Most studies have focused on tailoring the electrode, by modifying the surface electronic structure. However, it is of fundamental importance to understand how to tailor the electrolyte side of the interface. Oxygen reduction is the most studied electrochemical reaction, as it limits fuel cells and metal air batteries.

In our earlier studies, we mapped out the experimental *Sabatier* volcano for the oxygen reduction reaction in 0.1 M HClO4 using the Cu/Pt(111) near-surface alloy. We experimentally confirmed the theoretical notion that the most optimal catalyst should exhibit OH binding 0.1 eV weaker than Pt(111).[1] However, numerous reports suggest significant divergences in the catalytic performance of noble metals between acid and base. [2,3]

In the current study, we extend our previous studies on the Cu/Pt(111) to alkaline media. By focusing on surfaces with the (111) orientation, we can orthogonalise surface orientation and the reactivity of the surface. Remarkably, we observe that the same trend persists between OH binding and oxygen reduction activity in acid and alkaline media. Moreover, all surfaces show a ~8 fold improvement in activity in 0.1 M KOH, relative to the same surface in 0.1 M HClO4. At the peak of the volcano, we observe an exceptionally high activity of 107 mA/cm2 at 0.9 V with respect to the reversible hydrogen electrode. Curiously, stepped surfaces with the same binding to OH are markedly less active than Pt(111).[3] Taking these findings together, we deduce that in alkaline media, surface orientation may play a non-trivial role on electrochemical kinetics; i.e. binding to the reaction intermediates is not the only effect that controls activity.

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Keynote: Katherine Holt

Deprotonation of graphene nanoflake electrode edge groups studied using *in situ* IR spectroelectrochemistry

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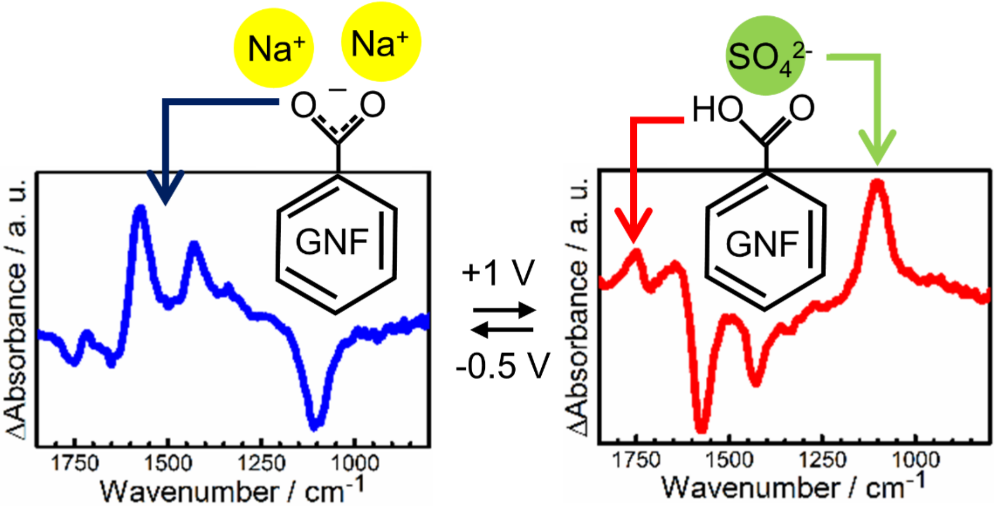
The ubiquity of acid moieties at electrode interfaces, as defect sites on carbon electrodes and as polymer electrolytes of solid supercapacitors, makes understanding their response to applied electrode potential an essential area of study. In this study we use *in situ* IR spectroscopy to monitor the protonation state of carboxylic edge groups of graphene nanoflakes as a function of applied potential[1].



Deprotonation of acid groups was found to take place on application of a negative potential, with positive potential resulting in their re-protonation. The deprotonation was found to be induced by a local increase in cation activity at the electrode interface on application of negative potential. The increase in cation activity has the effect of lowering the effective pK_a of the acid groups which induces deprotonation to take place.

The *in situ* measurements allowed concomitant changes in electrolyte composition to be determined. It was found that solution acid species, such as HSO_4^- and $H_2PO_4^-$ also undergo deprotonation when a negative potential is applied. This is also attributed to the migration of cations towards the electrode increasing their local activity and lowering the effective pK_a of the solution acids. This observation is important as it implies that speciation of acids near a biased electrode can differ significantly from bulk solution and this can be driven purely by cation migration in the absence of adsorption, redox chemistry or pH change.

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PF12

Study of Oxygen Reduction Reaction by Scanning Electrochemical Microscopy

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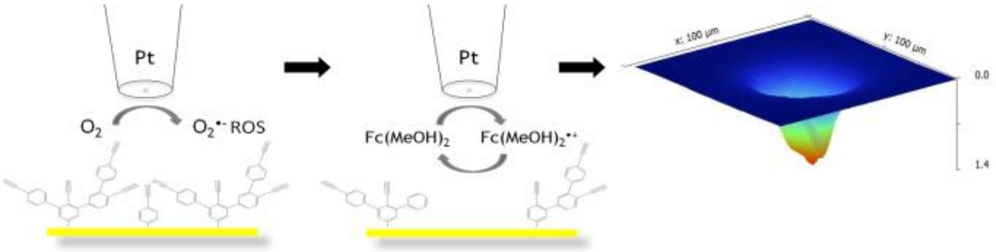
Multielectronic O_2 reduction reaction (ORR) and its catalysis is of general importance in natural and industrial processes.[1] The generally admitted description of ORR in water as simple competitive pathways between 2-electron (O_2 to H_2O_2) and 4-electron (O_2 to H_2O) reductions is often inadequate. The electron transfer steps could be accompanied by homogeneous or heterogeneous chemical steps and oxygen-oxygen bond breaking leading to possible numerous intermediates. This chemical reactions are usually so fast that the detection and characterization of intermediates, and thus the establishment of the reaction mechanism remains unknown.[2]

In this study, we have investigated the reduction of O_2 in water as function of different experimental parameters (pH, potential, additives…) by SECM using a foot-printing strategy.[2] This approach is based on the use of a sensitive surface to evidence the formation of reactive oxygen species (ROS), for example OH radicals during the ORR.

The role of added scavenger on the production of ROS was also examined. Considering the high reactivity of some of these ROS versus organic and living materials, these studies could have important consequences in several practical situations (biological sensors, fuel cell catalysts, reaction kinetics, porous membrane studies, corrosion mechanisms, etc.) as far as O_2 reduction is concerned.[3,4]



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Corrosion

Oral Abstracts

Improvement of sol-gel coatings and their anti-corrosion properties by doping with Titanium precursors

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Corrosion is a major oilfield flow assurance problem[1]. Paints and coatings are often used in oil production environment as a barrier to corrosion. In recent studies sol-gel materials draw increasing interest due to many promising properties like hardness, durability, scratch resistance and thermal stability and are gaining more worldwide recognition as an alternative for the preparation of glasses and ceramics at lower temperatures [2]. Beside the protection of metals and its alloys in corrosive environments, sol–gel-based coatings also exhibit high potential as an alternative to coatings that contain toxic compounds like chromate[3]. In this project silica inorganic sol-gel coatings were studied in order to follow the evolution of corrosion and to optimize their physico-chemical properties with particular attention to their corrosion resistance properties. To evaluate the protective properties stainless steel 304/304L coupons coated with inorganic coatings with or without doping material were subjected to a corrosive environment. I0 is considered as the reference. IM sample was synthetized with the same sol-gel structure and composition and was in addition doped with Titanium precursor. The coatings are a few µm thick. The kinetics of the degradation process were monitored throughout by electrochemical impedance spectroscopy (EIS). Besides EIS, electron microscopy was used to characterize the coating morphology before and after exposition to the corrosive environment. Chemical changes of the coating materials were determined by IR spectroscopy and Scanning Electron Microscopy (SEM). The achieved data allow to understand the failure mechanisms of these coatings and help to improve the formulation to enhance their resistance to corrosion.

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C2

AFM-SECM and Nanoelectric Liquid Imaging for Corrosion Research

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Corrosions often are redox reactions that involve metal oxidation by dioxygen, proton or water, and result in the release of hydroxyl groups, metal cations, or hydrogen. Localized processes, e.g. pitting, crevice, and galvanic corrosions, are primary forms, while even global uniform corrosion occurs heterogeneously on micro- or nanoscale. These local reactivity heterogeneities are the consequence of the local differences in structural, mechanical, electrical, and/or electrochemical properties. Therefore, approaches capable of simultaneously capturing correlated multidimensional information on nanoscale are highly desired. In addition, in these dynamic processes, *in situ,* non-invasive methodologies are also highly desired.

We have recently developed batch-fabricated, high-quality and robust nanoelectrode probes with the exposed Pt-coated tip apex of ~200 nm height and the end tip diameter of ~50 nm. These nanoelectrode tips are designed for Atomic Force Microscopes (AFM) platform to enable the AFM-based scanning electrochemical microscopy (SECM). AFM-SECM provides high-resolution, highly-multidimensional information. For example, PeakForce SECM and Force Volume SECM simultaneously images surface topography, quantitative nanomechanics, electrochemistry (at < 100 nm resolution), and tip-sample contact current.[1,2] The nanoelectrode probe is also the critical enabler of nanoelectric measurements in liquid, such as conductivity, surface potential and piezo response imaging in electrolyte environment.

In this talk, we will present the recently-developed nanoelectrode probe, a variety of AFM-SECM modes, nanoelectric liquid studies, and their applications in corrosion research. Examples discussed here include surface protection, reactivity hot spots revealed by *in situ* product detection, deposition and the subsequence stripping of metal products on the nanoelectrode tip, and nanoelectric liquid imaging of model samples. This work demonstrates the versatility of this suite of new techniques for corrosion research.

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Effect of the use of pulse plating techniques in electrodeposited Sn-Cu Coatings for Pb-free, environmentally-friendly applications

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The electrodeposition of lead containing alloys have found many industrial applications including electronics and other applications. However, lead is very harmful to health and the environment and the Restriction of Hazardous Substances Directive (RoHS) has been in force in Europe since 2003 restricting the use of certain hazardous substances (e.g. lead, cadmium, mercury etc.) in electrical and electronic equipment and this is likely to be extended to other industrial sectors. For this reason there is intensive research to find alternatives to lead alloys and one favourable candidate is Sn-Cu.
This paper will describe a study carried out to obtain a deeper understanding of some of the factors affecting Sn-Cu electroplating. Experimental work, by means of Hull Cell tests, ultrasonic agitation and pulse plating, has been undertaken to understand the effect of these factors on the properties of the Sn-Cu coatings. A number of advanced analytical techniques, including scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS) and white light scanning interferometry (WLS), have been used to evaluate the characteristics of the Sn-Cu coatings, in terms of their surface morphology, chemical composition and microstructure.
It was found that that pulse plating techniques combined with high speed magnetic stirring during deposition had a strong effect on the characteristics of the Sn-Cu electrodeposits and, in the short term, on Sn whiskers developing from the deposit.

This work is funded via the EU H2020 Fast Track to Innovation programme.

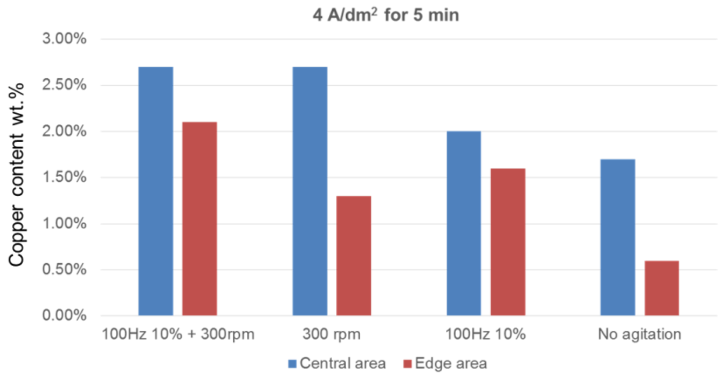

Figure 1. Effect of pulse plating on copper content of Sn-Cu alloy electrochemical deposition. All samples plated at 4 A/dm^2 for 5 minutes

C4

Effect of surface roughness on pitting behaviour of X65 carbon steel in saturated CO2 environment

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Surface finishing of steel can be interpreted in terms of roughness which may vary based on demand specifications. Pitting investigations are often conducted using polished samples which are not true reflection of in-service applications [1]. Machining and surface finishing impact on steel roughness which has been reported to influence pitting in low carbon steel [2]. Roughness on mild steel varies depending on speed and rake angle utilised during turning operations while corrosion tests revealed higher pit depth for rough surface compared to smooth surface [2].
Burstein et al. [3] examined the influence of surface roughness on metal stable pitting of stainless steel. They reported that smooth surfaces have low chance of metastable pitting but that emerged metastable pits have high probability for survival. Chen et al. [4] study on influence of SRB and surface roughness on carbon steel pitting revealed that surface roughness play significant role in carbon steel pitting. Eyu et al. [5] assessed the effect of surface roughness on carbon steel employed for coal steam application and observed that corrosion potential decreased as surface roughness increased; indicating higher ferrite dissolution with increase in roughness. Their work as well reported higher pitting with increase in surface roughness. Melchers et al. [6] work on mild steel corrosion in marine environment reported that surface roughness influence carbon steel pitting only at the early stage. FeCO3 and Fe3C are the common corrosion products formed on low carbon steel. FeCO3 film adheres to steel surface and retards corrosion under suitable conditions but pitting could still progress beneath FeCO3 film. There is yet no known literature comparing the influence of surface roughness on pit initiation/propagation beneath formed FeCO3 and under film-free conditions.

This work therefore investigated the effect of surface finishing on pitting beneath FeCO3 film formed on API 5L X65 (UNS K03014) carbon steel as well as under film-free conditions in saturated CO2 environment. X65 carbon steel was polished to 3 different finishing: 120 grit; 1,200 grit; and 0.25ηm. LPR/OCP measurements were conducted for the different samples under 3.5 wt% NaCl, 80°C up to 96h at pH3.8 and pH6.6. Top view SEM image was observed before cleaning sample in Clarke's solution followed by surface profilometry of corroded sample surface. Results revealed that pitting progressed beneath both Fe3C and FeCO3 films with less pitting recorded for FeCO3 films. As expected, pitting was observed to increase as surface roughness increased.

Keywords: Carbon steel, surface roughness, sweet corrosion, pitting, profilometry

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C5

Towards realistic atmospheric aerosol deposits – automated ultrasonic deposition

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The study of atmospheric corrosion, where contaminants collect on metal surfaces through aerosol deposition, has previously been investigated using a variety of methods with various benefits and drawbacks, such as thin-film electrochemistry, high throughput droplet tests, and salt-fog style experiments.(1-3)

Ultrasonic plates have been used to more accurately replicate the process of atmospheric aerosol deposition through solution atomisation; the duration and intensity of the ultrasonic pulse may be accurately controlled, and result in a controllable droplet size profile.(4) In this paper we extend the use of an ultrasonic atomiser to create an automated, localised aerosol deposition system, capable of repeatable deposition profiles over a contained area. This allows for high-throughput, realistic spray tests to be undertaken

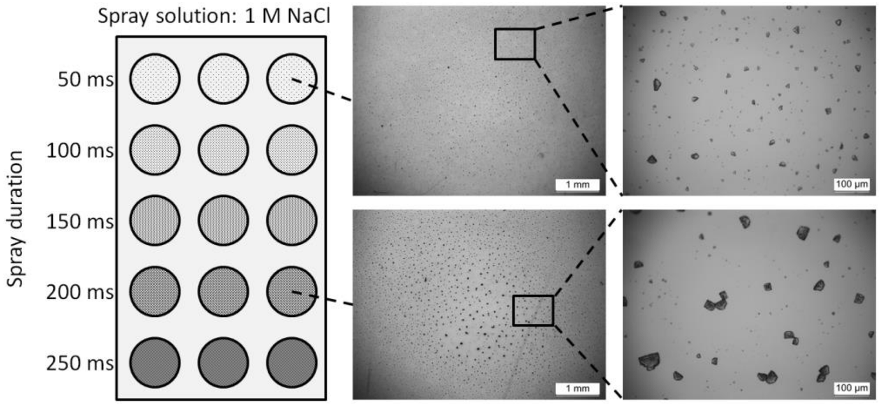

Figure 5 Example deposition scheme over a single sample, with micrographs of representative dry NaCl deposits

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Characterisation of Corrosion Products of a Ti-Based Metallic Glass in Artificial Pits by In Situ Synchrotron X-ray Diffraction

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Current standard corrosion tests of metallic biomaterials are carried out in vitro in simulated body conditions on bulk components or specimens. These test conditions may not be sufficient to predict the actual behaviour of an implant in vivo. Indeed, it was demonstrated recently that titanium implants can corrode in the absence of wear, generating pro-inflammatory corrosion products leading to revision surgery [1]. The observed corrosion products may have been produced through a localized form of corrosion called mechanically assisted crevice corrosion. Conventional corrosion testing on passive surfaces is not able to predict those corrosion products. More aggressive tests like artificial pit methods, provide more realistic conditions leading to corrosion products similar to the ones found in vivo. Synchrotron X-ray methods can be employed to identify and characterise in situ such corrosion products [2].

Titanium-based metallic glasses hold promise for use in small implants due to their high yield strength. So far, their corrosion behaviour has been characterised using standard polarisation methods on passive bulk specimens. Most of them are passive and have a relatively high pitting corrosion resistance in simulated body conditions.

In this work, we use in situ synchrotron X-ray diffraction to characterise corrosion products generated by a Ti-based bulk metallic glass, i.e. $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ (at.%) [3], inside artificial pits formed in 0.9% NaCl (+ 4% albumin; + 0.1% H_2O_2; + 4% albumin + 0.1% H_2O_2). In all electrolytes, the pit cavity contains a black layer, predominantly Pd, with $PdCl_2$ in some cases, and closer to the interface CuCl typically within ≤100 µm. This suggests Pd nanoparticles may be generated by the glassy $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ alloy during service. The effect of Pd nanoparticles on cell behaviour will be determined in future work.

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C7

Analysis of X65 Carbon Steel Surfaces After Erosion-Corrosion Testing Using a Submerged Impingement Jet

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Erosion-corrosion in the oil and gas industry, caused by the mechanical removal of material due to the impingement of sand particles and carbon dioxide (CO_2) corrosion, is a significant problem that can result in high degradation rates of carbon steel pipelines. Erosion-corrosion material loss is typically greater than the sum of the individual erosion and corrosion components, due to the interaction between the two wear mechanisms, resulting in an enhanced total material loss. Erosion-corrosion research has shown how parameters such as sand concentration and flow velocity affect the contributions of corrosion, erosion, corrosion-enhanced erosion and erosion-enhanced corrosion to total erosion-corrosion material loss. However, further investigation into the causes of corrosion-enhanced erosion and erosion-enhanced corrosion of carbon steel in conditions representative of oil and gas pipe flow conditions is required.

This work presents analysis of X65 carbon steel surfaces after erosion-corrosion tests in a submerged impingement jet (SIJ). The SIJ is capable of replicating harsh erosion-corrosion operating conditions, with high flow velocities and sand concentrations (20m/s and 1000mg/l) used to create a highly erosive and corrosive environment to investigate the interactions between erosion and corrosion. Computational fluid dynamics (CFD) was used to predict the trajectories of sand particles through the SIJ nozzle to determine impact angles and impact velocities on the surface of the X65 sample. Various surface analysis techniques were used to examine the surfaces of the carbon steel samples after erosion-corrosion tests to give a better understanding of the causes of corrosion-enhanced erosion and erosion-enhanced corrosion and how the interaction between corrosion and erosion contribute to the total erosion-corrosion wear of carbon steel.

C8

Potentiodynamic Anodic Polarisation Parameters as Indicators to Erosion-Corrosion of Stainless Steel

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Most of the studies that have dealt with the issue of erosion-corrosion resistance of stainless steels have focused on investigating the effect of influencing parameters such as flow velocity, sand loading and impact angle amongst others. These parameters are mostly linked to the resistance of a material to erosion. It is known that a corrosive environment can exacerbate erosion. Temperature is known to play a noticeable role in corrosion but only few published literature assess the effect of temperature on erosion-corrosion.

It is known that the corrosion resistance of corrosion resistant alloys reduces when the Critical Pitting Temperature (CPT) is reached. There is no literature that has examined the corrosion resistance of materials at their CPTs under erosion circumstances. This work therefore aims to investigate the effect of temperature (below and at CPT) on the erosion-corrosion of stainless steels in a (10% NaCl) CO_2-Saturated oilfield environment. It is known that erosion-corrosion resistance depends on the ability of the material to re-passivate after impact by sand and so if the temperature is above the CPT, this will be changed. The erosion-enhanced corrosion of UNS S32760 and UNS S31803 stainless steels at 20 m/s flow velocity and 1500 ppm sand concentration at different temperatures (25, 48 and 61) ^{o}C was evaluated by in-situ electrochemical measurements using Submerged Impingent Jet (SIJ). A potentiodynamic anodic polarisation was used to evaluate the corrosion resistance parameters. Results showed that correlation exists between the erosion-enhanced corrosion and static corrosion resistance parameters of the studied materials.

C9

Finite Element Modelling of Corrosion Product Deposition in Nuclear Plants

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Corrosion Related Unidentified Deposition (CRUD) in nuclear power plants can cause severe issues due to the corrosion of the major metal alloy components of piping and tubing under high temperature, high pressure water environments, as shown Fig 1. The corrosion products can become deposited on complex flow geometries. These deposits reduce heat transfer efficiency, cause Tube Support Plate (TSP) blockage and Flow Induced Vibration (FIV), and generate occluded sites where radioactive species (such as Co60) and water treatment chemicals (e.g. LiOH, B(OH)3) can accumulate. Such uncontrolled chemistry can accelerate the localised corrosion, which may lead to the reduction of tube wall thickness, cladding cracking, fuel leakage and subsequently increased radiation doses for plant workers [2].

The primary objective of this work is to facilitate the development of an all-inclusive deposition model, which will reproduce the morphology of deposits found in actual plants and assist in elucidating the electrokinetic mechanism. In this paper the development and verification of an electric model will be presented. In the model, coupled anode and cathode regions were found at the inlet of a pipe restriction, associated with a region of recirculating flow following the front facing step (FFS), as shown in Fig 2. The corresponding current densities and overpotential at the metal/solution interface were calculated. The coupled anode and cathode may explain the observed deposition process – generating deposits at the front facing step first, followed by a region free of deposits and then repeating ripples of deposited material. At the restriction outlet, a cathode was found.

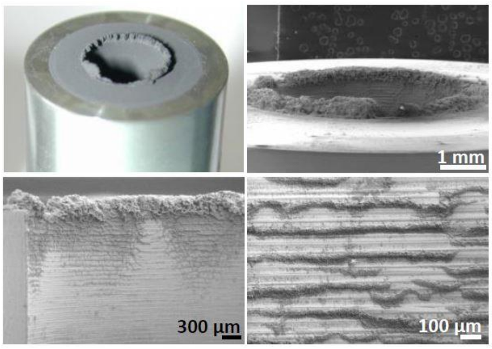

Fig 1. Deposits on Alloy 600 TT in secondary coolant chemistry (T=275°C, P=90 bar) [1]

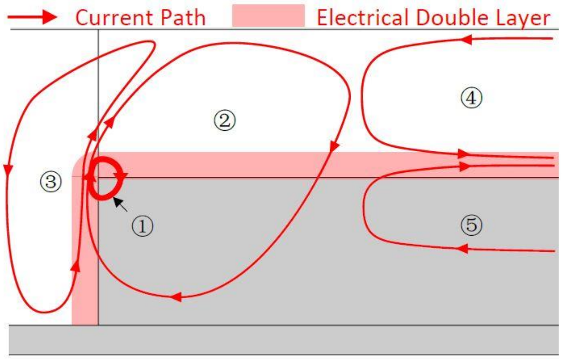

Fig 2. Schematic current path between solution and metal at the inlet of a restriction

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C10

Novel assessment of atmospheric corrosion of brass under sodium chloride-containing water droplets using the scanning Kelvin probe

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Imitating gold at a fraction of the cost is an attribute of brass that has driven watchmakers and minters to utilise this alloy, providing their products with desirable aesthetics while being commercially feasible. Unfortunately, tarnishing under atmospheric conditions reveals the imitator all too soon. This study aims to simulate and measure a fundamental corrosion mechanism on brass.

As a NaCl water droplet becomes deficient in oxygen, a differential aeration cell is established whereby cathodic oxygen reduction becomes preferable at the droplet circumference. This region draws sodium cations to counteract the electronegativity associated with an accumulation of hydroxide anions producing a secondary spreading phenomenon – originating at the droplet perimeter and proceeding radially outside its boundaries.

A combination of time-lapse photography and height-regulated scanning kelvin probe (SKP) potentiometry is used to study cathodic secondary spreading phenomenon, following exposure to NaCl containing water droplets. The rates at which these highly alkaline electrolytic films proceed from the droplet edge are measured and are shown to follow parabolic kinetics. NaCl droplet concentrations ranging 0.1 – 5 mol/dm^3 exhibit significant rates of secondary spreading as shown using time-dependent E_{corr} vs distance plots, though visual analysis was inadequate in measuring similar rates at lower NaCl concentrations. Cl^- sequestering corrosion product under the droplet coupled with migration of Na^+ ions from the droplet bulk lower the solute concentration causing progressive evaporation under constant humidity, shown to be most extreme at lower NaCl droplet concentrations.

C11

Preferential Weld Corrosion of High Strength Pipeline Steels

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The preferential or selective corrosion of weldments can occur due to differences in chemical composition and microstructure between the parent material (PM), heat affected zone (HAZ) and weld metal (WM). A potential difference and galvanic currents generated in the weldment in different environments can sometimes lead to serious localised corrosion.

In practice, the galvanic currents are generally controlled by the addition of a corrosion inhibitor and by ensuring that the composition of the weld metal is selected is slightly more-noble than the parent material. However, it has been shown that a current reversal occurs in some conditions, which result in the weld material becoming more active than the parent metal and severe attack of the weld occurs.
The aim of the project is to study the effect of flow rates on preferential weld corrosion in high strength pipeline steel by investigating the hydrodynamic conditions under which current reversal takes place.

A submerged jet-impingement flow loop enabled a weldment in X65 carbon steel (parent material, weld metal and heat affected zone) to be evaluated at flow rates of 0, 5 and 10 m/s, in brine solution saturated with CO_2 at 1 bar. The self-corrosion rate and galvanic currents from the weldment regions were monitored using linear polarisation resistant measurements and zero-resistance ammeters. Electrochemical impedance spectroscopy was used to complement the LPR measurements and confirm the self-corrosion rates of each part of the weldment in different environments. The total corrosion rates were determined and the effects of oxygen and efficiency of a typical oilfield corrosion inhibitor on this form of corrosion are discussed. The role of surface films that form in brine containing dissolved carbon dioxide will be examined.
The research will support corrosion prevention activities and make an important contribution to corrosion control in the oil and gas industries operating in Indonesia and elsewhere. In this way, it is envisaged that the research will provide advances in terms of improved safety, equipment reliability and associated economic benefits.

Key words: weld corrosion, X65 carbon steel, inhibitor, carbon dioxide

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C12

Influence of Ca^{2+} ions on CO_2 corrosion of X65 carbon steel at elevated temperature

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The effect of Ca^{2+} ions on the corrosion behaviour of carbon steel in a CO_2-containing sodium chloride solution was evaluated using the mass loss technique. Both general and localised corrosion behaviour was investigated over periods from 6 to 96 h at both 80°C and 150°C. In the absence of Ca^{2+} ions, high corrosion rates of 8.6 mm/year and 9.8 mm/year were observed after 6 h of exposure at 80 and 150°C, respectively. Film formation was already recorded at the higher temperature under these conditions. The general corrosion rates after 96 h reduced to 2.5 mm/year and 0.59 mm/year for 80 and 150°C due to the formation of crystalline iron carbonate ($FeCO_3$). In the presence of 5000 ppm Ca^{2+} ions there was more significant effect on the general corrosion rate at the lower temperature of 80°C where the protection afforded by the corrosion product layer was reduced. The extent of localised/pitting corrosion increased through the addition of Ca^{2+} ions at 80°C, indicating that Ca^{2+} plays a role in promoting localised corrosion (as chloride content was maintained compared to NaCl experiments). However, at higher temperature Ca^{2+} addition made little difference to general and localised corrosion rates. Results gathered from scanning electron microscopy and X-ray diffraction indicated that the addition of 5000 ppm of Ca^{2+} modified the corrosion product morphology at both temperatures from surfaces covered entirely by $FeCO_3$ to surfaces covered by iron-calcium carbonate and calcium carbonate.

C13

Comparison of two electrochemical methods (ENM and EIS) for detection of Corrosion under Insulation (CUI)

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Corrosion Under Insulation (CUI) is corrosion that occurs on the metal (normally steel) substrate underneath a heat insulating material. This can develop and progress quickly dependent on the available moisture, oxygen, contaminants and the temperature. CUI is hard to find because the insulation covers all the corrosion signs. Removing and reinstating insulation is a very costly way of inspecting for CUI. So the aim of this work is to develop a good inspection method to identify CUI. Initially an Electrochemical technique is being investigated eg EIS (Electrochemical Impedance Spectroscopy) or ENM (Electrochemical Noise Measurement). This depends on a good ionic path which may exist already or can be created by applying a probe eg a wet pad to the outside of the pipe. The real world situation has been being simulated in the lab by laying a detached piece of vinyl coating whose DC resistance is known and constant on top of different materials which are at different corrosion stages and investigating their electrochemical response. The three types of substrate used are : 1) clean stainless steel, 2) clean carbon steel, 3) rusty carbon steel. The way the EIS data has been analysed is to compare the impedance and phase data at particular frequencies and see if there are any significant differences. Regarding ENM results, the data has been treated to remove drift and spikes and the values of resistance noise (R_n) , voltage noise (V_n) and current noise(I_n) have been calculated and then been compared to see if the level of corrosion can be related to one or more of these numbers. Future work will be to investigate a non-electrochemical method eg pulsed eddy current and then move on from model experiments in a lab environment to investigate real insulation on real pipes.

C14

Corrosion control of magnesium alloys with its hydroxide (using a hydrothermal route).

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Magnesium-based alloys are the lightest engineering alloys with energy saving potential due to the favourable strength to weight ratio. However, the high chemical activity of magnesium can cause corrosion problems. Various protective coating methods are reported to improve the corrosion resistance of magnesium alloys such as conversion coatings, anodising, electrochemical and electroless plating, gas phase deposition and organic coatings[1][2].

The development of a $Mg(OH)_2$ coating on magnesium alloys by a hydrothermal route has recently been explored by Ishizaki and Zhu[3][4]. This coating not only provides protection but is also environmentally friendly. The research reported here concerns hydrothermal coatings deposited on an AZ31B magnesium alloy with de-ionised water at 120°C and 160°C. Coating thicknesses were measured and microstructure was characterised by scanning electron microscopy. The relationship between the thickness and heat treatment time was determined. X-ray diffraction and energy-dispersive X-ray spectroscopy was used for identification. The corrosion behaviour was studied by immersing hydrothermal coated samples into 3.5%wt NaCl solutions for 24 hours and/or 48 hours. Open-circuit-potentials and electrochemical-impedance-spectroscopy was used to evaluate the corrosion resistance of the hydrothermal coatings with respect to immersion time. The hydrothermal coating significantly improved the corrosion resistance of Mg alloy samples and the results and behaviour are discussed.

(This abstract is to be submitted for the ***Corrosion Science Symposium****)*

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C15

Optical Microscopic In-situ Observation of Crevice Corrosion of a Duplex Stainless Steel

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Introduction

Due to the characteristic γ/α duplex phase structure and the special compositional arrangement, Duplex stainless steels (DSS) have excellent corrosion resistance and mechanical properties without sacrificing economic performance. Therefore, DSS are used in severe corrosive environments like high chloride concentration solutions, oil and gas wells. However, it has been reported that DSS suffers from crevice corrosion in the seawater applications. The purpose in this study is to clarify dissolution behaviour on crevice corrosion of DSS by means of optical microscopic in-situ observation and electrochemical measurements to elucidate the crevice corrosion mechanism.

Experimental Procedure

Specimen used in this study was a DSS UNS S31260 (25Cr-7Ni-3Mo-0.15N mass%). Solution was 0.6 M NaCl (50±5 °C). The metal / poly methyl methacrylate (PMMA) crevice was prepared between the specimen and a transparent PMMA cell wall with Ti bolts and nuts. Thus, micro dissolution behaviour of crevice corrosion on a specimen surface was observed in-situ by means of an optical microscope. The specimens were immersed in the solution, and then they were held at 0 mV vs.SCE. Corrosion area was taken a photogragh every 15 s by the microscope during the potentiostatic test.

Results

The crevice corrosion initiated just beneath the edge of PMMA washer, it grew concentrically toward the outside direction of the crevice with time. On the early stage of the crevice corrosion growth, γ phase had already dissolved preferentially at the outer part of the corrosion area. And then α phase of this area started dissolving with corrosion area extending. Finally, α phase dissolved preferentially at that area. Bubble evolution was observed around the corrosion area, and the bubble moved toward the outside of the crevice.

Discussion

The galvanic cell between inside crevice anode and outside crevice cathode consisted of IR drop with large solution resistance is induced, because of tight shape of the crevice. As a result of the IR drop, potential gradient form from the outside to the inside in the crevice. Dissolved metal ions decrease solution pH by its hydrolysis. The bubble observed around the corrosion area was probably hydrogen gas proceeded from the reduction reaction of hydrogen ions. It seems that the low pH solution diffused toward the outside direction of the crevice. It is for these reasons that the distribution of the dissolution behavior1)-2) was observed inside the crevice in this study.

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Comparison of corrosion behaviour of X65 steels in water-containing supercritical CO_2 environments with NO_2/O_2

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Corrosion experiments were performed on X65 carbon steel in water-supercritical CO_2 (SC-CO_2) and under-saturated SC-CO_2 conditions at 80 bar and 35°C in the presence of 100 ppm (mole) NO_2 and 1000 ppm O_2. Results indicated that no corrosion occurs in dry conditions, and the reduction in water concentration from 1770 to 300 ppm results in the general corrosion rate reducing from 0.68 to 0.05 mm/year. There is no significant difference in the extent of localized corrosion observed on the surface. Pitting (or localized attack) rates for X65 ranged between 0.65 and 0.51 mm/year by varying the water concentrations between 1770 and 300 ppm in the presence of 100 ppm NO_2 and 1000 ppm O_2. For water-saturated CO_2 conditions, the general corrosion rate was 0.3 mm/year after 48 hours and approximately 20 times lower than the pitting/localized corrosion rate of 6.8 mm/year recorded in the presence of 100 ppm NO_2 and 1000 ppm O_2. Only crystalline $FeCO_3$ was observed on the surface in water-saturated CO_2 condition with or without adding 100 ppm NO_2 and 1000 ppm O_2. The introduction of both 100 ppm NO_2 and 1000 ppm O_2 inhibited the formation of crystalline $FeCO_3$ for under-saturated conditions.

Additional tests involving solution replenishment over 48 hours in the water-saturated system containing 3ml, 40ml and 100ml solutions were also conducted and indicated that no significant difference in general corrosion rates occurred through adding more water in the system, but the localized corrosion rate reduced from 6.8 to 5.2 mm/year if the water condition increased from 3ml to 100ml in the system.

Analysis of corrosions products formed on the steel surface was performed using X-ray diffraction, X-ray photoelectron spectroscopy, Raman and Scanning electron microscopy. The results suggest that the 100 ppm NO_2 and 1000 ppm O_2 would dissolve into the aqueous water phase quickly and can cause high localized corrosion in water-saturated CO_2 conditions. However, the localized corrosion rate observed in under-saturated condition is far less than that in water-saturated CO_2 condition.

C17

Comparative Studies of corrosion Behaviour of Casting and Laser-treated Mg-1Ca Alloy in Simulated Body Fluid and 0.9 wt% NaCl Solution

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Magnesium alloys used as biodegradable medical implants in physiological environment experience complex forms of corrosion, compared with those in a solution only containing chloride ions. In this study, we performed a comparative study on corrosion behaviour of Mg-1Ca alloy in simulated body fluid (SBF) and in 0.9 wt% NaCl solution, and investigated the effects of laser surface melting.

The results showed that the main corrosion products formed on the cast alloy are MgO and $Mg(OH)_2$ in 0.9 wt% NaCl solution, whereas thick, multilayer Calcium/Magnesium phosphates are formed in SBF solution on top of the MgO. In the SBF solution, for the first two hours, the magnesium hydroxide dominated the whole Mg alloy surface, and phosphates started to build up for longer immersion times. The formation of multilayer phosphates provided a partial protection for the alloy against further corrosion. Such protection was absent in the 0.9 wt% NaCl solution due to the dissolution of MgO and $Mg(OH)_2$.

Excimer laser surface melting in ambient atmosphere induced calcium-rich magnesium solid solution and generated a layer of MgO on the alloy surface. The laser-treated surface was immediately covered by a Calcium/Magnesium phosphates layer, once exposed in the SBF solution, leading to a remarkable decrease in corrosion rate. In 0.9 wt% solution, the laser treated alloy exhibited much less improvement.

C18

Investigating Corrosion Using High-Speed AFM

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The unpredictable nature of stress corrosion cracking (SCC) calls for further research into the mechanisms under which SCC and other forms of destructive corrosion occur. Observation of crack initiation at the nanoscale could give valuable insight into the processes that take place within metals during SCC.

Atomic force microscopes (AFMs) build up topographic maps of a surface by measuring the mechanical response of a sharp probe as it moves across the sample. They are capable of high-resolution imaging of structures and the measurement of mechanical properties at nanometre scales in varying gaseous, liquid and vacuum environments[1]. As a result, AFMs are considered one of the most versatile tools in nanoscience. However, a typical map is formed over a period of 100-1000 seconds, with a finite number of pixels per image, limiting it to static snapshots over small scan areas[2].

The clear potential of AFM quickly gave rise to considerable effort to enhance the image rate and address other limitations, ultimately resulting in the development of high-speed atomic force microscopes (HS-AFMs)[2]. The HS-AFM developed at Bristol Nano Dynamics Ltd. operates at speeds orders of magnitude faster than conventional AFMs, and is capable of capturing multiple frames per second. This allows for direct observation of dynamic events in real-time, with nanometre lateral resolution and subatomic height resolution[2]. Furthermore, HS-AFM is a valuable tool for studying solid-liquid interfaces and as such has the potential for *in situ* corrosion studies[2]. Additionally, the high pixel rate of the HS-AFM means it is capable of mapping macro-sized areas with nanoscale resolution, for detailed pre- and post-corrosion comparisons. The applications for HS-AFMs are still relatively unexplored, and advances in HS-AFM technology are ongoing.

Investigations were carried out into corrosion mechanisms of thermally sensitised AISI 304 stainless steel using the contact mode HS-AFM. Hardness induced topological maps of the surface have been produced, in which chromium carbide precipitation can be clearly seen by means of proper surface preparation[3]. Furthermore, a micro strain rig was custom built such that samples could be imaged under stress, alongside corrosive conditions, for investigations into SCC initiation. Laferrere et al. have previously demonstrated the use of HS-AFM to image nanoscale corrosion events, with parallel electrochemical control[4]. The research carried out builds upon this previous investigation, further substantiating the capability and potential of HS-AFM for applications in materials and corrosion science.

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C19

Using the Scanning Droplet Cell to Accelerate the Formation of Copper Patina Detected in the Marine Environment

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When copper is exposed to the marine environment it reacts with chloride ions to form a copper patina which usually has a green/blue appearance (Marušić, Otmačić-Ćurković, Horvat-Kurbegović, Takenouti, & Stupnišek-Lisac, 2009). The copper patina that forms tends to consist of the crystalline phases; atacamite, paratacamite or clinoatacamite, all of which are complex copper hydroxychlorides ($Cu_2Cl(OH)_3$) (Graedel, Nassau, & Franey, 1987). In certain circumstances patination may not be desirable (Bastidas, Criado, Fajardo, & La Iglesia, 2013) therefore it is important to understand the process of patination and the mechanisms by which the different phases form.

Using the Pourbaix diagram for copper in sea water it was found that a neutral pH would allow the formation of a copper hydroxychloride. However, maintaining a constant pH while polarising copper to generate patina products is difficult in a static solution. Therefore to maintain the neutral pH while applying a potential, the Scanning Droplet Cell (SDC) was used. The SDC provides a localised environment from which corrosion measurements can be made, under a constantly refreshed droplet of solution.

By comparison, when polarising copper in a static solution with the three electrodes in the same solution the pH was noted to become more alkaline. Similarly, when separating the counter electrode from the working and reference electrode using a salt bridge the solution containing the working electrode became more acidic.
XRD analysis found that when polarising copper in a static solution clinoatacamite was formed. However polarising copper under the SDC formed nantokite on the surface of the copper coupon, while paratacamite was detected in the waste solution. These results help to identify the conditions required to form the different phases of copper hydroxychloride.

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Energy & Environmental

Poster Abstracts

EE31

New Mechanical Route for Screening OER Catalysts

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The search for new, highly active, inexpensive electrochemical water splitting catalysts is of growing interest since the latter are a key component in solar-drived water-splitting solar cells. In such cells, whilst H_2 is produced on the cathode, it is the reaction on the anode, the Oxygen Evolution Reaction (OER) which is the most kinetically demanding step in the overall process.[1] The screening of OER materials routinely involves fabricating thin films of the catalysts on conducting substrates from powder dispersions.[2] This process can be extremely time consuming and produce results which are often hard to compare and reproduce, due to a variety of reasons, including mass loading effects. In this study, a novel mechanical route for producing reproducible electrodes of new OER catalysts in powder form is described. These electrodes can then be readily utilised in a rotating disc electrode (RDE).

In order to test our mechanical fabrication procedure, RuO_2, was synthesised by the Adams method, and used as the active OER material.[1, 3] The RDE electrodes were produced by pressing a known amount of Pt powder with Ru Adams, and minimal amount of PTFE binder powder on top, using an infra-red die and hydraulic press. The resulting Ru/PTFE and Pt layered disc is illustrated in Fig. 1(a) and (b). The Ru/PTFE/Pt disc has exceptional OER properties when compared to literature values for RuO_2; e.g. the overpotential at 10 mA cm^{-2} is 0.26 V, Fig. 1(c), and exhibits a Tafel slope of 30 mV dec^{-1}.[1] Additionally, this mechanical technique provides a facile and reproducible route for OER electrode fabrication from powders. Thus this approach allows for the rapid screening of any new potential OER material, which will also be explored in this study.

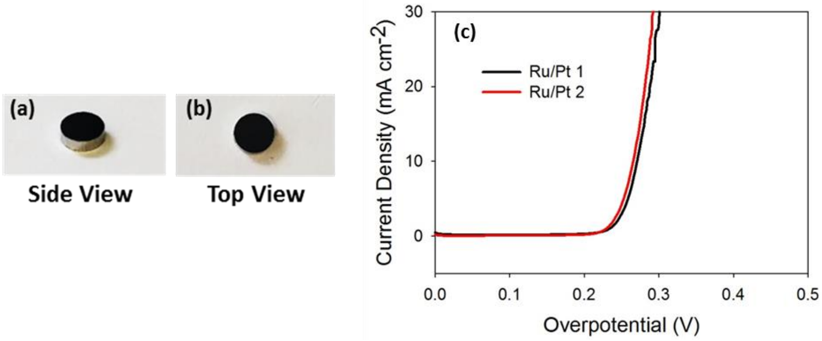

Figure 1 (a) XRD analysis of the Ru Adams with COD reference pattern for RuO_2 (b) Picture of the pressed Ru Adams top and Pt powder disc and (c) OER Linear sweep voltammograms.

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EE32

Electrochemical Behaviour of H_3PO_3 on Pt Electrode in Hot Concentrated H_3PO_4 Electrolyte

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Concentrated H_3PO_4 represents the most widely utilised proton-conductive phase in membranes for high temperature proton-exchange membrane fuel cells (HT PEM FC) operating at 120-200 °C. Acid is usually immobilized in polybenzimidazole-type polymer.

However, application of H_3PO_4 is connected with several drawbacks. Firstly, its aggressive nature leading to corrosion of Pt catalyst is widely known. Secondly, adsorption of $H_2PO_4^{2-}$ anions on Pt surface negatively influences kinetics of O_2 reduction reaction. The stability of H_3PO_4 is also an issue, though this fact is not widely known. In particular, H_3PO_4 is at elevated temperature reduced at Pt surface by H_2 to phosphorus impurities. Understanding of this process is still far insufficient, although Pt-P and H_3PO_3 were already confirmed as the products of H_3PO_4 reduction [1]. Effect of these impurities on HT PEM FC performance has not been investigated yet. Our previous work was focused mainly on H_3PO_3 electrochemical behaviour on Pt electrode in aqueous electrolytes at ambient temperature [2].

The goal of this work is to qualitatively describe electrochemical behaviour of H_3PO_3 on polycrystalline bulk Pt electrode in 99% H_3PO_4 electrolyte. These conditions are directly relevant to HT PEM FC operation. Measurements were performed using voltammetry techniques in a specially designed electrochemical cell. Impact of H_3PO_3 concentration and electrolyte temperature on shape of measured voltammograms was studied as well as H_3PO_4 stability at various temperatures. Results pointed out several important features of H_3PO_3 electrochemical behaviour on the Pt which will be presented. This data can eventually contribute to optimisation of HT PEM FC operational regime and, quite possibly, even to increase of its lifetime.

Financial support by the FCH JU within the framework of the DEMSTACK project, contract No. 325368, by MSMT CR project No. 7HX13002 and financial support from specific university research (MSMT No 20-SVV/2017) is gratefully acknowledged.

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EE33

Electrochemical CO_2 reduction and formic acid oxidation on $Pd_{Ml}Pt(111)$ and $Pd_{Ml}Pt(100)$ electrodes

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Formic acid oxidation occupies an important role in fuel cell technology and has been considered as a model reaction for providing a simplified example of more complex organic molecules that can also be applied to this field. Although general agreement exists that Pd is more active towards formic acid oxidation than Pt and Au, the true nature of the underlying reaction mechanism is still open for discussion. As the reverse reaction, efficient production of formic acid from CO_2 reduction has been reported on PtPd nanoparticles from our previous study. We study here the formic acid oxidation on epitaxially grown Pd monolayer on Pt(111) and Pt(100) single crystals by means of cyclic voltammetry with rotating electrodes and online electrochemical mass spectrometry. Our results show that $Pd_{ML}Pt(111)$ exhibits enhanced formic acid oxidation activity at low potential without CO poison formation and considerably lower overpotential for the reduction of CO_2 to formic acid. In the case of $Pd_{ML}Pt(100)$, we find the unique mass transport controlled formic acid oxidation for the first time. These new research results help to understand elementary steps during the conversion of CO_2 and formic acid on Pd based catalysts and highlights the effects of electrolyte pH and surface structure.

EE34

Control of Thickness and Morphology of Poly-(3,4-ethylenedioxythiophene) by Electrochemically Growth (E-PEDOT) and Manipulation of its Conductive State for Use as Anodic Buffer Layer in Organic Photovoltaic Cells

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This contribution presents the electrochemical growth and manipulation in the conductance, thickness and morphology of the polymer film poly[3,4-ethylenedioxythiophene] electrochemically (CV or CA) obtained (E-PEDOT), from the monomer 3,4-ethylenedioxythiophene (EDOT)[1] onto the transparent conductive anode indium-tin oxide (ITO). For this study, different mixtures of anhydrous organic solvents were used, resulting in low polymerization kinetics of the monomer EDOT[2] in Toluene-Acetonitrile (4:1, v/v). Also was found which a low concentration of the monomer and a suitable potential of electropolymerization, allowed us to gain better control the growth of the polymer.[3] Finally, these E-PEDOT films were used as buffer layers in organic photovoltaic cells (OPVs) with bulk heterojunction architecture and their performance was compared with those constructed with the classical spin cast deposited PEDOT:PSS buffer.

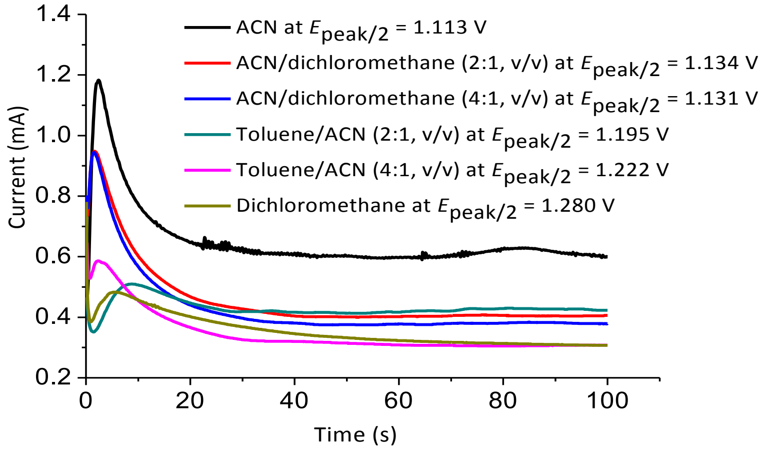

Figure 1. Potentiostatic polymerization of EDOT, in the different organic media at the anodic half-peak potential ($E_{peak/2}$)

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EE35

Synthesis of highly durable and methanol tolerant Pt catalyst for oxygen reduction reaction by ultraspray method

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Direct methanol fuel cells (DMFCs) are attractive for their possible implementation in portable applications, due to the high energy density of methanol, and their relatively high energy-conversion efficiency. Despite the potential commercialisation of DMFCs, the sluggish kinetics of the oxygen reduction reaction (ORR) that occurs at the cathode is slowing down their development [1]. Current state-of-the-art of catalysts for ORR, highlights Pt-based materials as the most efficiency catalysts in terms of activity [2] although further improvements in their durability are necessary [3]. Additionally, DMFCs might suffer the problem of methanol crossover, the non-reacted methanol permeates the cathode compartment through the polymer membrane causing a decrease in the performance of the cathode catalyst. Therefore, the improvement in the durability and the tolerance to methanol crossover of Pt catalysts are the main challenges for large scale commercialisation of DMFCs.

Herein, we report an ultrasonic spray pyrolysis (USP) method combined with annealing process for the synthesis of active and highly durable platinum nanoparticles embedded in carbon microspheres (PtNP@CMs) as electrocatalysts for ORR. Materials prepared also showed excellent tolerance to methanol crossover in acid environments. The catalytic activity for the ORR has been strongly influenced by the Pt loading used as precursor, resulting in an effective method of synthesis for the reduction of the Pt content in the final catalysts. Moreover, low Pt loadings and higher heat treatments yield high durable catalysts for the ORR in acid environments. Notably, the most durable PtNP@CM catalyst synthesised display no statistical difference in mass activity after 3500 cycles. The better stability of this catalyst might be promoted by the fact that Pt nanoparticles are more embedded in the spherical carbon structures, based in microscopy analysis. Furthermore, the most active catalysts showed an excellent tolerance to the addition of 3 M of methanol measured via a current-time (i-t) chronoamperometric method at 0.55V. We discuss the structural and chemical properties that might be at the origin of the excellent durability. The intrinsic scalability of the proposed synthetic method holds promise for commercial applications of these materials.

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EE36

Versatile 3D-Printed Electrodes for Electrochemical Flow Reactors

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Porous electrodes in flow-by configuration afford significantly higher active surface area, mass transport and space time yield in comparison to planar electrodes. These electrodes are applied in numerous industrial processes, including inorganic and organic electrosynthesis, treatment of process streams, metal recovery and electrolysis reactions. In this contribution [1], we present a novel 3D-printed flow reactor electrode with a complex, intricate geometry impossible to replicate by computer numerical control (CNC) machining or other classical manufacturing methods. Such 3D-printed electrodes offer an alternative to the currently available metal and carbon-based meshes, foams and felts, delivering a new genre of free-form porous electrodes having tailored composition, catalytic activity, active surface area, fluid flow characteristics and mass transport properties.

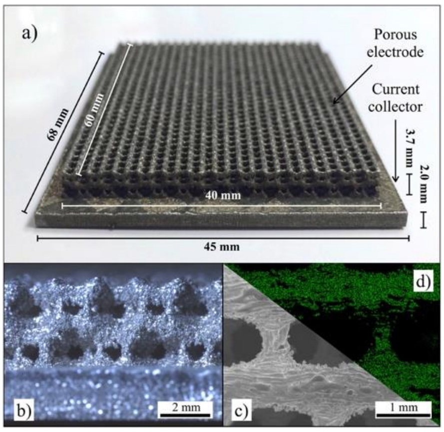

Fig 1. 3D-printed Ni/SS porous electrode. a) the macro structure, b) micrography of the electrode, c) SEM of an individual pore, d) nickel EDS mapping for the same pore opening.

The mass transport characteristics of a Ni/SS 3D-printed porous electrode compare well and exceed those observed in typical planar, mesh and RVC electrodes. This opens the possibility to employ geometrically complex structures produced by additive manufacturing techniques as high performing, robust electrodes in specialised electrochemical flow reactors. Electrodes having different roughness, microstructure, orientation, composition, electrocatalysis and fluid flow environment can be 3D-printed.

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EE37

Targeting the Electrochemical Activity of Biofilms

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Microbial fuel cells (MFCs) have sparked interest within the portable electronics industry where bacteria can be used to power low energy devices through the formation of a redox-active biofilm at an electrode surface. This study explores supercapacitors and targets the electrochemical activity of biofilms to harness the energy that bacteria produce. This could significantly increase the energy that can be generated in applications involving MFCs and potentially provide an alternative renewable fuel source for use in small electronics. A supercapacitor was designed and different carbon-based electrode materials were prepared and tested including carbon nanotubes, graphite and graphene oxide. The electrode materials were also modified with MnO_2 and a redox-active *Pseudomonas Fluorescens* biofilm was grown on electrode surfaces. A range of electrochemical techniques were then employed to quantitatively study the redox activity of the biofilms and determine the bacterial contribution to charge storage. These techniques included cyclic voltammetry, galvanostatic charge/discharge measurements, differential pulse voltammetry and electrical impedance spectroscopy. The outcome of the investigation has shown promising results. The specific capacitance of the MnO_2-modified CNT supercapacitor for example, increased significantly from 79 ± 7 $\mu F\ g^{-1}$ in the absence of bacteria, to 170 ± 9 $\mu F\ g^{-1}$ after the formation of a 72-hour biofilm. These results indicate that bacterial biofilms could well be the future for energy production in small electronic devices.

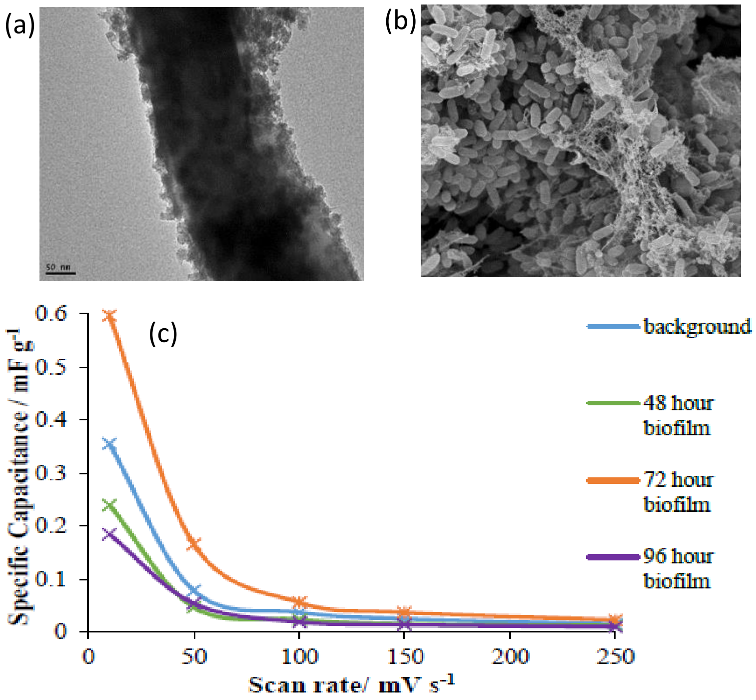

Figure 6. a) TEM image showing the uniform deposition of MnO_2 at the surface of a CNT b) SEM image showing formation of biofilm after 48 hours on CNT:MnO_2 (4 to 1 by mass), c) Comparing the specific capacitances of the supercapacitor in the absence and presence of a biofilm at different scan rates

Capacitive Properties of Nitrogen Doped Amorphous Carbon Materials for Electrocatalytic Applications

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Non-crystalline carbon materials play an important role in electrochemical energy storage and energy conversion technologies.[1] Disordered graphitic carbon scaffolds structures typically result in excellent performance in capacitive and electrocatalytic applications.[2] Nitrogenation of the carbon matrix is an effective way of introducing disorder in different forms, including changes in morphology, electronic structure and surface functional groups.[3] However, it is not well understood how to control the interplay between these effects in electrochemical applications. The aim of this project is to improve our understanding of how compositional changes in the carbon translate into different electrochemical properties by synthesising nitrogenated amorphous carbons (a-C:N) with smooth topography but different levels of nitrogenation. a-C:N electrodes were deposited via sputtering deposition and characterised by XPS, Raman spectroscopy and determination of capacitive properties. In this study the synthesis of N doped amorphous carbon is discussed in addition to how annealing affects the properties of N-doped amorphous carbons. The capacitive properties of deposited a-C:N electrodes were investigated in aqueous and organic electrolytes. XPS studies reveal that the density of N-sites increases with the amount of nitrogen gas used in the deposition, while annealing has the effect of reducing N-site concentration. Raman studies reveal that initial N-doping and disorder can affect the number and size of sp^2 clusters of a-C. Capacitive properties of these electrode materials were analysed by using Electrochemical Impedance Spectroscopy (EIS). Capacitance of amorphous carbon increases with N-doping. Annealing at 900 °C for 1 h also decreases the capacitance of N doped amorphous carbon electrodes. These results are important for an improved understanding of nitrogenated carbon materials for energy conversion and other applications.

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EE39

Transition Metal Coordination Complexes with Redox Non-Innocent Ligands for Flow Battery Energy Storage

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Due to inherent, and often unpredictable intermittency in renewable technologies, a network dependent on such electricity is not feasible. To be completely reliant on renewables whilst still guaranteeing an uninterrupted supply, efficient grid-scale energy storage devices are necessary, to store excess energy at off-peak times for use when demand increases. Redox-flow-batteries (RFBs) are electrochemical energy storage devises which are suitable for grid-scale energy storage due to their easily scalable design; RFBs store complementary redox materials, dissolved in liquid electrolytes, in separate storage tanks which are cyclically pumped through a flow-cell stack where they are reversibly charged or discharged. Hence, RFBs decouple battery power and capacity allowing either property to be independently scaled; by increasing the electrode area or electrolyte volume respectively.[1] Furthermore, RFBs offer long lifetimes, high energy efficiencies and require low maintenance due to their simple modular design making them attractive for various applications including back-up and off-grid installations.

Aqueous flow batteries such as the all-vanadium RFB have achieved commercial success however their energy densities have reached the maximum that can be reasonably achieved, $\cong$ 33 W h L^{-1}, due to the narrow 1.23 V electrochemical window of water and maximal solubility of their redox material.[2] In contrast, non-aqueous RFBs can theoretically achieve much higher energy densities by use of solvents which offer larger stability windows (acetonitrile is stable over 5 V for example), and redox materials which undergo multiple electron transitions at high redox potentials. Many non-aqueous systems have been studied thus far, utilising a wide range of chemistries from small organic molecules to transition metal coordination compounds,[3] however significantly higher energy densities than aqueous RFBs have not yet been realised due to low solubilities and cell potentials which do not fully exploit the solvent stability window. The work by our group aims to surpass these limitations by utilising transition metal complexes with redox 'non-innocent' ligands which are capable of multiple electron transfers.[4] Such ligands are known to be redox active and interfere with the metal electronic states, imparting a degree of electron delocalisation across the molecule, allowing numerous oxidation states to be accessed.[5] Hence, a single species, two or three electron battery may be created with double or triple the energy density of previously studied non-aqueous RFBs.

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EE40

Synthesis and Electrochemistry of Advanced Electrocatalysts Based on Ternary Metal Nitrides

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Recently, attention is being drawn to ternary metal nitrides as new applications for them arise. Metal nitrides have attracted much interest in terms of their structural type and their activity as catalysts in a number of reactions.

Electrochemical systems are currently heavily dominated by expensive noble metals, hence transition metal nitrides have been applied to various electrochemical systems such as fuel cells as a viable alternative[1]. Bonding and structural features contribute to their attractive electronic conductivity and catalytic activity, whilst their high melting points and resistance against corrosion make them an attractive choice with regards to electrode materials[2].

In this work, a range of compounds have been synthesised by adding small cobalt additions (between 0 % and 20 %) to the parent phase Ni_2Mo_3N, using a modification of the Pechini method[3]. XRD analysis showed a single phase with a linear increase in lattice parameter as further cobalt is doped into the system. Particle sizes of 90 nm were calculated.

The compounds synthesised show a good activity towards the hydrogen evolution reaction, showing an attractive onset potential and high activity. Initial analysis suggests the 15 % cobalt sample ($Ni_{1.7}Co_{0.3}Mo_3N$) possesses the most desirable activity towards the HER, with a more positive onset potential and greater activities.

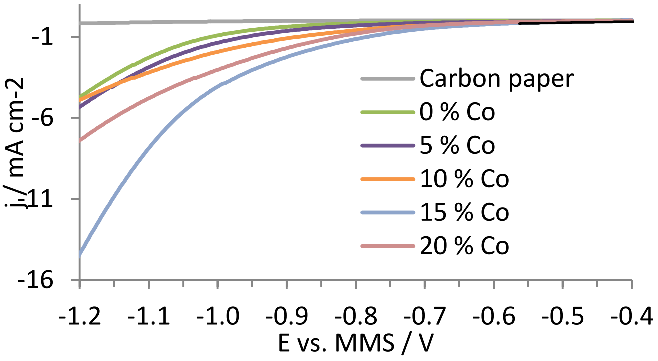

Figure 7 Linear sweeps of electrodes in 0.1 M H_2SO_4, purged with N_2 (*ca.* 30 min.) prior to measurements being taken. Scan rate 5 mV s^{-1}.

X-ray absorption spectroscopy (XAS) suggested the incorporation of cobalt into the structure made both metal centres redox active, as oxidation was seen of the molybdenum, cobalt and nickel at open circuit potential with subsequent reduction at more negative potentials. These results were not, however, seen for Ni_2Mo_3N.

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EE41

Catalytic Activity of Electrodeposited MoS_2 Films for Hydrogen Evolution

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Electrolysers are expected to play a major role in the green hydrogen economy, as they offer a clean and sustainable approach to the production of hydrogen fuel. These devices utilize (renewable) energy to split water, with catalysts required to efficiently generate oxygen at the anode and hydrogen at the cathode. In the latter case, platinum is regarded as the benchmark due to its high activity and stability.[1] However, there is a need substitute this critical metal catalyst with earth-abundant alternatives, in order to reduce device costs and improve sustainability. In recent years, molybdenum disulphide has received much attention as one such alternative to platinum for the hydrogen evolution reaction (HER).[2]

In addition to chemical and physical routes, amorphous and nanostructured MoS2 and MoS3 films can be prepared by electrodeposition, with the stoichiometry and structure of the final catalyst being dependent on the deposition parameters.[3, 4] In this work we compare the HER behaviour of MoS2 films prepared by various electrochemical approaches including cyclic voltammetry, constant potential electrolysis and rapid potential pulsing. We demonstrate that the catalytic acitivity and short-term stability of the film is governed largely by film thickness, which can be controlled by the number of voltammetric cycles or deposition time (Fig. 1).

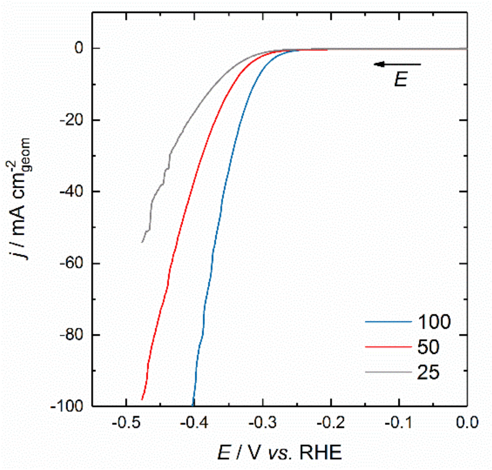

Fig. 1: Linear sweep voltammograms of HER at electrodeposited MoS_2, measured at a scan rate of 5 mV s^{-1} in H_2-saturated 0.5 M H_2SO_4, under rotation at 1600 rpm. The catalyst films were deposited on glassy carbon substrates by cyclic voltammetry; the legend indicates the number of CV cycles used to prepare the films.

In addition to HER testing using a rotating disk electrode, we use Atomic Force Microscopy and Raman spectroscopy to monitor the catalysts *in situ*, enabling the performance metrics of the films to be correlated with their chemistry and morphology.

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EE42

Developing magnetic resonance imaging (MRI) for studying batteries

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There is significant interest in the development of improved energy storage devices, in particular, the development of high performance advanced batteries. In order to improve such energy storage devices, a full understanding of the distribution of chemical species, ion transport, side reactions and structural changes of the electrodes, *in operando*, is required.

Magnetic resonance imaging (MRI) is a promising tool to visualize and understand the electrochemical processes inside batteries and it can provide significant insight in a non-invasive way[1]. There have been ^{7}Li MRI studies of lithium-ion batteries[2-4]. Potential replacements for Li-ion batteries are zinc[5] and aluminium[6] based batteries. However, in order to study zinc and aluminium batteries, an alternative method should be developed to study the electroactive species using ^{1}H NMR signal from the electrolyte[5].

This project focuses on using MRI techniques to determine the speciation and distribution of electroactive zinc species in novel electrolytes, such as room temperature ionic liquids (RTILs) and deep eutectic solvents (DESs). Studying the effect of Zn^{2+} on the NMR parameters, such as T_1 and T_2 relaxation times, of the electrolyte will facilitate visualization of the distribution of zinc species in RTILs or DESs based batteries.

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EE43

An Electrochemical Impedance Study of the Oxygen Evolution Reaction at Nickel-Cobalt Oxides in Base

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First row transition metal oxides (Co_3O_4, NiO, Fe_2O_3, MnO_2…) catalyst are promising materials for superconductors, water splitting, microelectronics and electro-sensing.[1] The singularity of transition metal oxides proprieties lie in the nature of the partly electron filled d-shell which produces an easy transfer electron back and forth between free oxygen and transition metal ions shell.[2] Although these materials have many applications, this project focuses on the oxygen evolution reaction (OER). Poor OER catalyst limits the efficiency of H_2 production from water electrolysis making the process economically unfavourable. It is widely believed that NiO along with Co_3O_4 generates a synergetic metal oxide, $NiCo_2O_4$, which has been reported as a stable catalyst in alkaline media for oxygen evolution reaction.[3, 4] In this perspective, the investigation of the oxygen evolution reaction in an aqueous alkaline solution using different composition ratio of Nickel-Cobalt oxide prepared by thermal decomposition is presented. The research herein focuses on the analysis of different physical electrode properties such as film resistivity and double layer capacitance, along with the kinetics and reaction mechanism during the OER. These proprieties were studied using electrochemical impedance spectroscopy (EIS) and Tafel plot analysis. The oxide films were synthesised using thermal decomposition method of the precursor salt ($Ni(NO_3)_2$ and $Co(NO_3)_2$) at 400°C in air. Titanium wire (0.6 cm^2 area) was used as electrode support. All the experiments were carried out in 1M alkaline solution and iR (solution resistance) corrected.

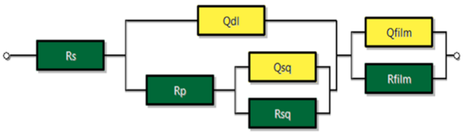

Fig 1. Equivalent circuit used in the CNLS fitting of the impedance data presented in Fig 2.

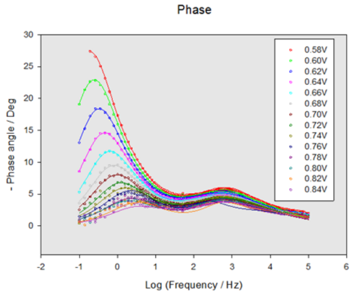

Fig 2. Electrochemical impedance spectra recorded in 1 M NaOH at a series of potentials associated with OER in Bode format.

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Sensors & Analytical

Poster Abstracts

SA13

VOLTAMMETRIC ANALYSIS OF VITAMIN B_1 B_2 & B_6 USING SCREEN PRINTED CARBON ELECTRODES

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Vitamins are an important group of organic compounds which are essential for healthy growth and nutrition. They can be found in pharmaceutical products, foods, and drinks. Most vitamins have been reported to possess electroactive behaviours in media of a specific pH. These reports have involved various electrode materials such as platinum, mercury, and glassy carbon. Only a few reports have appeared which describe the application of unmodified screen printed carbon electrodes (SPCEs) to vitamin analysis. However such devices offer advantages such as mass production in a wide range of geometries and low cost; consequently they can be considered disposable.

Cyclic voltammetry has been used to ascertain the electrochemical behaviour of the water soluble vitamins thiamine (B1), riboflavin (B2), and pyridoxine (B6) using SPCEs with a selection of buffer solutions. All three vitamins produced well defined oxidation peaks in a phosphate buffer at pH 11. In the present investigation square wave voltammetry was employed to quantify the three vitamins simultaneously, with a single scan performed in only 8 seconds. The successful application of the rapid square wave voltammetric assay, employing SPCEs, to both a multi-vitamin supplement and a food product will be presented.

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Acknowledgments

The authors would like to thank Gwent Electronic Materials Ltd (GEM) for supplying the screen printed carbon electrodes.

SA14

Development of an Assay for the Beta-Agonist Salbutamol in Serum using Voltammetry in Conjunction with a Disposable Screen-Printed Carbon Electrode

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Salbutamol, [1-(4-hydroxymethyl phenyl)-2-(t-butylamino) ethanol] also known as albuterol is a beta-2, non-catecholamine partial agonist, used to treat asthma and other airway diseases. Salbutamol may be exploited by healthy individuals to enhance performances in sport through its anabolic and stimulatory effects on the body. Therefore, the World Anti-Doping Agency (WADA) have drawn up strict regulations to prevent unfair, competitive advantages in sport by people using the drug above a designated therapeutic level.

The aim of the present study was to develop a simple, economic assay to determine salbutamol in serum which may have application in determining possible abuse of the drug in sport. Screen-printed carbon electrodes (SPCEs) have been attracted great interest due to the possibility of their mass production in a wide range of geometries at low cost; therefore these devices can be considered disposable. Our group have successfully developed electrochemical sensors and biosensors based on SPCEs for the determination of a wide range of biologically important compounds. Consequently we decided to explore this approach in the present investigation.

Initial studies were performed using cyclic voltammetry, with phosphate buffers over a wide pH range in order to understand the nature of the electrochemical reaction and to deduce the optimum buffer for quantitative analysis. Well-defined voltammetric peaks were obtained over the pH range studied with currents of highest magnitude being produced under alkaline conditions. Several different voltammetric waveforms were compared and square wave voltammetry was selected as it resulted in the best sensitivity and selectivity for the measurement of salbutamol. In order to evaluate the assay, known concentrations of salbutamol were spiked into serum, a simple solvent extraction step was performed and the reconstituted residue was analysed by square wave voltammetry; the results suggest that the method holds promise for screening salbutamol in serum samples.

SA15

Electrochemical Detection of Cellular Iron Reduction in Epithelial Cancer Cell Lines

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Iron is an essential nutrient required for the functionality of many living organisms. In mammals, iron plays a key role within a variety of processes. These include the transport and storage of oxygen, as well as the catalysis of key reactions throughout the body. Extracellular iron has been shown to be reduced via transplasma membrane electron transport systems (TPMETS). We have utilised the electrochemical mediator ferricyanide as a tool to measure the reduction capacity of three epithelial cancer cell lines (A549, Calu-3 and H1299) toward iron. Linear sweep voltammetry was used to monitor the magnitude of oxidation current which could be correlated to the concentration of iron reduced. Viability studies were also carried out to ensure our iron compound, potassium ferricyanide, did not cause cytotoxicity upon incubation. The capability of both cell lines to reduce iron hints at the presence of ferrireductase enzymes present in the membrane of the cells. Our further work will seek to confirm and quantify these enzymes, with further implications for understanding the underlying biochemical modulation of iron transport via transplasma membrane electron transport systems. This work is important for the understanding TPMET systems in more detail, and in particular adsorption of ions onto membranes.

SA16

The Role of Electrochemistry in Understanding the Drugs Targeting Copper Complexation for Alzheimer`s Disease

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Complexation of certain metals with therapeutic compound is assumed to be significant in metal dependent diseases. The medicinal uses and applications of metals and metal complexes are of increasing clinical and commercial importance. In the search for new therapeutic tools against Alzheimer's' disease, complexation of copper with ligands that target prevent aggregation of beta amyloids in presence of metal ions such as Cu^{2+}, were characterized using voltammetry and spectroscopic techniques. Chelation therapy has been scientifically proven to remove excess toxic metals before they can damage the body, but at the same time chelation is not completely risk free. Henceforth the challenge of well-designed metal-based drugs is to minimize possible toxicity. Oxygen is required for many life-sustaining metabolic reactions. Oxygen and its activated intermediates, ROS (reactive oxygen species), however, may react with cellular components with resultant degradation or inactivation of essential molecules. This work reports results on the complexation of ligands with copper (II) using glassy carbon electrode. The drugs were designed to cross the blood brain barrier (BBB). The basic aim of this study is to understand the role of drugs targeting copper complexation for Alzheimer`s disease. The binding parameter such as the binding constants was determined from voltammetry data.

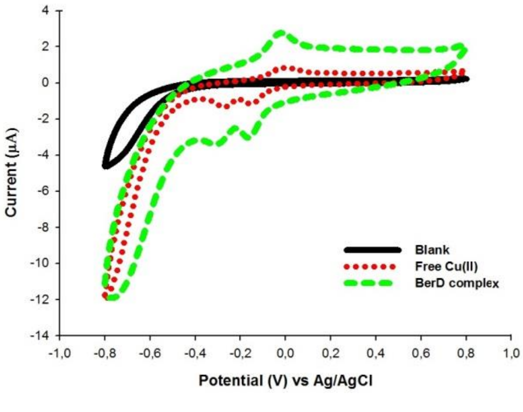

Fig. 1 Overlaid voltammogram of bare glassy carbon electrode, free copper and Cu-BerD complex.

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SA17

Detection of Biomarkers of *Pseudomonas aeruginosa* Bacteria by Electrochemistry at the Interface between Two Immiscible Electrolyte Solutions

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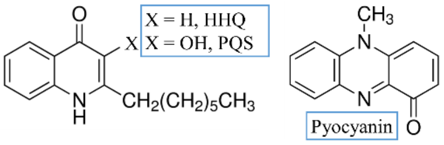
Chronic lung infections with ***Pseudomonas aeruginosa*** are directly responsible for the large majority of premature deaths in CF patients [1]. After initial colonisation, a window of opportunity exists, during which establishment of chronic infection may be prevented or delayed by aggressive antibiotic eradication therapy in the majority of patients [2]. *P. aeruginosa* bacterial populations synchronise group behaviour (such as biofilm development, swarming motility, *etc.*) by Quorum Sensing (QS), a chemical cell-to-cell communication process regulated by small extracellular signalling molecules [3]. Molecules used in QS, such as ***2-heptyl-4(1H)-quinolone (HHQ), pseudomonas quinolone signal (PQS) and pyocyanin***, are unique indicators of the presence of *P. aeruginosa* in clinical sputum samples (see Figure).



In this presentation innovative ***electrochemical sensors*** to detect *P. Aeruginosa* QS biomolecules will be demonstrated that generate characteristic signals from their adsorption at polarised immiscible water-oil interfaces. The latter approach offers several significant advantages: (i) soft interfaces are pristine and defect-free, thus the time-consuming step of polishing electrodes between measurements is eliminated; (ii) pre-concentration steps can be implemented with stripping voltammetry to provide sub-nM limits of detection; and (iii) the hydrophilic/hydrophobic nature of the sensors completely circumvents any issues due to analyte solubility

The premise of this research is to take advantage of the inherent amphiphilic nature of QS molecules, a trait developed to facilitate their interaction with bacterial cell membranes. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) responses at *pristine* polarised water/1,2-dichloroethane interfaces give clear unambiguous signals in the presence of each QS biomolecule. Variables such as pH of the aqueous phase are investigated.

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SA18

Interactions of thiolated gold nanoparticles with lipid membranes

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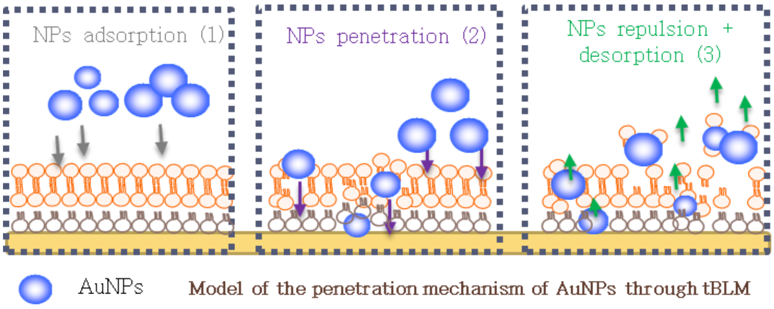
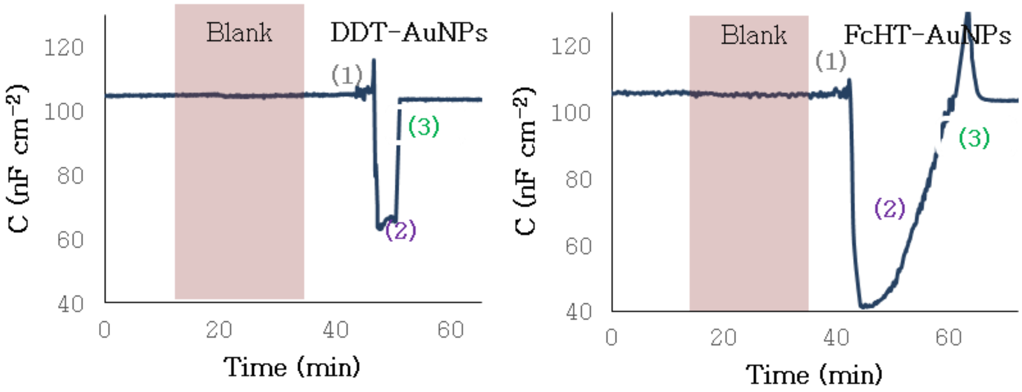
Gold nanoparticles (AuNPs) have shown to have very unique physiochemical properties; they are widely used as materials in the development of devices within the nanotechnology field in their use in pharmaceuticals, medical and biological applications.[1] There are many advantages to NPs in the biomedical field; these have a high surface area to volume ratio giving advantageous properties as good drug carriers, manipulation of size and charges allows the enhancement of the surface reactivity of NPs.[2]
The work reports the study of non-electroactive and electroactive thiol-stabilised AuNPs and their interactions with artificial cell membranes (tBLM models) using electrochemical and microscopic techniques.



Model of the penetration mechanism of AuNPs through tBLM



CVs of the SAM-modified gold electrode in 0.1 M KNO_3 at 60, 120, 240, 360, 480 and 900 min immersion times. Scan rate: 50 mV/s.

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SA19

Cellulose in Sensors and Logic Gates: Ionic Diode Phenomena Based on Surface Charges in Reconstituted Cellulose Films

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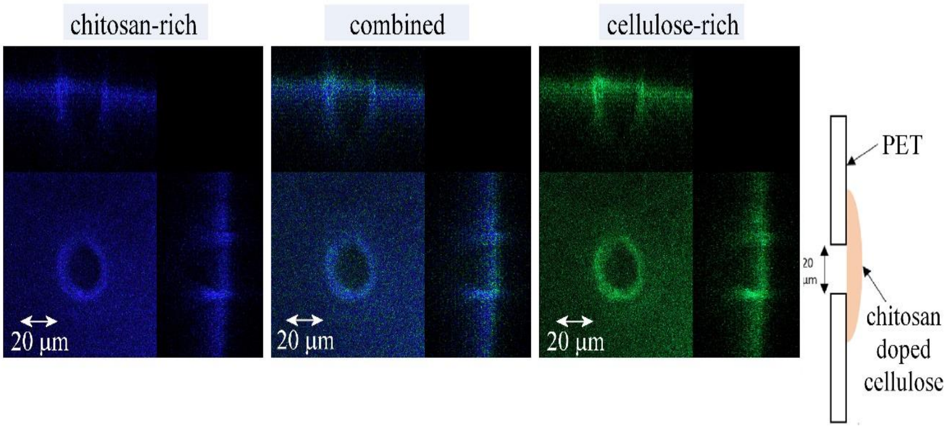
Cellulose materials provide the most abundant polymeric material on earth and there are many applications deriving from modified forms of cellulose. In particular, new fields are developing in sensing and in "paper electronics". Here, the ion flux through reconstituted cellulose is investigated with the aim of employing ion flux in ionic diode sensors [1-3] to detect environmental pollutants, DNA, or disease bio-markers. Ion flux is measured as current through the membrane (which is deposited onto a microhole). The surface charge of cellulose (negative) and, for example, of chitosan a modified version of cellulose (positive) are employed to control the ionic current signals. Modified cellulose surfaces with switchable charge are employed in sensors.



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SA20

Simultaneous Determination of Epinephrene and Homovanilic Acid on Bromophenol Blue Modified Glassy Carbon Electrode

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Development of rapid methods for the determination of neurotransmitters and their metabolites is significant in clinical diagnosis. Herein, we report the development of a sensitive and reliable voltammetric technique suitable for the simultaneous determination of epinephrine (EP) and homovanilic acid (HVA) based on the electrochemical oxidation of these compounds on polybromophenol blue modified glassy carbon electrode (GCE). Bromophenol blue was electropolymerized on the GCE surface by cyclic potential scanning from -1 V to 1.8 V using a solution of 0.5mM of bromophenol blue prepared in PBS (pH=6). The modified electrode was characterized by SEM and EIS. Under optimized conditions, the oxidation peak current of EP and HVA showed a linear dynamic range from 2.0 µM to 50.0 µM for each with detection limits 0.82 µM for EP and 0.50 µM for HVA respectively. The effect of coexisting species on the electrochemical determination was also investigated. The potential of the sensor to be used for simultaneously determining these species in real samples needs to be explored further.

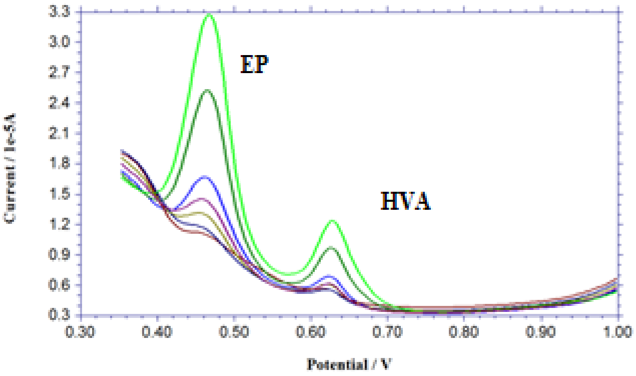

Figure 8 Simultaneous determination of EP and HVA on modified electrode

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Physical & Fundamental

Poster Abstracts

PF13

Electroplating of Aluminium from Novel Ionic Liquids

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In various applications, such for automobiles, aviation, household appliances, containers and electronic devices, aluminium is used. This due to Al having many excellent properties such as good electrical and thermal conductivities, low density, high ductility, and good corrosion resistance.[1] Electroplating of Al is normally achieved from classic ionic liquids, which are expensive, toxic and highly sensitive to air.[2] This work will show, for the first time, the electrodeposition of Al from novel ionic liquids, where these liquids are about ten time cheaper than traditional ionic liquids, easy to prepare, and less sensitive to moisture. The novel solvents were (1.5:1) $\mathrm{AlCl_3}$:acetamide, (1.5:1) $\mathrm{AlCl_3}$:*N*-methylacetamide and (1.5:1) $\mathrm{AlCl_3}$:*N,N*-dimethylacetamide eutectic liquids.[1, 3] Thick and adherent pure Al coatings have been achieved on copper and mild steel substrates from these types of solvents. The electrochemical properties of the plating liquids have been studied using cyclic voltammetry, and the resultant surface morphologies and composition of the Al coating were revealed by SEM/ EDX (Fig 1). XRD was used to examine the crystal structures of the Al coatings. In addition, corrosion of the Al deposit in brine (0.1 M $\mathrm{NaNO_3}$) was measured, where it was found that the Al coatings achieved from the $\mathrm{AlCl_3}$:acetamide and $\mathrm{AlCl_3}$:*N,N*-dimethylacetamide eutectic liquids had a higher resistance to corrosion compared to the Al films produced from $\mathrm{AlCl_3}$:*N*-methylacetamide based liquid.

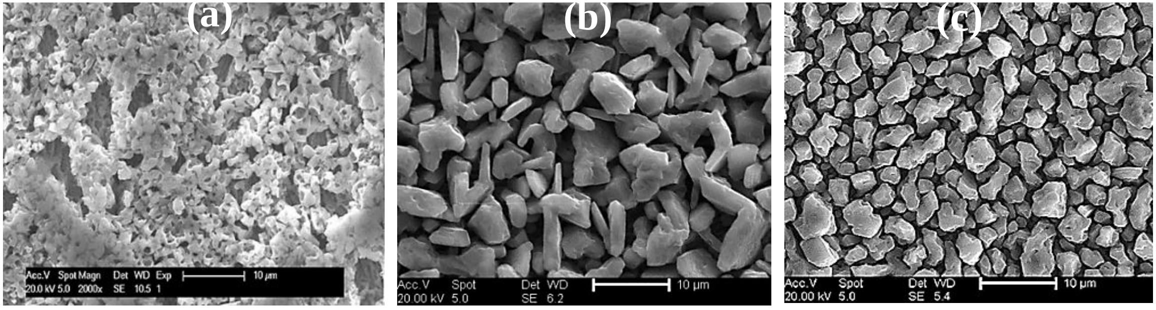

Fig 1: *SEM morphology of Aluminium electrodeposition from* ***(a)*** *$AlCl_3$:acetamide,* ***(b)*** *$AlCl_3$:N-methylacetamide, and* ***(c)*** *$AlCl_3$:N,N-Dimethylacetamide-based IL.*

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PF14

Development of an X-ray cell for electrochemical studies of ionic liquids on single crystal surfaces

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Ionic liquids (IL) present an interesting alternative to traditional aqueous electrolytes for use in fuel cells and Li-ion batteries[1]. IL are molten salts consisting or organic cations and organic/inorganic anions. Due to their large asymmetric shape they do not crystalize and are liquid at room temperature, their ionic nature makes them intrinsic ionic conductors. IL have several unique properties which make them promising alternate electrolytes, these properties include: large electrochemical window, high thermal stability and an extremely low vapour pressure[2].

The Electrochemistry of ILs on single crystal surfaces Au(111) has been investigated with the aim of elucidating the fundamental interactions at the electrode/electrolyte interface. Since the electrochemical behaviour of ILs often depends critically on the interfacial structure of the liquid adjacent to the electrode, a molecular level description is necessary to understand and improve their performance.

During this project an ionic liquid electrochemical cell has been developed which can be used in UHV and for in-situ surface X-ray diffraction experiments (SXRD). SXRD has been used to investigate structural changes at solid-electrolyte interfaces[3]. The final experimental design can be seen in **Error! Reference source not found.**a. Predominantly cyclic voltammetry has been carried out. Three generations of electrochemical cell have been conceived and tested. A cyclic voltamogram from the final set up is shown in Fig 1b. First results obtained with the setup will be presented.

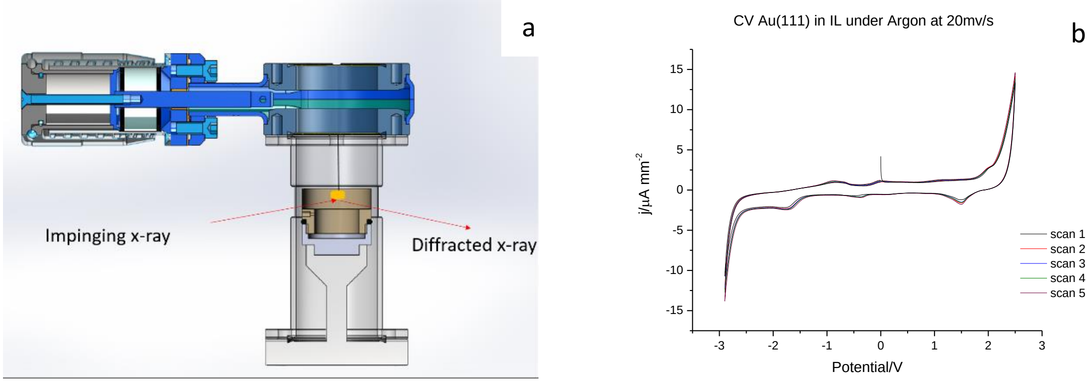

Figure 9: a) Final Experimental set up showing an electrochemical cell in vacuum in an alumina casing b) Cyclic voltamogram of ionic liquid BMPyr TFS on Au(111)I recorded using experimental set up shown in b at 20mv/s

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PF15

Phosphate-mediated electrochemical adsorption of cisplatin on gold electrodes

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Cancers have been the biggest cause of mortality to human population over ages. Since its discovery, the use of cisplatin (CP)[1] has led to a massive improvement in cancer treatment with cure rates of certain cancers reaching over 90%. Although CP has proven to be a very effective anti-cancer drug, its associated toxicity has limited the use.[2] As a cytotoxic drug, it can damage both healthy and tumorous cells causing severe side effects.[3]

The concept of electrochemical adsorption of metalorganic drugs, such as CP, is at its very early stages but the idea behind is to create a novel system that adsorbs the CP at the electrode modified with a receptor. The system would then filter out the CP thus reducing its accompanying side effects. The electrochemical adsorption would also allow us to monitor the level of cisplatin. It has been reported that the most likely sites of cisplatin are nitrogen atoms of nucleobases and thiol-rich molecules.[4, 5] There are also some evidences that DNA's phosphate groups may interact with Pt-based drugs through hydrogen bonds.[6]

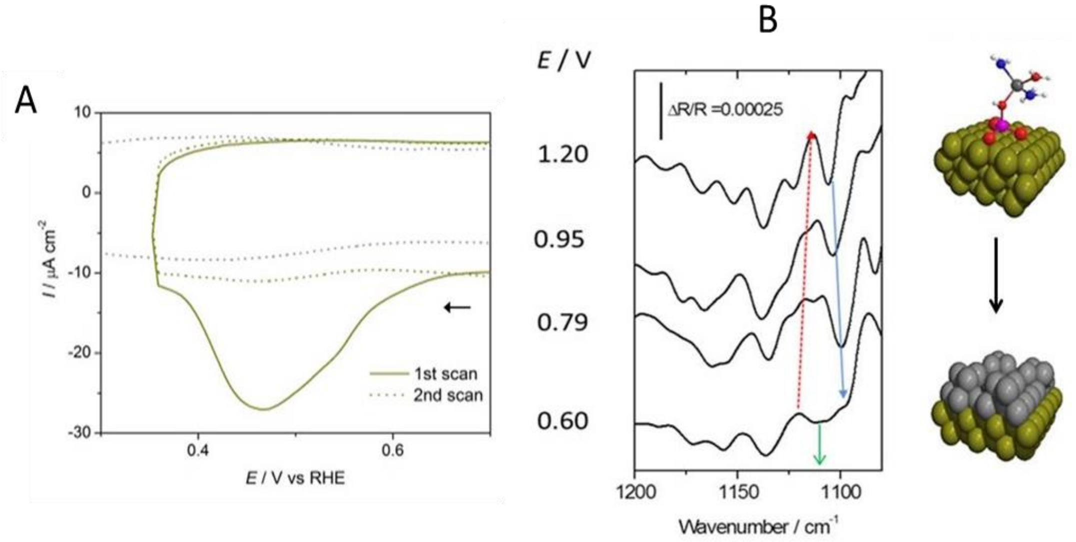

Figure 10: (A) Consecutive voltammetric profiles in a cisplatin-free DPBS solution of surface-modified Au(poly) electrode. Surface modified electrodes were obtained by immersing the electrode in 2.6 mg L^{-1} solution of cisplatin solution during 1 min at at 0.85 V vs RHE. The scan direction is indicated by the arrow in the figure. (B) Potential-difference FTIR spectra of polycrystalline Au electrode recorded in the presence of cisplatin in DPBS accompanied with corresponding hard-sphere models.

Here we report for the first time the adsorption of cisplatin on polycrystalline gold surfaces under electrochemical control. It was found that the process is mediated by the adsorption of phosphate anions on the gold surface and that the maximum coverage of platinum adsorbed is given by the maximum coverage of phosphate adsorbed at a given potential. The interaction of cisplatin with the phosphate groups was confirmed by in situ FTIR spectroscopy under external reflexion configuration.

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PF16

Temperature dependence of Cu-UPD on Au(111) in 0.1 M sulphuric acid

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Underpotential deposition (UPD) of a metal is the deposition of a monolayer of metal on a substrate at a potential positive of the bulk deposition and it is well suited to study the influence of the substrate on the deposition process, as they are in close proximity and thus strongly interact [1]. As most studies on the UPD process have been carried out at room temperature, and most industrial processes using metal deposition use elevated temperatures [2], a systematic electrochemical study of the UPD process has been carried out to investigate the effect of the temperature on the UPD process. Cu-UPD on Au(111) in 0.1 M sulphuric acid has been chosen as a model system, as it is widely studied and well understood [3,4].

Using a thermostat to regulate the temperature, cyclic voltammograms (CVs) were taken at selected temperatures (Figure 1). Both peak position and peak shapes of the CVs at different temperatures are compared. Deposition peak B sharpens and shifts towards higher potential with increased temperature. Peak A also shifts towards higher potential with increasing temperature, although the shift in potential does not happen as a gradual process but rather at certain threshold temperatures, in particular around 30°C and between 40°C and 50°C. A clear influence of the temperature on the UPD process can therefore be seen.

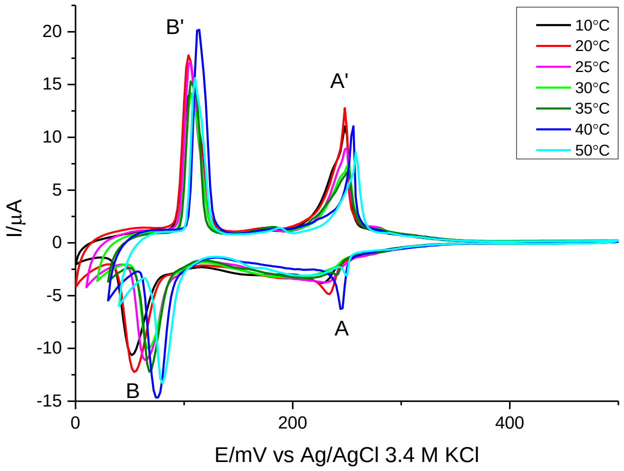

Figure 11 Temperature dependent CVs of Cu-UPD on Au(111) in 0.1 M H2SO4 1 mM CuSO4 at 5 mV/s

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PF17

Ionic Diode Characteristics at a Polymer of Intrinsic Microporosity (PIM) | Nafion "Heterojunction" Deposit on Microhole Poly(ethylene-terephthalate) Substrates

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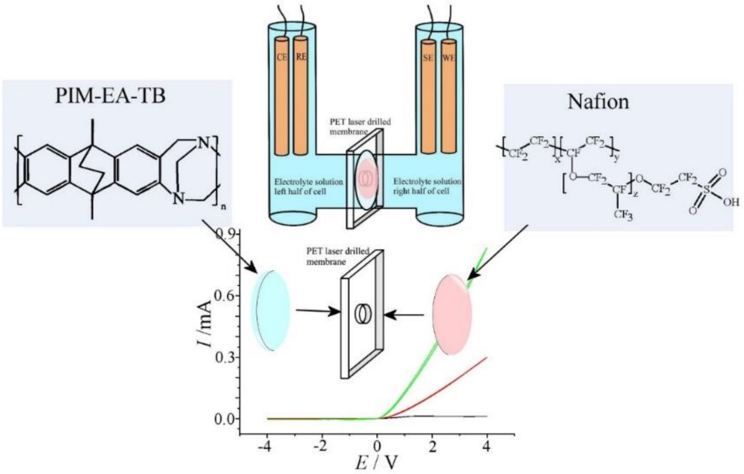
Abstract

Ionic diode phenomena occurs at asymmetric ionomer | aquoues electrolyte microhole interfaces. Depending on the applied potential, either an "open" or a "closed" diode state is observed switching between a high ion flow rate and a low ion flow rate[1]. The phenomenon is characterized via voltammetric, chronoamperometric, and laser confocal scanning microscopy. We had explore a "heterojunction" based on an asymmetric Nafion ionomer | polymer of intrinsic microporosity (PIM) microhole interface. Improved diode characteristics and current rectification are observed in aqueous NaCl and the effect to the PIM is investigated. When it was investigated about the precipitation reaction of potassium cations with perchlorate anions to give insoluble $KClO_4$ at the microhole interface, it is shown that inversion of the rectification/diode effect occurs.



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PF18

Microporous Heterocarbon Flakes as Catalyst for Ammonia Oxidation

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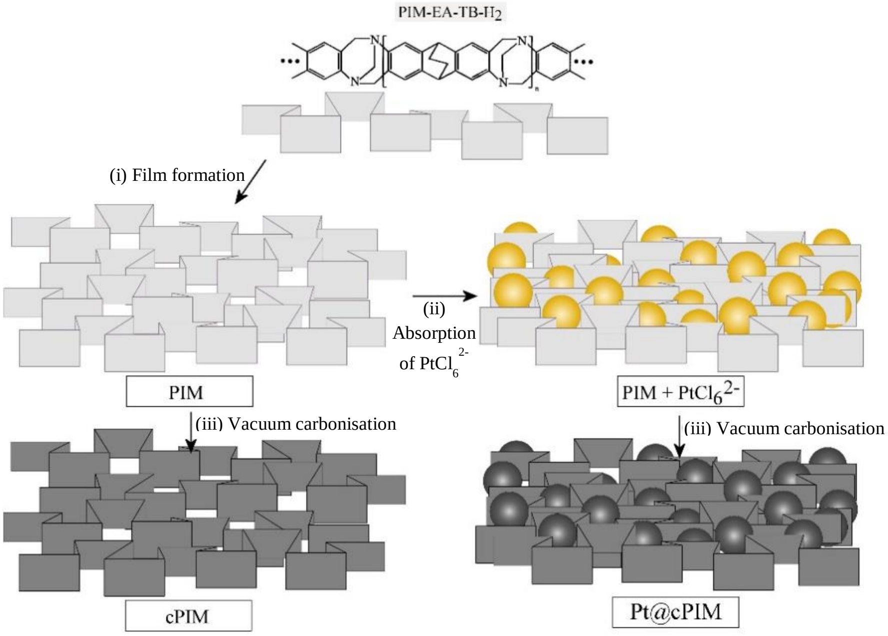
Polymers of intrinsic microporosity (PIMs[1]) are developed into gas diffusion electrodes for ammonia oxidation. PIMs offer molecularly rigid structures[2] with the ability to carbonise into morphologically stable heterocarbon[3] with micropores that can be impregnated with active nanoparticle catalysts.[4] After carbonisation, flake-like materials are obtained and tested for catalytic activity. Pore size effects and catalyst loading effects are observed.



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PF19

Microporous Nafion Composites in Electroanalysis

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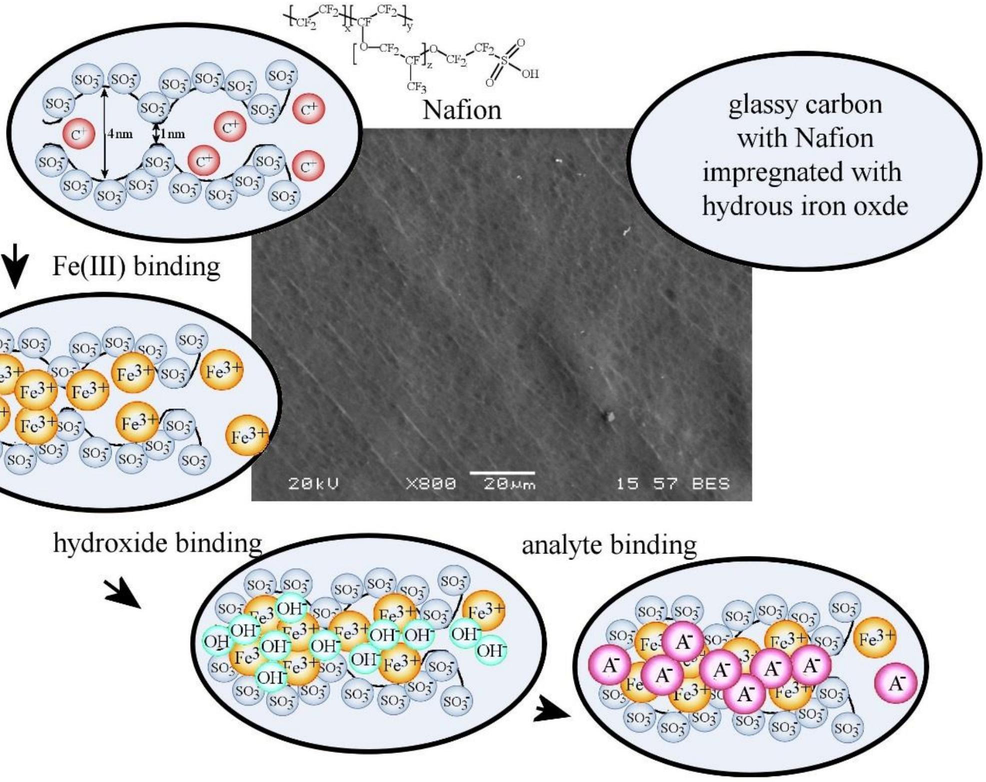
Nafion offers microporous channels for ion exchange and it has recently been shown that the cation exchanging properties of Nafion can be inverted[1] to anion exchange by pre-filling the hydrophilic channel structure. Here, prefilling is performed with hydrous iron oxide and sensitivity to anionic analytes is investigated. A voltammetric sensor response is obtained either indirectly (Fe(III/II) or directly for redox active anions.



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PF20

A Polymer of Intrinsic Microporosity (PIM-1) in Electrochemical Membranes and Diodes

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Polymers of intrinsic microporosity (PIMs [1]) offer rigid molecular backbone polymer structures with permanent microporosity and high processibility. Films [2,3] can be readily deposited by drop-casting. Here, the material PIM-1 is investigated for ion conductivity, membrane properties, and for diode/rectification effects when deposited asymmetrically over a microhole in a PET substrate. Reactivity changes in alkaline solution environments are highlighted and future water purification applications discussed.

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Corrosion

Poster Abstracts

An experimental investigation into the effects of water condensation rate and surface temperature on top of line corrosion in a CO_2 environment.

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Top of Line Corrosion (TLC) is a corrosion phenomenon occurring in pipeline transportation of wet gas when there is a significant difference of temperature between the produced fluids and the surrounding environment. If the gas/liquid flow is stratified, saturated water vapour condenses on the inside walls of the pipeline and forms small water droplets which become saturated with acid gases leading to severe corrosion.

This paper provides a comprehensive experimental investigation into on the effect of condensation rate, surface temperature and iron carbonate saturation on TLC and $FeCO_3$ precipitation rate on carbon steel (X65) in a CO_2 environment. TLC is found to be governed by surface temperature regardless of water condensation rates (WCR) at surface temperature lower than 32°C. The results also show that WCR influences the TLC, precipitation rate and scale film formation at surface temperature higher than 32°C. On the basis of the experimental data, a new empirical model to predict the TLC rate in the absence of $FeCO_3$ films is described and a new kinetic constant for the calculation of $FeCO_3$ precipitation rate under condensing condition at the top of the line is proposed.

The Influence of Pulsed Electrical Charge on Electrochemical Remediation of Steel Reinforcement

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Cathodic protection is the most common technique used to prevent/mitigate corrosion of the steel in concrete. However, many authors[1,2], have demonstrated that the application of a current to a steel sample produces severe side effects such as softening of the cement paste, bond strength degradation and loss of adhesion to the cement layer. Research by Koleva[3] has however indicated these side effects can be reduced and controlled by applying the current in a pulse form, which proves to be less detrimental to the bulk concrete as well as the steel-cement interface.

This work investigates the effect of different pulse signatures to find the optimum pulse regime. Once the effect of pulse regime is understood, the research will look to investigate how the pulse duty cycle affects the distribution of current within a reinforced concrete specimen. The pulse technique will then be applied to a number of other electrochemical rehabilitation techniques which commonly have a constant current applied to them.

Preliminary studies for a reinforced concrete sample investigated the distance along the sample where a potential of 100mV is achieved. It can be concluded that when using a pulsed current with a square waveform and a duty cycle of 50%, a potential decay of 100mV is witnessed further along the specimen when compared to 10% and 30% duty cycles and constant current 100%. Although currently in its preliminary phase of research, once the optimum pulse regime has been determined, further experimental work will be conducted to investigate how the use of a pulse current can affect the electro migration of ions or particles through the bulk concrete to restore the passivity of the rebar or provide a protective barrier.

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