

Butler2016

RSC Scotland and North of
England Regional
Electrochemistry Symposium

April 20th 2016

University of Glasgow

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RSC Electrochemistry Interest Group

Welcome to the Royal Society of Chemistry Scotland and North of England Regional Electrochemistry Symposium, 2016! The following contains safety information, abstracts and a running order for the symposium. This meeting would not be happening without the hugely generous support of our sponsors, so please do visit them in the exhibition area and show your gratitude for keeping the Butler meetings free to attend. Many thanks also to my students (Isolda Roger, Giacomo Cioncoloni and Mike Shipman) for their helping in organising this meeting. I hope you enjoy Butler2016.

Mark

Meeting Information

Registration will be in the conference room (A4-41a) of the Joseph Black Building, while talks will be held in the main lecture theatre (B4-19), which is accessible from floors 4 and 5 (the ground floor of the Joseph Black Building is level 3). **Breaks, lunches** and the **poster sessions** will take place in the conference room in the Joseph Black Building. We would be grateful if poster exhibitors could put up their posters as soon as they can in order to allow people more time to read them during breaks.

Fire and Security information

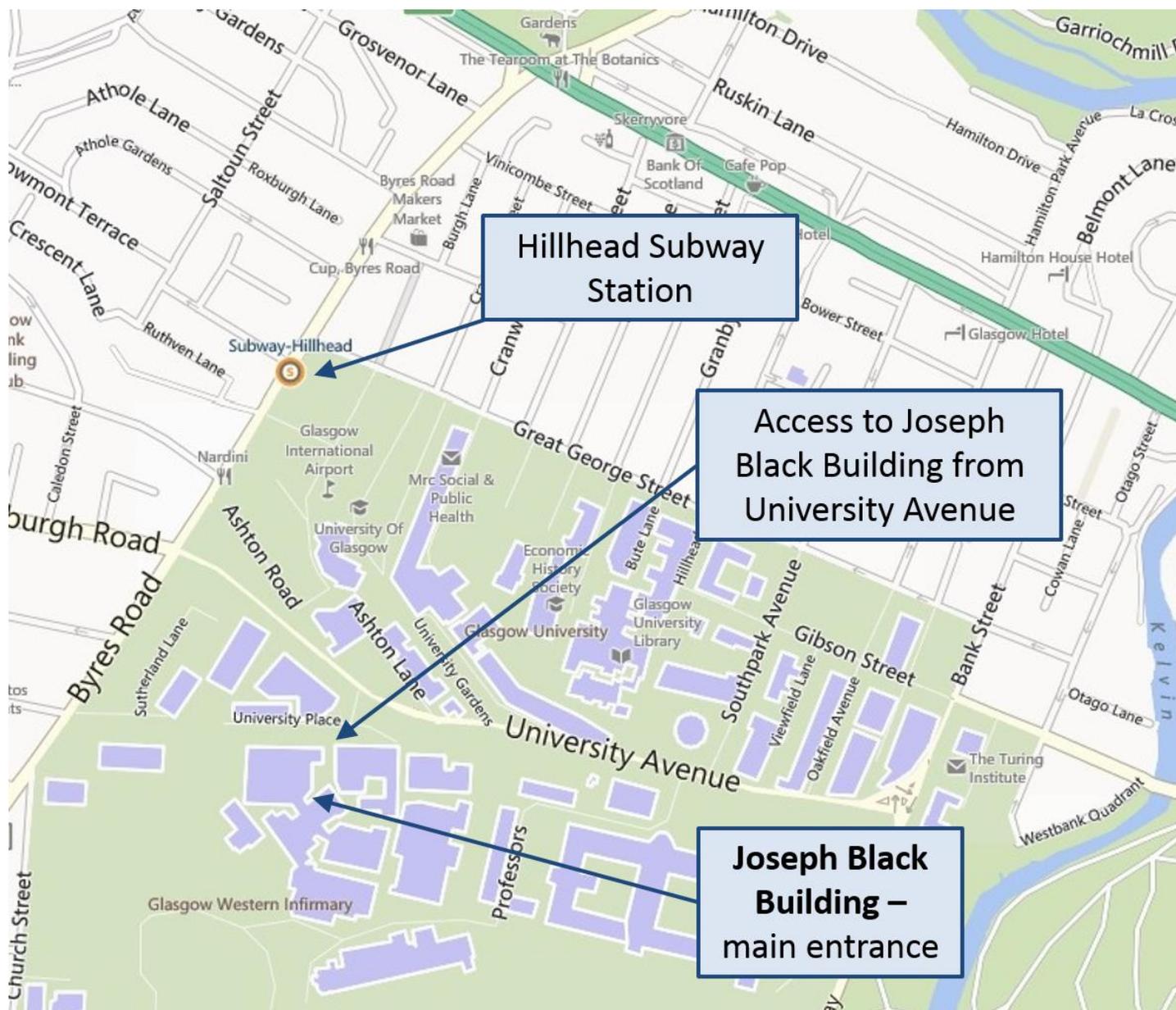
In case of a fire alarm in either building please leave in an orderly fashion and assemble in front of the Wolfson Medical Building, which is across University Place from the Joseph Black Building (see map below). In case of emergency on campus, please dial 0141 330 4444 (int. ext. 4444).

Internet Access

UK delegates should use the Eduroam wireless internet service. For details on using Eduroam please see: <http://www.its.qmul.ac.uk/network-services/Eduroam.html>

Please note that although we will attempt to resolve any technical issues people have with the wireless networks we may need to refer you back to your home institutions for technical support in the case of the Eduroam network.

Map – Please enter the Joseph Black Building by the entrance indicated



Local Information

The University of Glasgow (G12 8QQ) is located in the West End of Glasgow, approximately 2 miles from the city centre. It can be accessed from the centre of Glasgow by the subway system (alight at Hillhead Station, G12 8SH), by bus (First buses Number 4 service), by taxi (£5-10) or on foot (allow 35-40 minutes). For more detailed information see the following link:

<http://www.gla.ac.uk/about/maps/howtogether/>



2016 RSC Butler Symposium

20th April, School of Chemistry, University of Glasgow

Programme

10:00 Registration and coffee

10:45 Welcome / safety notes

Session 1 – Session Chair: Alexey Ganin

10:50 – 11:10 *Isolda Roger – University of Glasgow*

11:10 – 11:30 *Victoria Camus – University of Edinburgh*

11:30 – 11:50 *Damion Corrigan – University of Edinburgh*

11:50 – 12:10 *Mwanda Jonathan Amolo – University of Aberdeen*

12:10 – 12:30 *Hirepan Chávez-Cárdenas – University of St Andrews*

12:30 – 13:30 Lunch and posters

Session 2 – Session Chair: Mark Symes

13:30 – 13:50 *Irene Munaò – University of St Andrews*

13:50 – 14:10 *Yousillya Bunga – Durham University*

14:10 – 14:30 *Tobechi Nnamdi Okoroafor – Newcastle University*

14:30 – 14:50 *Jiabo Le – University of Aberdeen*

14:50 – 15:15 Coffee and posters

Session 3 – Session Chair: Serena Corr

15:15 – 16:00 Keynote lecture – *Prof. John Irvine, University of St Andrews*

16:00 – 16:15 Prizes and close

With thanks to the RSC Electrochemistry Interest group and our industrial sponsors:



Talks

Talk 1: Efficient Electrocatalytic Water Oxidation at Neutral and High pH by Adventitious Nickel at Nanomolar Concentrations¹

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Abstract: Electrolytic water oxidation using earth-abundant elements is a key challenge in the quest to develop cheap, large surface area arrays for solar-to-hydrogen conversion. There have been numerous studies in this area in recent years, but there remains an imperative to demonstrate that the current densities reported are indeed due to the species under consideration, and not due to the presence of adventitious (yet possibly highly active) contaminants at low levels. Herein, we show that adventitious nickel at concentrations as low as 17 nM can act as a water oxidation catalyst in mildly basic aqueous solutions, achieving stable (tens of hours) current densities of 1 mA cm⁻² at overpotentials as low as 540 mV at pH 9.2 and 400 mV at pH 13. This nickel was not added to the electrolysis baths deliberately, but was found to be present in the electrolytes as an impurity by ICP-MS. The presence of nickel on anodes from extended-time bulk electrolysis experiments was confirmed by XPS. In showing that such low levels of nickel can perform water oxidation at overpotentials comparable to many recently-reported water oxidation catalysts, this work serves to raise the burden of proof required of new materials in this field: contamination by adventitious nickel at trace loadings must be excluded as a possible cause of any observed water oxidation activity.

References

- 1 I. Roger, M. D. Symes, *J. Am. Chem. Soc.*, 2015, **137**, 13980-13988.

Talk 2: Monitoring Changes in Intracellular Redox Potential and pH in a Prostate Cancer Model System

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Abstract: From the necrotic core to the outer compartments of a tumour there exist gradients of redox potential, lactate, pH and drug penetration. Tumours also have inadequate vasculature resulting in a state of hypoxia. Hypoxia is a key player in metabolic and redox dysregulation and can also provide cells with resistance to cancer treatments, particularly chemotherapy and radiation therapy. Radiation therapy is received by almost two-thirds of prostate cancer patients. The ionising radiation destroys cancerous cells through the generation of oxidative species such as reactive oxygen species (ROS) that damage vital cell components, including DNA and proteins. ROS are also implicated in the regulation of intracellular redox potential (IRP), the disruption of which has been linked to the progression of disease, cancer and even aging.

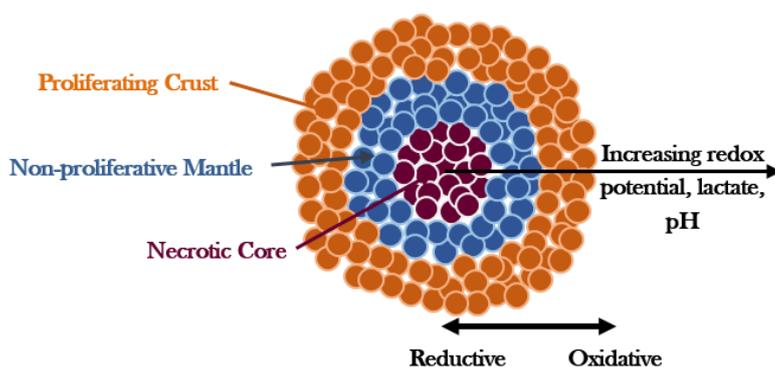


Fig. 1 Schematic of the organisation of cells within a tumour and spheroid model, showing gradients in redox potential, lactate and pH. The necrotic core is low in $[O_2]$, pH and glucose, but all increase towards the proliferating crust upon approaching blood supply or in the case of spheroids media.

Using two nanosensors, MeNQ and *p*MBA,¹ and Surface-Enhanced Raman Scattering (SERS), we can quantitatively measure both IRP and pH, respectively, within the cell cytosol of Multicellular Tumour Spheroids (MCTS) (Fig. 1). These are 3D cell cultures that possess their own microenvironments, similar to those found in tumours. A 3D *in vitro* model is used as an alternative to 2D monolayers as spheroids recapitulate the *in vivo* features of a tumour, enhancing clinical relevance. Oxidative and reductive stress have been chemically induced to model the intracellular behaviour of the probes, validating their use in cell culture. A nanoshell targeting approach has also allowed for spatial quantification of pH and redox potential throughout the MCTS following drug treatment, and more recently the effects of x-ray radiation on cell redox biology is being explored, looking at dosage and fractionation schedules.

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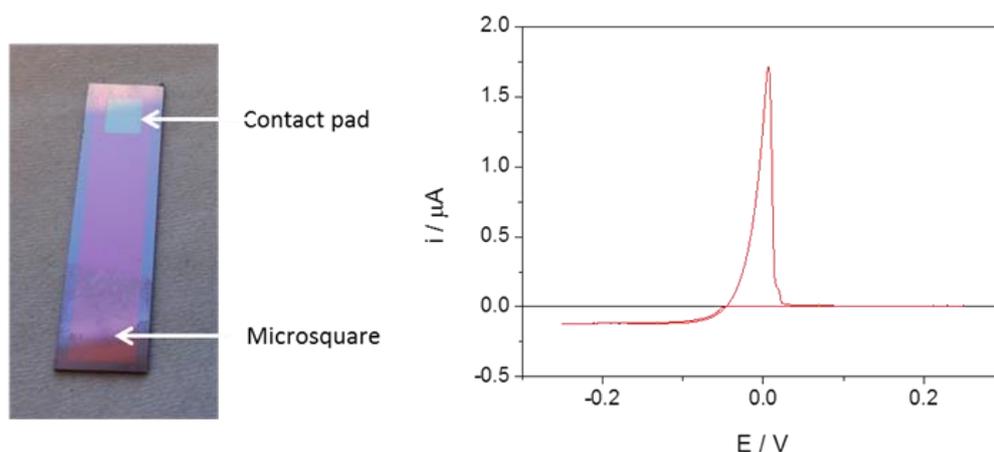
Talk 3: Development of robust microelectrode sensors for the nuclear fuel cycle

Damion K Corrigan¹, Ewen Blair², Justin Elliott¹, Simon Reeves¹, Ilka Schmäuser², Anthony J. Walton² and Andrew R. Mount¹.

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Abstract: The EPSRC REFNE project is an interdisciplinary collaboration between five UK universities and the National Nuclear Laboratory (NNL). The aim of the project is to develop high temperature reprocessing of spent nuclear fuel using molten salt media (pyroprocessing). Improving the efficiency of the nuclear fuel cycle will be a tremendous advantage in terms of meeting future global energy demands. In Edinburgh, our role is to develop a robust microelectrode capable of operating at the high temperatures (450-500°C) and in the often corrosive environments found in molten salts. Ultimately, the electrode will be employed for online measurements in pyrochemical reprocessing of spent nuclear fuel. Microelectrodes have the well-known analytical advantages of improved signal to noise, reduced iR drop and relative insensitivity to convection. Producing devices for use in molten salt media represents a significant materials challenge and in order to meet this challenge, microfabrication approaches for electrode production have been employed. This talk will discuss the analytical advantages of the microelectrode for molten salt measurements, detail the fabrication processes and materials combinations employed to produce functioning devices and showcase example measurements of relevance to the reprocessing of spent nuclear fuel.



Left – image of a microelectrode chip designed for use in molten salt
Right – Cyclic voltammogram recorded using a sweep rate of 100 mVs^{-1} and a $50 \mu\text{m}$ tungsten square electrode in LKE + 10 mM Bismuth (III) chloride at 450°C .

References

- 1) E. O Blair, D K Corrigan, I Schmäuser., J G Terry, S Smith, A R Mount and A J Walton (2016) *ICMTS* - accepted
- 2) D K Corrigan, J P Elliott, E O Blair, S J Reeves, I Schmäuser, A J Walton and A R Mount. (2016) *Faraday Discussions – Liquid salts for Energy and Materials* - accepted
- 3) E O Blair, D K Corrigan, J G Terry, A R Mount and A J Walton (2015) *JMEMS* Feb 2015.
- 4) D K Corrigan, E O Blair, J G Terry, A J Walton and A R Mount (2014) *Analytical Chemistry*, 86 (22):11342-8.

Talk 4: Deposition of silver and palladium on cyanide-modified Pt (111) electrodes

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Abstract: The demand to increase electronic power densities has led to extensive research into the use of molecules as conductors as a means to attain the ultimate miniaturisation of electric components. The transport of electrons across single-molecule junctions has been the object of intense research. Less attention, however, has been devoted to developing contacts across small groups of molecules, and to studying the transport of electrons across this kind of contacts (which will most likely be required for future applications of molecular electronics). One viable method to establish this kind of contacts is to sandwich small areas of molecular monolayers between a metal substrate and electrodeposited 2-dimensional metallic nano islands.

Metal cations have been shown to attach to the surface of cyanide-modified Pt (111) electrodes via non-covalent interactions between the negative end of the cyanide dipole and their positive charge.^{1,2} In the case of Cu²⁺ the interaction is irreversible, and reduction yields Cu bidimensional nanoislands on the cyanide adlayer in a Pt/CN/Cu 'sandwich' configuration.³ We have attempted the metallization of cyanide-modified Pt (111) electrodes with palladium and silver using the same sequence of irreversible adsorption followed by electrochemical reduction. Cyclic voltammetry in both sulfuric acid and perchloric acid solutions show that also in these cases the attachment of Pd²⁺ and Ag²⁺ via non-covalent interactions is irreversible, but a gradual change in both cyclic voltammograms upon cycling suggests a slow migration of palladium and silver underneath the cyanide adlayer, in direct contact with the Pt (111) substrate.

In-situ STM imaging also shows evidence of the slow migration of the silver and palladium to creep underneath the cyanide adlayer and directly deposit onto the Pt (111) substrate. In-situ STM imaging of Cu deposition on the cyanide modified platinum (111) clearly shows the formation of bidimensional islands that grow via an Ostwald ripening process.³ Comparison of these results with those obtained with Cu provides further support to our previous conclusions² that the cyanide adlayer on Pt (111) can be successfully metallised with bidimensional Cu nanoislands.

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Talk 5: Search for Novel Oxide Ion Conductors: Lanthanum Titanate Based Compounds for Electrochemical Applications.

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Abstract: A new family of ion conductors based on the cuspidine structure has been proposed to be used as electrolytes in solid oxide fuel cells due to the fast ion conducting behavior displayed¹. It has been reported that the creation of oxygen vacancies on La₂TiO₅ by partial substitution of Ti⁺⁴ sites has improved its ionic conductivity².

In this work, the effect of replacing La⁺³ by Sr⁺² on the electrical properties of La₂TiO₅ was studied. Replacement of Ti⁺⁴ by Ga⁺³ was also investigated. Dual substitution on both La⁺³ and Ti⁺⁴ sites was studied as a means to optimize the ionic conductivity. The samples $La_{2-x}Sr_xTiO_{5-\frac{x}{2}}$ ($x = 0.0375; 0.05$), $La_2Ti_{1-y}Ga_yO_{5-\frac{y}{2}}$ ($y = 0.35; 0.5$) and $La_{2-x}Sr_xTi_{1-y}Ga_yO_{5-\frac{x+y}{2}}$ ($x = 0.0375$ and $y = 0.35; 0.5$) were synthesized using a wet method. The samples were characterized by X-ray diffraction and SEM. The impedance measurements were collected under static air in the temperature range 500-900 °C. The dopants (Sr⁺², Ga⁺³) increased the ionic conductivity of the La₂TiO₅. The highest value of conductivity at 900 °C was achieved for the dual substitution sample.

References

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Talk 6: $\text{NaFe}_3(\text{HPO}_3)_2((\text{H},\text{F})\text{PO}_2\text{OH})_6$: a potential cathode material and a novel ferrimagnet

*Irene Munaò*¹, *Elena A. Zvereva*², *Olga S. Volkova*^{2,3,4}, *Alexander N. Vasiliev*^{2,3,4}, *A. Robert Armstrong*¹ and *Philip Lightfoot*¹

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Abstract: A novel iron fluoro-phosphite, $\text{NaFe}_3(\text{HPO}_3)_2((\text{H},\text{F})\text{PO}_2\text{OH})_6$, has been synthesized by a dry low temperature synthesis route. The phase has been shown to be electrochemically active for reversible intercalation of Na^+ ions, with an average discharge voltage of 2.5 V and an experimental capacity at low rates of up to 90 mAh/g. Simple synthesis, low cost materials, excellent capacity retention and efficiency suggest this class of material is competitive with similar oxyanion-based compounds as a cathode material for Na-batteries. The characterization of physical properties by means of magnetization, specific heat and electron spin resonance measurements confirms the presence of two magnetically non-equivalent Fe^{3+} sites. The compound orders magnetically at $T_C \sim 9.4$ K into a state with spontaneous magnetization.

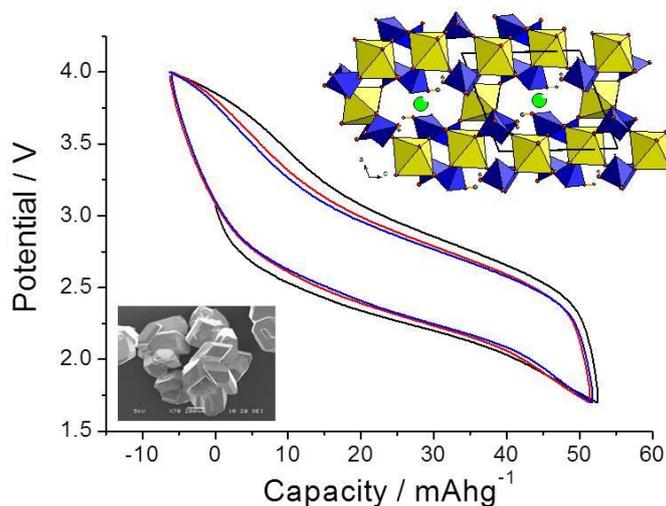


Fig. 1 Polyhedral representation, SEM picture and load curves for $\text{NaFe}_3(\text{HPO}_3)_2((\text{H},\text{F})\text{PO}_2\text{OH})_6$

References

- 1 I. Munaò, E. A. Zvereva, O. S. Volkova, A. N. Vasiliev, A. R. Armstrong and P. Lightfoot, *Inorg. Chem.* 2016, DOI: 10.1021/acs.inorgchem.5b02922 (in press)
- 2 C. Masquelier and L. Croguennec, *Chem. Rev.* 2013, 113, 6552-6591.
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Talk 7: Metal nanoparticles and their interactions with lipid membranes immobilized on gold electrodes

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Metallic nanoparticles (NPs) such as gold, silver and copper 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

One of the advantages of metal NPs is their small sizes which enhances the reactivity of the NPs surface area (larger surface area) thus greater toxic potential even at low nanoparticle concentration.² There has been an increasing interest in the development of novel and modification of existing antimicrobial compounds in the hope of improving the antimicrobial activity of nanomaterials against the fight of increasing drug-resistant properties of some bacterial strains.³

The work reports the comparison of metal NPs (gold, silver and copper) and their interactions with artificial cell membranes using different models of bilayer lipid membrane (BLM) formation using electrochemical and microscopic techniques.

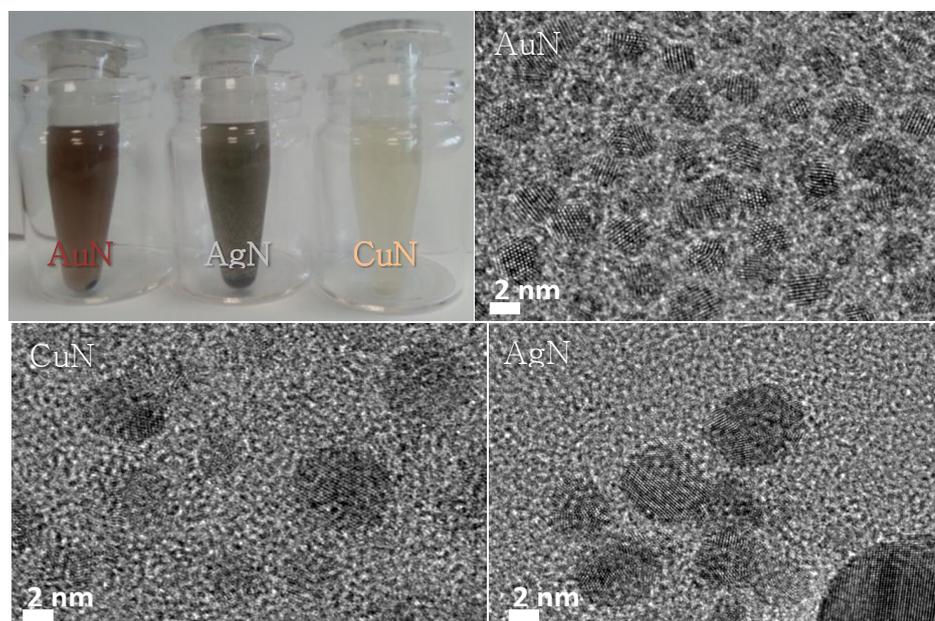


Fig. 1: Optical image of metal NPs, TEM images of AuNPs, CuNPs and AgNPs.

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Talk 8: Bioelectricity generation using mixed culture from anaerobic sludge in dual chambered bioelectrochemical system

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Abstract: Bioelectrochemical systems (BESs) can be broadly defined as devices that catalyse electrochemical reactions through the use of biocatalysts at either or both electrodes.¹ They are capable of producing electricity or other value adding compounds from electron transfer between electrodes and electrochemically active microbes or biomolecules.² As microbial fuel cells (MFCs) its operation results in the production of electricity and in recent years rapid progress has been made in MFC research going by the exponential increase in number of journal publication in the last 10 years.³ Electricity can be produced using bioelectrodes comprising of either pure cultures such as *Geobacter*⁴ and *Shewanella*⁵ or mixed culture.⁶ However, the attention of the research community have focused more on mixed culture due to their stability, nutrient versatility, stress resistance and overall performance.³ This study investigates the ability of mixed culture to produce electricity in BES using acetate as the sole carbon source.

Two H-type MFCs consisting of two anaerobic chambers were set-up. The chambers were separated by a proton exchange membrane with each chamber containing carbon form electrode. An Ag/AgCl reference electrode (+197mv vs. SHE) was also placed in the anode chamber. Titanium wires were used to connect the working and counter electrodes to a voltage generator for potential supply with potential change recorded using a data logger. The two chambers were filled with 180 mL of minimal medium containing 10 mL each of both Wolfe vitamin and modified mineral solutions. The pH of the medium was set at pH 7.0 ± 0.1 and the whole system purged with ultra-pure nitrogen before start-up. Anaerobic sludge from an existing anaerobic digester was used as the bacterial source. Measured potential was used to calculate current according to the relationship between current and potential at 200 Ω.

The BES with the most optimum bioanode produced a maximum current density of 73.75 mA/m² after 21 days of operation. Analysis using cyclic voltammetry and electrochemical impedance spectroscopy showed that it had the greatest redox activity of electroactive bacteria on its electrode surface and the lowest internal resistance which reduced progressively over time from 2347-1676 Ω with increased current generation.

References

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Talk 9: Determining Potential of Zero Charge of Pt(111) from Density Functional Theory based Molecular Dynamics

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Abstract: The potential of zero charge (PZC) is the potential at which no excess charge exists on the surface of the electrode. As an intrinsic property of the electrode, PZC is only dependent to the nature of the metal and the contacting solution. Experimentally, PZC can be used to check the cleanness of the metal surface. Furthermore, it specifies the position where the Gouy-Chapman capacitance reaches its minimum when no specific adsorption occurs, thus, determining the PZC has become a key prerequisite for studying the electric double layer.

This project aims at determining the PZC and the structure of the Pt(111)/water interface. Based on DFTMD simulation and hydrogen insertion method,¹ we present a new method that connecting the electrostatic potential of bulk water in the interface model to the electrostatic potential of pure water, thus saves a large amount of computational time. In this method, the H⁺ serves as the reference ion so that we can directly estimate the PZC vs. SHE.

The Pt(111)/water interface is modelled by periodic Pt(111) 6 × 6 supercell slab of 4 atomic layers with fully filling the water molecules in between. The whole model contains 144 Pt atoms and 151 water, the density of the bulk water is 1 g/cm³. Born Oppenheimer DFTMD simulations are carried out by the CP2K/Quickstep package, employing Perdew-Burke-Ernzerhof (PBE) functional to describe the exchange correlation effects.

The PZC of Pt(111)/water interface is determined to be 0.2 V after 8 ps simulation, which reproduces the experimental results² with a small uncertainty. We also find the charge-transfer between Pt and interfacial water can decrease the workfunction of Pt(111) surface, which is the dominant factor for the workfunction change. Two sub-layers are observed in the interfacial water, the first sub-layer has a preferred orientation (30 degrees with the surface) and adsorption site (top site of Pt), and the second sub-layer contains part of H-down water and the others are disordered.

References

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Talk 10 – Plenary Lecture: *Electrode Evolution in Solid Oxide Cells*

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Fuel cells will undoubtedly find widespread use in this new millennium in the conversion of chemical to electrical energy, as they offer very high efficiencies and have unique scalability in electricity generation applications. The solid oxide fuel cell (SOFC) offers certain advantages over lower temperature fuel cells, notably its ability to utilise CO as a fuel rather than being poisoned and the availability of high-grade exhaust heat for combined heat and power or combined cycle gas turbine applications. Although cost is clearly a key barrier to widespread SOFC implementation, perhaps the most important technical barriers currently being addressed relate to the electrodes, particularly the fuel electrode or anode. In terms of mitigating global warming, the ability of the SOFC to utilise commonly available fuels at high efficiency, promises an effective and early reduction in carbon dioxide emissions and hence is one of the lead new technologies to improve the environment. In the longer term the ability to utilise waste derived fuels such as biogas will be of critical importance.

The electrochemical reactions in fuel cells and electrolyzers occur at the interface between electrodes and electrolyte. Here we look at attempts to nanoengineer this interface to enhance performance and also probe the changes in local structure that relate to activation or ageing during operation.

Posters

Poster 1: Cobalt phosphide supported on Nitrogen-doped graphene as catalyst for the hydrogen evolution reaction

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Abstract: Hydrogen is proposed as a major energy carrier for the future world. The electrochemical hydrogen evolution reaction (HER), which generates hydrogen from water and electricity, underpins many clean-energy technologies.¹ Generally, the HER is catalysed by Pt-based/noble metal catalysts² but the utility of these noble metals at global scale is limited due to the high price and low abundance. Therefore, alternative electrocatalysts for the HER are highly prized.³ In this work, a nanocomposite cobalt phosphide and nitrogen-doped graphene (NGr) catalyst was synthesized by pyrolysis. XRD and XPS results confirm the presence of cobalt phosphide, showing a small peak which could be belonged to the presence of N-graphene in the hybrid. The cobalt nanocomposite exhibited good HER activity as catalyst for the HER under acidic conditions; with a small onset potential of ca. 65 mV. In comparison to a commercial 20wt. % Pt/C (Alfa Aesar, a Johnson Matthey Company) tested under the same conditions the CoP based catalyst had only a 20 mV higher onset potential but a greater Tafel slope.

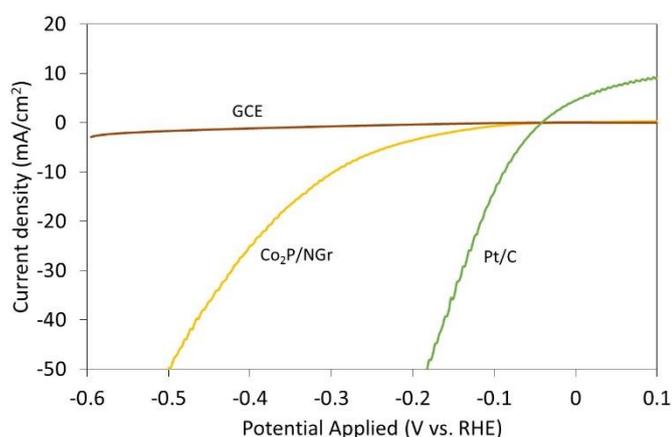


Fig. 1 Linear sweep voltammograms of the Co₂P/NGr nanocomposite, bare GCE and Pt/C catalyst in 0.5 M H₂SO₄ with a scan rate of 0.1 V/s.

References

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Poster 2: A Fundamental Study of Microsquare Nanoband Edge Electrodes (MNEE) and Their Use in Biosensing

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Abstract: Nanoelectrodes are defined as electrodes which have a critical dimension of the order of nanometers. We have previously reported the design, fabrication and characterisation of a novel nanoelectrode design in conjunction with Engineers from the Scottish Microelectronic Centre (SMC) in Edinburgh.^{1,2} Microsquare Nanoband Edge Electrodes (MNEEs) consist of an array of holes with nanoscale Pt bands (formed by sandwiching the metal between insulating layers) exposed around their perimeter. These have enhanced mass transport, which results in the rapid establishment of an enhanced steady-state diffusion profile and a greater Faradaic current density, along with a smaller relative double layer capacitance, which together gives a significantly increased signal to noise ratio compared to macroelectrodes.³ Building on our previous expertise in biosensing, e.g. in MRSA detection, this poster will present work aimed at comparing the enhanced biosensing performance of MNEE to macroelectrodes.⁴ It will cover the design, fabrication, characterisation and fundamental principles of these nanoscale biosensors; as well as covering the characteristics of electrochemical biomolecule detection.

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Poster 3: Synthesis and characterisation of DNA-templated Ternary metal sulphide (CdZnS₂) for application in gas sensing

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Abstract: The synthesis and characterisation of DNA templated semiconducting nanowires were studied in order to determine their viability for use as transducers in gas sensing applications. Nanowires are particularly promising as transducing materials for sensor design because their large surface/volume ratio shows that their electrical resistance is highly sensitive to chemical events at their surface. This resistance can be measured in a simple two-terminal device. The ability of semiconducting metal sulphides DNA-templated nanowires to act as a transducer in gas sensor is due to the change in electrical conductivity of nanowires as a result of interaction between the active sites of the nanowires surface and the absorbed target gas¹. The doping of semiconducting metal sulfides provide an extra way of tuning the sensing properties.

The λ-DNA templated CdZnS₂ nanowires was synthesised by reacting an aqueous solution of λ-DNA with Cd(NO₃)₂, Zn (NO₃)₂ and Na₂S in solution. This produced smooth, uniform and continuous 1-dimensional nanowires. The chemical composition and morphology of the synthesized nanowires was characterised by Fourier transform infrared (FTIR) spectroscopy, Atomic Force Microscopy (AFM), Powder X-ray Diffraction (XRD) and Raman Spectroscopy. These characterisation has shown that these nanowires has potentials to be used in gas sensing applications.

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Poster 4: Characterisation of the hybrid ZnBr₂ flow battery

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Abstract: The zinc-bromine hybrid redox flow battery (RFB) is one of the few battery systems that have seen commercial implementation for medium-to-large scale energy storage. One of the issues identified with this flow battery is that of bromine crossover from the positive electrode to the zinc electrode, leading to a loss of current efficiency. This problem can be overcome through the use of organic-based complexing agents that tie up the bromine as an immiscible liquid phase which is pumped from the electrode surface and stored in an external reservoir. It is recirculated back to the positive electrode during discharge of the battery.

The primary aim of the research is to investigate the nature of the complex formed and the effects these complex agents have on the kinetics of both the electrogenerated bromine species and on the deposition of the zinc metal. Different carbon composites and complexing agents have been employed to examine the energy efficiency. The characteristics of the reactions have been examined using electrochemical impedance spectroscopy, potentiodynamic polarisation as well as galvanic cycling (Figure 1).

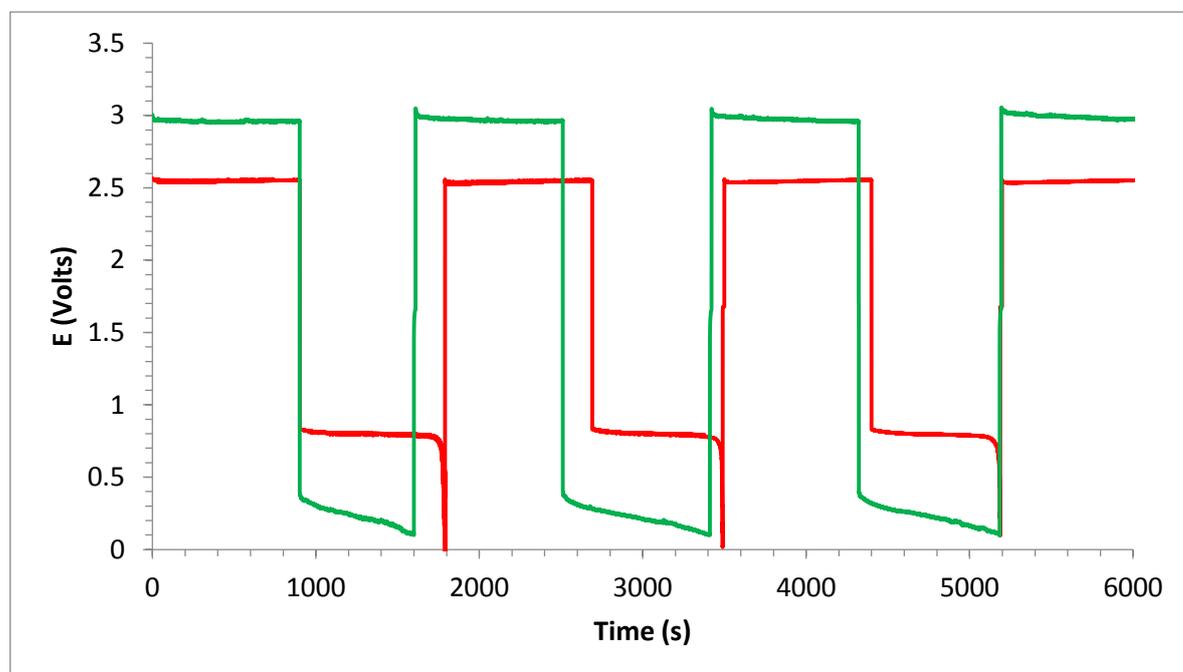


Fig. 1 Galvanic cycles showing the differences in the charge/ discharge cycle between the electrolyte solution with MEP (Green) and without MEP (Red)

Poster 5: Improving the catalytic properties of the (La,Sr)(Cr,Fe,Ni)O₃ perovskite by in situ nanocatalyst exsolution

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Abstract: In the present study the (La,Sr)(Cr,Fe,Ni)O₃ perovskite was synthesized and characterized for the fuel oxidation layer of Oxygen Transport Membranes. The catalytic properties of the perovskite were improved by the incorporation of a catalyst with the method of in situ nanocatalyst exsolution, which tends to grow pinned metal nanoparticles on the reduced oxide surface.¹

La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O₃ (LSCF) perovskite with partial substitution of the B site by 5 mol% of Ni was synthesized via a modified Pechini method. X-ray diffraction showed that LSCF exhibits an orthorhombic structure and after doping the B site with 5 mol% of Ni the perovskite is retaining its structure with a small decrease on the unit cell parameters. The formation of exsolved nanoparticles (30-50 nm) on the LSCF_{Ni} surface was observed by SEM, after reducing the samples in 5%H₂/Ar at 900°C. TEM-EDX analysis of these nanoparticles indicated that their composition is an Fe-Ni alloy. The exsolution of the nanoparticles can be controlled by changing the reduction conditions. Catalytic testing of the LSCF and LSCF_{Ni} was conducted at 900°C with a gas composition of CH₄, CO₂ and H₂. LSCF_{Ni} showed a 21.7% CH₄ conversion, which was 5 times higher than LSCF, confirming the catalytic activity of the exsolved nanoparticles and suggesting potential improvement of the performance for the Oxygen Transport Membranes.

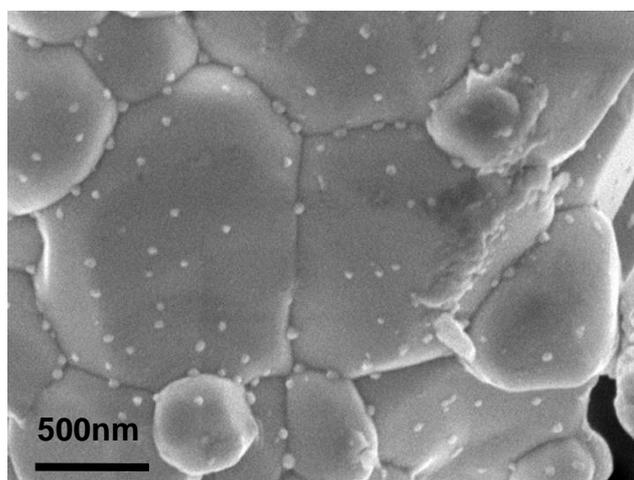


Fig. 1 SEM micrograph of the exsolved Fe-Ni alloy particles on the surface of LSCF_{Ni}

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Poster 6: Pulse deposition of copper using an additive-bearing EnFACE electrolyte

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Keywords: pulse deposition, EnFACE technology, copper, additives

Abstract: A new electrodeposition process called Electrochemical nano and micro Fabrication by flow and Chemistry (EnFACE) allows mask-less pattern transfers onto a metallic substrate. EnFACE uses an acid-free, additive-free plating bath containing low concentrations of metal salts^{1,2} as the process requires electroplating under conditions of fast kinetics and low electrolyte conductivity³.

Additive agents are known to improve the quality of electroplated deposits^{4,5}. The current work reports on the influence of commercial additives, namely, Copper Gleam series (Dow chemicals) and chloride ions (Cl⁻), on the properties of copper electroplated using an EnFACE electrolyte containing 0.1 M CuSO₄ in pulsed current mode.

Copper films were pulse plated on stainless steel coupons from electrolytes containing different concentrations of additives. Electron backscattered diffraction (EBSD) was used to analyse grain size and deposit topography, while

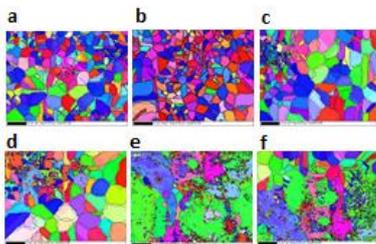


Figure 1. EBSD map for pulse plated copper at different additive concentration (a) 17%, (b) 33%, (c) 50%, (d) 100%, (e) 200% and (f) standard.

mechanical property was evaluated using the universal testing machine (UTM). The resistivity (Rs) of the copper films was measured using the four-point probe. Results indicate that grain size of the deposit decreased with increasing additive concentration. This grain refinement resulted in an increase in resistivity, yield strength, and tensile strength, and a decrease in ductility. These changes in properties may be related to the increase in the grain boundary area of the copper deposits.

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Poster 7: Electrochemical biosensors for protease activity: the influence of redox tag, linker and surface configuration

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Abstract: Proteases are enzymes that catalyse the cleavage of amide bonds at specific sites in a protein or peptide. Among their myriad of physiological roles, these enzymes are involved in many pathophysiological conditions, including inflammation and cancer. There is an increasing demand in clinical research for selective and sensitive analytical tools for the detection of the enzymatic activity in patient samples. Electrochemical biosensors have proved to be valuable tools for the detection of enzyme activity.

Here the the ability of different redox-tagged peptides, tethered to a gold surface, as a sensor platform for the electrochemical detection of protease activity was explored. Cleavage of the substrate causes removal of the electrochemical label, leading to a decrease in the electrochemical signal as measured by square wave voltammetry (Fig. 1).

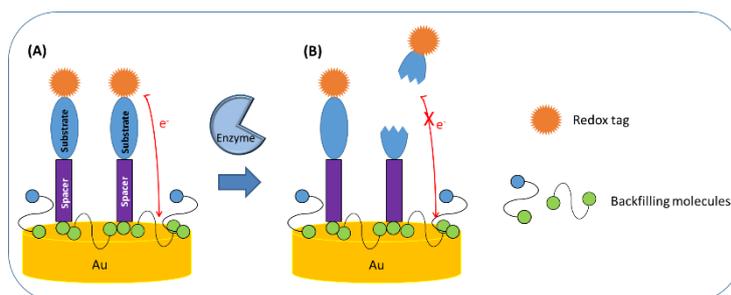


Fig. 1 Scheme of principle of detection. (A) Sensing phase consisting in a mixed self-assembled monolayer containing a redox-tagged peptide. (B) Cleavage of the substrate by the enzyme under interrogation.

With this aim, different cleavable redox-tagged peptides were designed and synthesised. Two modifications were introduced into the substrate sequence: a redox tag (ferrocene or methylene blue) at the amino-terminus and a spacer (an alkyl or polyethylene-based chain), with a cysteine moiety at the C-terminus enabling peptide attachment to a gold surface through the thiol group. The sensing phase composition/optimisation was carried out by producing thiol-modified peptide films and evaluating their stability and performance upon the addition of trypsin.

Sensing phases prepared with methylene-blue peptides showed better stability and signal gain. A systematic study on the influence of spacer and film configuration on the analytical features of the sensor is presented¹.

Acknowledgements: The authors acknowledge financial support from the EPSRC-funded Implantable Microsystems for Personalised Anti-Cancer Therapy (IMPACT) programme (Grant ref. EP/K034510/1).

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Poster 8: p-Type NiO Hybrid Visible Photodetector

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Abstract: A novel hybrid visible-light photodetector was created using a planar p-type inorganic NiO layer in a junction with an organic electron acceptor layer. The effect of different oxygen pressures on formation of the NiO layer by pulsed laser deposition shows that higher pressure increases the charge carrier density of the film and lowers the dark current in the device. The addition of a monolayer of small molecules containing conjugated π systems and carboxyl groups at the device interface was also investigated and with correct alignment of the energy levels improves the device performance with respect to the quantum efficiency, responsivity, and photogeneration. The thickness of the organic layer was also optimized for the device, giving a responsivity of $1.54 \times 10^{-2} \text{ A W}^{-1}$ in 460 nm light.

Poster 9: Microwave synthesis of nanostructured electrodes for Li-ion batteries

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Abstract: Nowadays, Li-ion batteries play a key role in the growing demand of portable electronics and hybrid electric vehicles (HEVs).¹ The development of fast and low temperature syntheses of nanostructured electrodes are then vital. Microwave treatment of metal alkoxides presents a rapid and low cost route to high quality nanocrystalline phases for Li-ion battery applications. Here, we demonstrate the significant reduction in processing times and energy consumption during the preparation of nanostructured battery materials when using single source metal alkoxides in comparison to commercial starting materials. In particular, we show the formation of olivine LiMPO_4 ($M=\text{Fe}, \text{Mn}$) nanostructures *via* a simple and energy efficient route employing metal alkoxides, which affords electrode materials exhibiting excellent electrochemical performances.^{2,3} Co-location of two transition metals in these metalorganic precursors is believed to bypass the need of diffusional mixing and allow the reactions to proceed faster and at lower temperatures generating highly crystalline materials. We also present neutron pair distribution function (PDF) analyses of some of our phases in an effort to examine the local structure and show that microwave processes produce highly crystalline olivine structured materials. Finally, we also include cycling studies in order to probe the relationship between the synthetic route, composition and electrochemical performance.

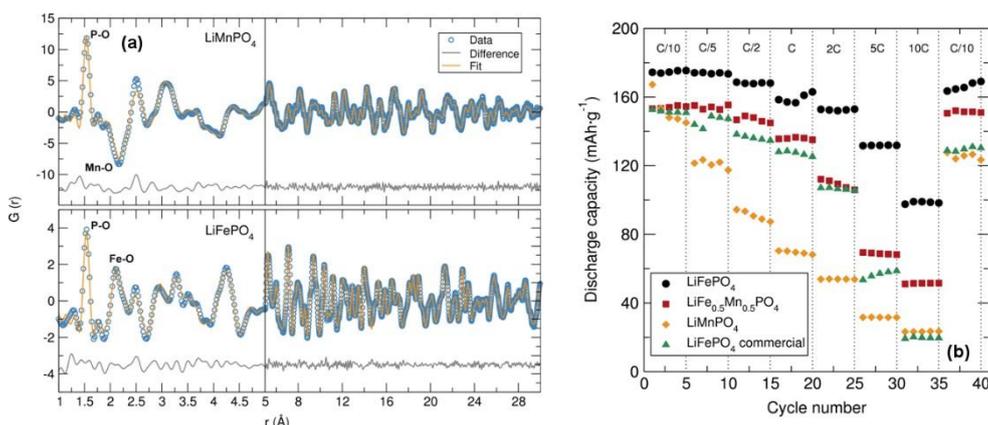


Fig. 1 (a) Neutron PDF analysis of LiMPO_4 ($M=\text{Fe}, \text{Mn}$) samples prepared from commercial starting materials and **(b)** rate performance of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ nanostructures prepared from heterometallic alkoxide precursors.

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Poster 10: Development and investigation of micro liquid electrodes for application in pyro electrochemical nuclear waste processing

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Abstract: Electrochemical pyroprocessing is a promising technology for the reprocessing of waste nuclear fuel. However, the high temperatures and corrosive environment of a molten salt, as used in pyroprocessing, presents unique challenges. To implement an electrochemical pyro-reprocessing system, it is necessary to develop robust and reliable electrochemical sensors in order to examine the fundamental electrochemistry (alloy formation, separation efficiency, diffusion coefficients, etc.). They will also provide a means to analytically detect relevant redox species.

This work shows the development, fabrication and examination of liquid bismuth thin film microelectrodes for the study of reductive alloying and oxidative de-alloying in molten lithium chloride potassium chloride eutectic (LKE). The resulting electrodes were shown to be capable of operating in LKE. Cerium is considered an electrochemical surrogate for plutonium in molten salt systems. Thus, studies of cerium alloying and de-alloying on the liquid bismuth microelectrode were performed in LKE. Using cyclic voltammetry there was evidence for the formation of multiple alloys.

Poster 11: Investigation of suitable cathode materials for use in next generation thermal batteries

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Abstract: This work includes fabrication of thermal cells of transition metal sulfides such as ZrS_3 and $CoNi_2S_4$. These materials were synthesized by solid state reaction in sealed quartz tubes (10^{-3} Torr) and investigated as candidate cathode materials in thermal batteries. Li-Si alloy as anode, LiCl-KCl as electrolyte and MgO as separator were used. The electrochemical properties of the batteries were investigated at 500 °C by Galvanostatic Discharge. The structure of $CoNi_2S_4$ was determined by XRD and was an inverse spinel structure single phase material¹ and cell parameters refined by WinXpoW programme. $CoNi_2S_4$ has a 2 step voltage plateau vs Li-Si, the first one at 1.75 Volts and the second one at 1.4 Volts at a constant current of 20 mA with capacity of 266 mAhg⁻¹. A monoclinic structure² of ZrS_3 was determined by XRD and morphology of crystallites as needles was investigated by SEM. ZrS_3 at high temperature Li cells has a flat voltage plateau of 1.7-1.6 Volts at a constant current of 20 mA with capacity of 350 mAhg⁻¹.

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Poster 12: Nanowire Gas Sensors for a Range of Analytes of Industrial Interest

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Abstract: Gas sensor networks have a wide variety of applications in environmental and safety monitoring that can be very useful to businesses and the general public. Environmentalists can use sensors to measure atmospheric pollution and monitor industrial emissions, and safety monitors can use sensors to detect harmful chemical vapors and explosives in public spaces, government and military facilities, and chemical processing plants. However, gas sensor technologies are still developing and have yet to reach their full potential in capabilities and usage¹. Conducting polymers (CPs) are unique materials because they exhibit electronic, magnetic and optical properties of metals and semiconductors while retaining the attractive mechanical properties and processing advantages of polymers².

This research work reports the synthesis, chemical (FTIR, UV-vis and XPS), structural (AFM and TEM) characterisations, electrical measurements (I-V and C-V) and design of gas sensors for a range of analytes of industrial interest. The sensing elements were based on CP nanowire created using a simple and low cost fabrication method by employing DNA as a template on which to carry out the polymerization. The gas characteristics of the different CP-DNA nanowire were investigated by recording their electrical responses when exposed to different analyte vapour passed at different flow rate. The resistance of CP/DNA nanowire change when exposed to the vapours at different flow rate.

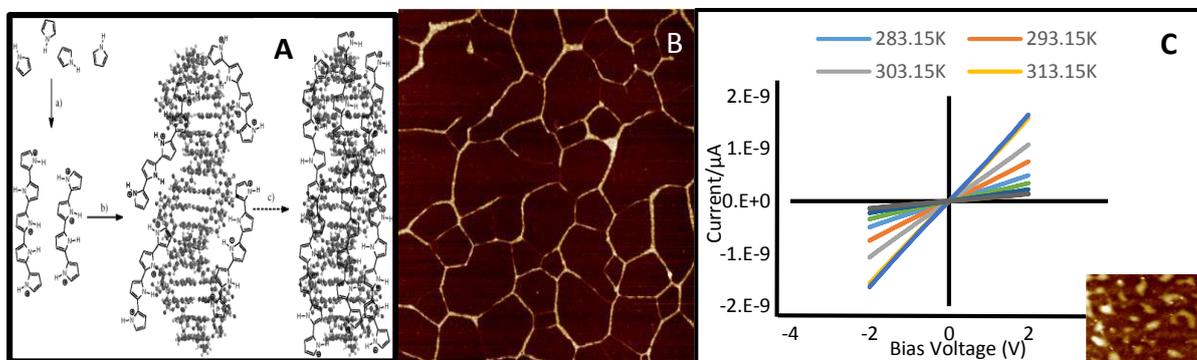


Fig. 1 (A): Proposed mechanism of self-assembly of DNA/CP nanowires, **(B):** Tapping mode AFM images of DNA/CP Nanowires and **(C):** Current-voltage (I-V) curves of a two-point contact Pt/DNA nanowire at a temperature range from 243.15 K to 283.15 K (Inset: An AFM height image of the network, the data scale is 5.2 nm, scale bar = 500 nm).

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Poster 13: Fast microwave-assisted synthesis and lithium-ion diffusion studies of lithium stuffed garnets

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Abstract: Lithium-stuffed garnets attract huge attention due to their outstanding potential as solid-state electrolytes for lithium batteries.¹ However, there exists a persistent challenge in the reliable synthesis of these complex functional oxides together with a lack of complete understanding of the lithium-ion diffusion mechanisms in these important materials. Addressing these issues is critical to realizing the application of garnet materials as electrolytes in all solid-state lithium-ion batteries. We have synthesised a cubic phase garnet of nominal composition $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_{2.92}\text{Zr}_2\text{O}_{12}$ through a microwave-assisted solid-state route for the first time, reducing considerably the reaction times and heating temperatures. Lithium-ion diffusion behaviour has been investigated by electrochemical impedance spectroscopy (EIS) and state-of-art muon spin relaxation (μ -SR) spectroscopy, displaying activation energies of 0.55 ± 0.03 eV and 0.19 ± 0.01 eV respectively.² This difference arises from the high inter-grain resistance, which contributes to the total resistance in EIS measurements. In contrast, μ -SR acts as a local probe providing insights on the order of the lattice, giving an estimated value of $4.62 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for the lithium diffusion coefficient. These results demonstrate the potential of this lithium-stuffed garnet as a solid-state electrolyte for all solid state lithium-ion batteries, an area of growing interest in the energy storage community.

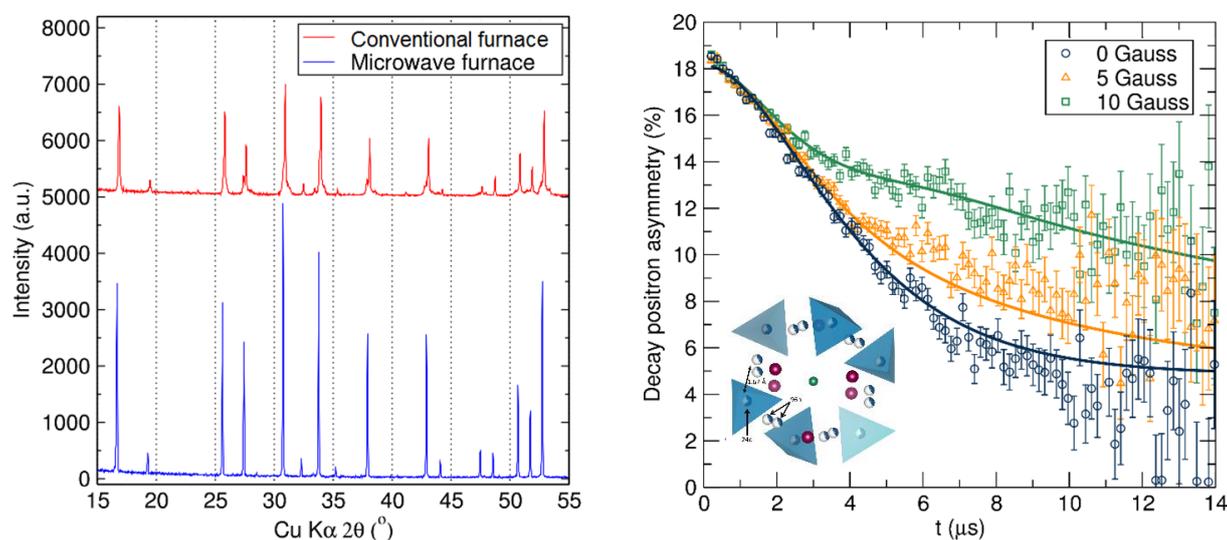


Fig. 1 (a) XRD pattern of the as-synthesized $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet by microwave-assisted vs conventional solid-state approach. (b) μ -SR raw data collected at room temperature at zero field (circles) and applied fields of 5G (triangles) and 10G (squares), fit (solid line) using the Keren function for the $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet.

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Poster 14: Surface-enhanced infrared spectroscopic detection of hydration shells at the electrochemical interface

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Abstract: Thanks to surface selectivity and low limits of detection, Surface-Enhanced Infrared Absorption Spectroscopy in the Attenuated Total Reflection mode (ATR-SEIRAS) is widely employed in the study of electrochemical interfaces. Hydration shells of Na^+ , Li^+ and NH_4^+ were detected with *in situ* ATR-SEIRAS by attracting the cations to the Au-electrolyte interface at potentials much more negative than the potential of zero charge (pzc). Migration of solvated cations to the interface caused a marked increase in the intensity of O-H stretching and H-O-H bending absorptions around 3450 and 1625 cm^{-1} , respectively. The H-O-H bending frequency suggested a lower degree of hydrogen bonding than bulk water, which is consistent with the structure of a primary solvation shell for a hydrophilic ion. At more negative potentials, a blue shift in H-O-H bending was observed. In the case of NH_4^+ , increased absorption due to H-N-H bending at 1440 cm^{-1} confirmed the accumulation of cations at the interface. The increase in O-H stretching and H-O-H bending bands are therefore attributed to the hydration shell of the cations. Electrochemical techniques coupled with *in situ* ATR-SEIRAS are shown to be an effective method for the study of solvation shells around ionic species.

Poster 15: Electrochemical Reduction of CO₂ in Organic Solvent to Chemical Fuels at Low Overpotential

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Abstract: The major challenge associated with the electrochemical reduction of CO₂ is finding a durable combination of electrocatalyst and electrolyte with which reduction of CO₂ can proceed with high energy efficiency and high product selectivity ⁽¹⁾. Depending on the electrolyte used, the electrode material, and the potential applied, a wide range of products can be obtained from this process, including, among others, carbon monoxide, formate (formic acid in acidic solution), formaldehyde, and ethanol etc ⁽²⁾. To achieve reduction of CO₂ with high energy efficiency and high product selectivity, a deep knowledge of the reaction mechanism, i.e. of the reaction intermediates and of the active sites on the catalyst surface is important. Due to the solubility of CO₂ and stability of anion radicals in organic solvents, amongst other reasons, CO₂ was reduced in acetonitrile to study this process. The first step was to determine the effect of water in the reduction process (water is necessary as a proton donor for the formation of CO or more reduced products, like alcohols or hydrocarbons) ⁽³⁾. CO₂ was therefore reduced in organic solvents, with different amounts of water to determine the effect of water in CO₂ reduction and the optimum amount of water required to obtain maximum efficiency and stability of the radicals (intermediates). This was done using classical electrochemical techniques like cyclic voltammetry. This work shows that water had an effect on the reduction of CO₂, also the controlling the amount of water present in organic solvents affects the reduction efficiency and stability of intermediates.

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Poster 16: Effect of water in metal electrodeposition processes from Deep Eutectic Solvents

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Although the plating industry currently uses mostly aqueous electrolytes, due to certain disadvantages Deep Eutectic Solvents (DESs) have been suggested as alternatives. These liquids have shown the potential to eventually replace aqueous electrolytes because of their innovative properties. Our group has reported electrochemical co-reduction of the DES, which could be avoided by the presence of water. Until now, most researchers have focused on using water free DES, and therefore, there is no substantial information on water content on the metal electrodeposition process. This study examines how water might affect the metal speciation, electrochemical parameters and microstructure properties of the deposits. Experimental results have demonstrated that the absorption band at 405 nm, characteristic of tetrachlorocuprate complex $[\text{CuCl}_4]^{2-}$ from which Cu is deposited, exhibited a diminution when 15 wt% of water was added to the solvent. A further increase in the amount of moisture (>30 wt%) triggered both the appearance of a new band at 270 nm and a strong reduction of the absorbance at 405 nm (Figure 1), showing that higher amounts of water might cause significant variations in the metal speciation. Hence, the content of water should be constantly monitored during a long-term electrodeposition process, which is the plan for future work.

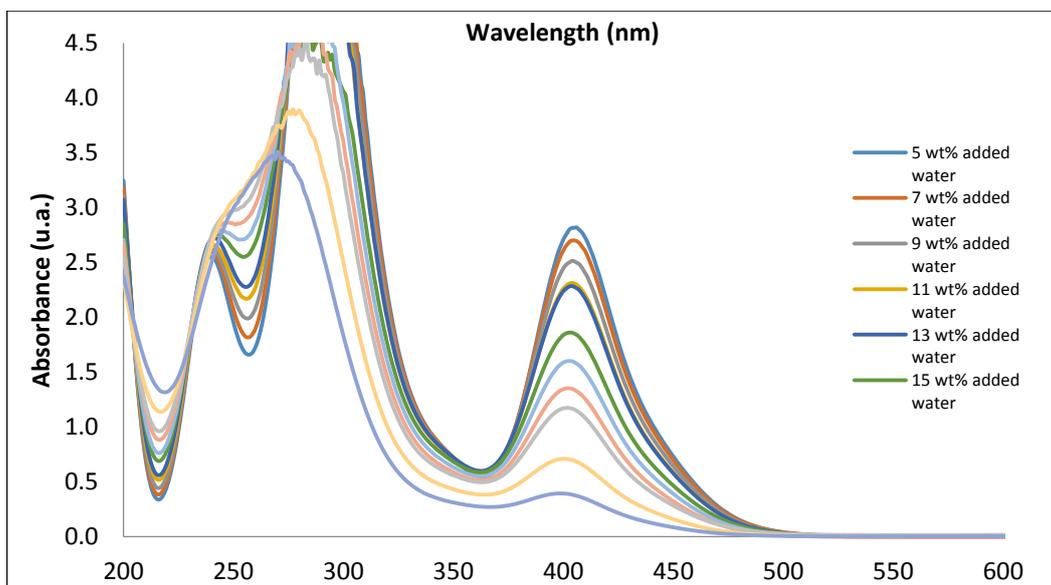


Figure 1. UV-Vis absorption spectra vs wavelength of 0.1 M Cu^{2+} -ethaline/water mixtures in a magnetic cuvette of 125 μm pathlength.

Poster 17: The effect of secondary doping on the properties of conducting polymers: an empirical and theoretical study

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Abstract: Conducting polymers (CP) also known as conjugated polymers, due to their structure; they have the distinctive property of conduct electricity. The most known families of CP are the polyanilines (PAni), polythiophenes (PTh) and polypyrroles (PPy). In addition to electrical conductivity, each of these families have other associated properties widely exploited such as, electrochromism, photocurrent and piezoelectricity and then they can be applied in many different types of electrochemical devices. Despite this properties, the major drawback of this class of materials is its poor durability, although they are quite resistant to severe environments, the time operation of devices based on CP is not long enough. Since the premature aging is related to electronic conduction mechanism itself, a viable strategy is attempting to inhibit this side effect¹. So several studies are being developed to minimize this disadvantage, among them we can mention the secondary doping². Thus, this work aims to explain and understand how the redox process of the chain polymeric behaves over the operation of electrochemical organic devices, using both experimental and theoretical data obtained by DFT calculations. Therefore, it was chosen to study layer-by-layer (LBL) systems of poly(o-methoxyaniline)(POMA) and poly(thiophene acetic acid)(PTAA) whose application is focused on supercapacitors. This choice is due to the fact of POMA acts like a polycation and PTAA like a polyanion and additionally, it is not electrochemically active at the potential window studied for the LBL film, so all the properties studied is due to POMA layers. Electrochemical characterizations were made by cyclic voltammetry and electrochemical impedance spectroscopy. While the simulations were done using DFT MOLOTOP basis set through CP2K program. As a blank sample, films made only by POMA was used. Interestingly, the durability increased drastically, in 3000 extensive charging and discharge cycles the LBL films were stable while POMA films quickly lost part of their properties. Furthermore, the specific capacitance of LBL compared to POMA films increased from 50.0 F g⁻¹ up to 140 F g⁻¹. These values agree to the minimization of mechanical stress due to the effect of the secondary doping as seen from calculations. The counter-ions of the solution no longer need to be intercalated by the active material layer (POMA). At its place, the PTAA chain substituents acts as counter-ions, being next to the chains of POMA and not needing to be intercalated to compensate for charge generated during POMA oxidation.

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Poster 18: Optimization of energy generation through stand-alone renewable energy systems

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Energy insecurity and pollution control are among the greatest challenges of our time. Addressing these challenges requires major changes in our energy infrastructure. The main aim of this research is to analyse the technical and economic feasibility of stand-alone renewable energy systems with option of hydrogen storage for a small community in the Scotland. The renewable energy system selected for this study is solar power plant and modelling is carried out by using MATLAB software. The results shows that although photovoltaic panels are highly fluctuating in nature and round trip efficiency of any long term storage system is always less than 50%, however considerable positive results were obtained by using tracker to effectively use the PV panel to generate more energy. Electrolyser performance over a wide range of loads are carried out and new gas turbine cycle is proposed to make the model much reliable and viable which results in round trip efficiency of storage system to about 63% and results in control of greenhouse gas emissions. From an economic point of view, the proposed system can deliver power at a price competitive to fossil fuel fire power plant only if the UK government funding like feed in tariff are placed.

Keywords: Energy efficiency; Optimization; Renewable energy; Solar PV, Hydrogen storage

Poster 19: Nanocomposite films as a gas sensor for organics

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Abstract: This research concerns the physical and structural properties of carbon nanotube /conductive polymer composites and their use in gas sensors. A good sensor should be sensitive, reliable, low cost, with fast response and a short recovery time¹. Carbon nanotubes (CNTs) are well-suited because of their unique properties; their small size, hollow centre, large surface area and good electric conductivity. However, it has been shown that pristine carbon nanotubes have a low response for volatile organic compounds – our target analyse - therefore we attempted to improve this property of CNTs by templating pyrrole on CNTs². Polypyrrole is simple to prepare by oxidation of the monomer and its resistance is very sensitive to organic vapours, although much larger than that of CNTs. TEM and AFM of polypyrrole/CNT composites prepared from single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) show polypyrrole coated the CNTs successfully. There are significant changes in the range of diameters of nano tubes for SWCNTs from (7-10) nm to (8-35) nm and from (2-10) to (21-50) nm for MWCNTs. The composites were tested for the variation in their resistance upon exposure to a range of organic vapours (acetone, chloroform) and to water. The sensing devices comprised simple two-terminal devices over which a layer of the composite was applied by drop-coating. We investigated the effect of the CNT: polypyrrole ratio on the sensor response, $S = (R-R_0)/R_0$ where R_0 is the resistance in an air atmosphere and R is the resistance at steady-state after exposure to an air/analyte mixture. In general, pure CNTs show a rapid response time, but very low response (typically $S < 0.1$) at room temperature. As the amount of polypyrrole in the composite is increased, S increases, the response time deteriorates. Interestingly, the response of the composites may even change sign as a function of target analyse concentration; this suggests that a simple mechanism based on swelling and its effect on the percolation behaviour of CNTs in the polypyrrole matrix is insufficient to explain the data.

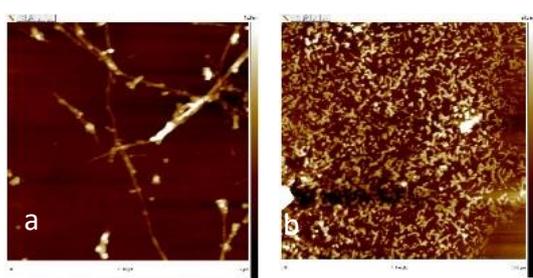


Fig1: AFM height images of (a) height distribution of SWCNTs after templated by Ppy. (b) Height distribution of MWCNTs after templated by Ppy. The heights were calculated by AFM

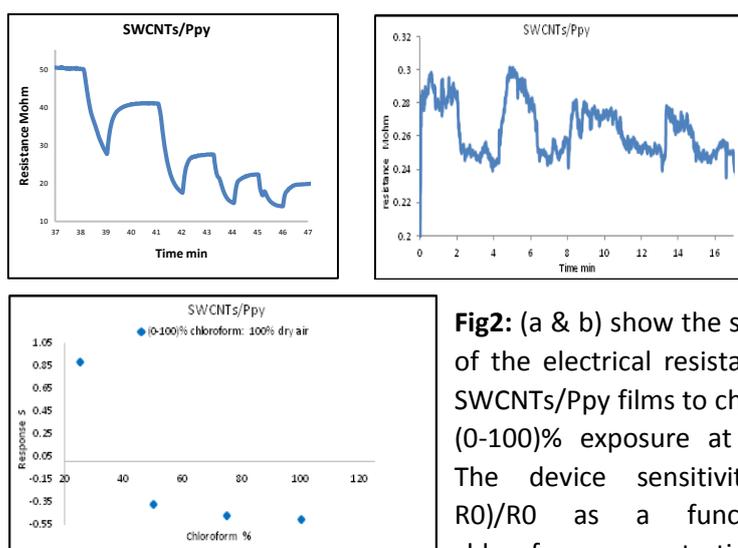


Fig2: (a & b) show the sensitivity of the electrical resistance R of SWCNTs/Ppy films to chloroform (0-100)% exposure at 17°C; (c) The device sensitivity $S = (R-R_0)/R_0$ as a function of chloroform concentration.

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Poster 20: The development of aluminium microelectrodes for online monitoring in nuclear pyrochemical processing

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Abstract: Molten salts are being extensively studied for effective pyroprocessing of spent nuclear fuel. The EPSRC funded REFINE collaboration is at the forefront of the UK's pyrochemical research effort. Within this collaboration our focus has been to develop "online" monitoring of chemical processing for use in the molten salt lithium potassium eutectic (LKE). The chemical species of interest for online monitoring are redox active, making electrochemical techniques a promising set of approaches for real time measurements. Using photolithographically defined patterns, we are developing a range of microelectrode sensors for use in LKE. Microelectrodes have the advantages of high signal to noise ratio, insensitivity to convection and rapid development of steady state diffusion profiles which make them an ideal candidate sensor for use in online monitoring of pyrochemical processing. The major challenge associated with the work is developing a sensor capable of withstanding the harsh environment in the melt (temperatures up to 500 °C and often highly corrosive). There are several metal candidates for the specific recovery of actinides during pyroprocessing. Of these candidates aluminium offers the best specificity for actinides over lanthanides. This poster will detail our research using aluminium microelectrodes for both online sensing and fundamental studies of the aluminium-actinide binary systems in LKE.

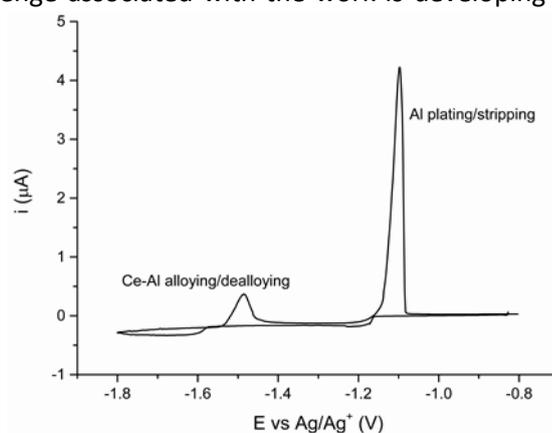


Fig. 1 Co-reduction of ~60 mM AlCl₃ and 11 mM CeCl₃ on a photolithographically fabricated tungsten microdisc electrode (15 μm radius) in LKE. T = 723 K, v = 100 mVs⁻¹. Cerium is used as a non-active surrogate for plutonium.

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Poster 21: Measurement of Double Layer Capacitance and Standard Rate Constants Using Bismuth Bulk Electrodes (BBE)

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Abstract: Bismuth is of interest in electroanalytical applications as a potential replacement for mercury because it has a smooth surface that can be re-formed by melting and, importantly, is environmentally benign by comparison¹. However, it is a semi-metal rather than a true metal and therefore it is important to establish the extent whether this has a large effect on the electron transfer kinetics. Bismuth bulk electrodes (BBE) have been employed in this study to determine the double layer capacitance (C_{dl}) in aqueous electrolytes and the standard rate constant (k^0) of the one-electron transfer process in hexaammineruthenium (III) chloride by the techniques of cyclic voltammetry (CV) and AC impedance spectroscopy. Electrode kinetics were confirmed to be too fast to measure by CV as the reactions were diffusion controlled and/or obscured by the uncompensated resistance. However, the Nyquist impedance plots showed a well-defined 'semi-circle' which was modelled using the Randles equivalent circuit, slightly modified to include a constant phase element instead of a pure capacitor. High quality data for the charge transfer resistance in a range of potentials around the formal potential were obtained. The results of the study gave a mean value of standard rate constant (k^0) to be $5.0 \times 10^{-3} \text{ cm s}^{-1}$ and a charge transfer coefficient (α) of 0.56 which demonstrate that reliable kinetic data can be obtained at bismuth electrodes. A figure demonstrating the variation of k^0 with potential for different concentrations of ruthenium hexamine is shown below.

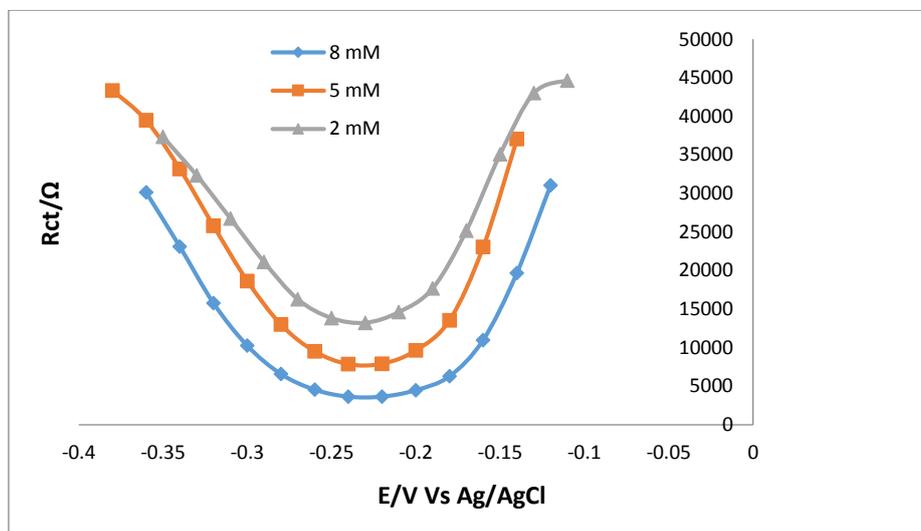


Figure1. Variation of charge transfer resistance with concentration of ruthenium hexamine

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Poster 22: Improving Flow Plate Design in Fuel Cells for Higher Efficiency

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Abstract: PEM fuel cell is gradually gaining dominance in the energy generation industry compared to other energy generation mediums. They are currently being developed actively for use in cars and buses and also in a number of portable applications. It is also used for combined heat and power systems (CHP). PEM is highly recommended for its patronage for NASA and Space Shuttle orbiter. It is sometimes even being argued by researchers that PEMFCs exceed all other electrical energy generating technologies with respect to the scope of their possible applications. They can power small portable devices like mobile phones and other electronic equipment like computers. Two components of PEMFCs are usually similar. The electrolyte used and the electrode structure and catalysts are the components in the PEMFCs that cut across all of them. There are other important parameters that hugely affect the performance of PEMFCs. These are the water management, the method of cooling the fuel cell, approach in connecting the cells in series, the pressure to operate the cell and even the reactants used are all factors that determines how efficient the PEMFCs is going to perform.

Modelling of PEM fuel cell has experienced a number of major landmarks in terms of research as it can be seen vividly in a number of literature. Most of these detailed work are centered on the internal heat and mass transfer of the cell but to achieve a good performance for any proton exchange membrane fuel cell stack, gas and water management remains critical factors that must be seriously considered. The field flow plates have to meet the conflicting requirement of providing good electrical contact and easy passage and even distribution of the gases concerned, hydrogen to the surface of the anode and air/oxygen to the surface of the cathode. A study of the input parameters affecting output responses will be performed, through experimentation of a single cell, and a comparison between three different configurations of flow plates of a proton exchange membrane fuel cell, the manufacturer's serpentine flow plate and two new configurations; the maze flow plate and the parallel flow plate. A study of the input parameters affecting output responses of voltage, current, power and efficiency of a fuel cell will be performed through experimentation. The results will be taken from direct readings of the fuel cell and from polarisation curves produced. The information will then be analyzed through a design of experiment (DOE) to investigate the effects of the changing parameters on different configurations of the fuel cell's flow plates.

Poster 23: Compare two structures of CO_2^- interacted with proton in aqueous from DFT based molecular dynamics

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Abstract: The structure of CO_2^- with proton is the key step of CO_2 reduction. In this research, two possible structures COOH and HCOO were investigated from Density Functional theory based molecular dynamics by using CP2K computational package. Based on the method from Jun Cheng^{1,2}, acidity constants and Gibbs free energy were calculated to evaluate those two pathways.

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Poster 24: Rapid Oxygen Transport Membrane evaluation at St Andrews

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Abstract: Oxygen transport membranes show promise as a replacement for cryogenic oxygen separation in the fields of oxyfuel combustion for CCS, production of syngas and lab-scale oxygen production. The causes and mechanisms of degradation are not fully understood, and there is potential to improve oxygen flux. Real-world systems are large and tubular, making evaluation of new materials expensive and difficult. Small planar architecture suits this rapid-screening process better, as cells are easier, quicker and cheaper to fabricate.

Oxygen transport membranes of the type being evaluated in the present study comprise a porous support layer, fuel oxidation layer, dual phase (ionic and MIEC) dense layer and an oxygen reduction layer. The dense layer's composition of an ionically conductive fluorite and a mixed ionic electronically conductive perovskite allows flow of electrons in the opposite direction to the oxide ion migration to maintain charge neutrality. Because no current is drawn (in contrast to SOFC) the driving force is chemical potential.

This study is primarily concerned with developing test capability for the rapid screening of cell assemblies, and understanding the causes and mechanisms of degradation in the fuel oxidation layer and dense layer.

Poster 25: Direct growth of Co-doped MoS₂ hydrogen evolution catalyst on F-doped SnO₂

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Transition metal chalcogenides (TMCs) are fascinating class of materials with a wide range of properties including electronic devices, sensing applications, energy storage and catalysis. Recently, TMCs have attracted significant interest as they can replace platinum in electrochemical water splitting reactions by acting as cathodes for proton reduction. In this function they can create both cheap and abundant platform for driving solar energy electrochemically into production of an ideal fuel: hydrogen.¹ Molybdenum sulfides of various compositions (Mo_xS_y) have been shown to be highly effective hydrogen evolution catalysts from aqueous solution over a wide *pH*-range.² Moreover, doping of molybdenum sulfides with other transition metals has also been proposed as a route to improving electrocatalytic activity for hydrogen evolution.³ However, existing methods to obtain such mixed-metal chalcogenides tend to produce materials in powder form which require post functionalization in order to be transferred onto a suitable substrate of choice, *e.g.* F-doped tin oxide. It remains very challenging to obtain ternary TMCs directly on a substrate and to unlock the true synergic benefits from interaction between a substrate and an electrocatalyst.

Herein, we show that metal-chalcogenides from a well-defined single-sourced molecular polyoxometalate (NH₄)₃(CoMo₆O₂₄H₆)·7H₂O precursor can be grown hydrothermally directly on a F-doped SnO₂ substrate. Electrochemical performance of tested materials indicates highly active hydrogen evolution electrocatalyst in aqueous solutions. The encouraging results offer the opportunity to develop a wide range of efficient catalysts by exploring a wide range of polyoxometalates as single-sourced precursors.

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Poster 26: Decoupled hydrogen evolution from a molecular metal oxide redox mediator and a catalyst in water splitting

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Abstract: The splitting of water via electrolysis is seen as a potentially renewable source of hydrogen for a green, sustainable future. A promising candidate for hydrogen storage is silicotungstic acid (STA) used as a recyclable redox mediator that can decouple the Oxygen and Hydrogen Evolving Reactions (OER and HER) during water electrolysis (see Figure 1).¹ With HER decoupled in space and time, the introduction of a catalyst allows for an on demand and spontaneous release of hydrogen gas with no additional input of energy. We report a platinum-catalysed system using STA that releases pure hydrogen at a rate 30 times faster than the equivalently loaded, state of the art proton exchange membrane electrolyser.

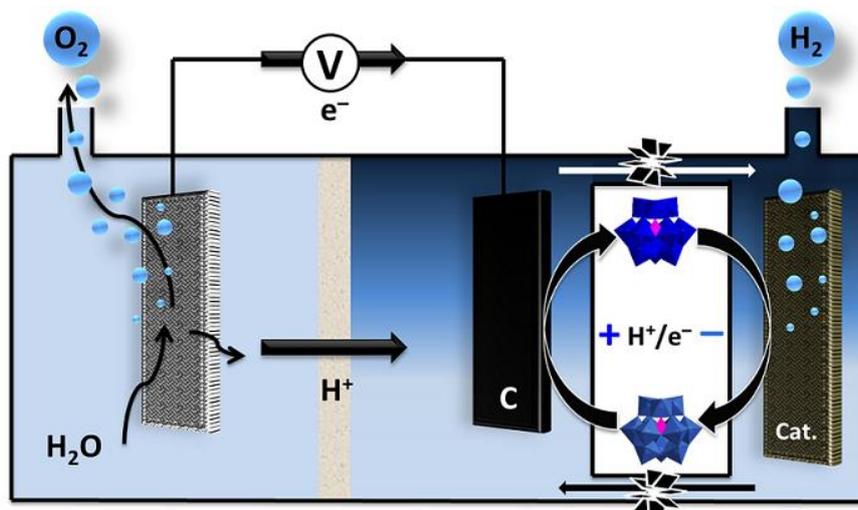


Fig. 1 A schematic representation of decoupled hydrogen evolution using an STA redox mediator and a catalyst during water splitting.

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