Oral Presentation Abstracts
Electrochemical Techniques & Tools

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Electrodes modified with surface-confined redox functionalities have a wide range of applications including sensors, optical devices, and batteries. Their rational design requires correlation of interfacial structure and properties, and accordingly a wide range of techniques has been used to provide insight into the chemical nature or, in the case of the STM and AFM, surface topography of the interface. The spatial distribution of material perpendicular to the electrode interface is one of the key parameters which determine the performance of a modified electrode device. This structure is central to the preservation of electroneutrality during redox processes as it determines the ease with which mobile species can enter and leave the film. Most measurements of electroactive film characteristics assume vertical spatial homogeneity, with respect to both the populations of mobile species (solvent, counterions) and the film matrix material (polymer, metal) through which they move. Although it is widely recognised that this is an unrealistic approximation, it is commonly used in the absence of better information. There is therefore a fundamental necessity motivating the development of a technique which is able to simultaneously characterise the spatial and temporal resolution of the individual components within the interior of electrochemical systems.

To address this capability gap, we have been developing in situ neutron reflectivity (NR). The unique penetrating power and selectivity of NR with isotopic contrast variation permits such dynamic analysis of compositional and structural changes of systems under electrochemical control. This allows the observation and quantification of diverse permeation characteristics of both conventional solvents and ionic liquids in electroactive conducting films. Due to instrumentation capabilities, the acquisition of NR data in electrochemical systems has previously been achieved at the cost of restriction to static measurements at fixed potentials. Here we report the first dynamic in situ NR measurements on electroactive films under dynamic electrochemical control, using state of the art event mode NR data acquisition.

Event mode data acquisition effectively records every neutron interaction with the surface, giving each neutron an individual time stamp. This permits setting of the averaging period (data “slices”) post-experiment, greatly improving the time resolution of NR experiments from hours to minutes or even seconds, which is consistent with dynamic electrochemical processes. This new capability has been exploited to perform temporally resolved specular NR measurements to profile different species at buried interfaces under dynamic electrochemical operating conditions during deposition, alloying and dissolution processes. Systems involving single and multi-component films of Cu, Ag and Sn on Au electrodes exposed to choline chloride / hydrogen bond donor (ethylene glycol, urea) ionic liquid media were studied providing new insights into transient population distributions.
In Situ Surface Enhanced Infrared Spectroscopy to Track Interfacial Processes Relevant to Non-Aqueous Lithium-Oxygen Batteries

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Non-aqueous lithium-oxygen (Li-O₂) cell generates electric current when lithium ions react with dioxygen molecules at the negatively polarised electrode forming Li₂O₂ during discharge process; the reverse happens during charging. One major factor affecting the reversibility of Li-O₂ cells is the poor stability of solvents in the presence of discharge products. The electrolyte environment also plays a critical role in promoting or hindering specific reaction pathways of the discharge products. Since the performance of Li-O₂ battery correlates closely with these reaction pathways, probing these mechanistic details using advanced analytical techniques is crucial for the realisation of practical Li-O₂ batteries [1]. Here we explore the prospect of using an advanced infrared spectroscopy technique, electrochemical attenuated total reflection surface enhanced infrared spectroscopy (ATR-SEIRAS), for a direct detection of the intermediates and reaction products formed during the oxygen reduction process. Compared to conventional infrared spectroscopy techniques, ATR-SEIRAS is particularly attractive for its strong sensitivity and selectivity to the interfacial region [2]. A schematic representation of the in situ ATR-SEIRAS setup is shown below.

The beam of infrared radiation propagating in the internal reflection element (IRE) undergoes total internal reflection at the interface where a thin layer of gold (ca. 20 nm) was deposited. Total internal reflection at the interface between two media of different refractive indices creates an evanescent wave that penetrates into the medium of lower refractive index. For the nanostructured gold film formed on the IRE, the plasmon absorption band tails well into the infrared region, which gives rise to enhanced electromagnetic fields resulting in an increased IR absorption in the interfacial region formed by the gold film working electrode (WE) which helps to detect the surface bound species selectively. As opposed to the commonly used silicon internal reflection element (IRE), we use a zinc selenide prism for our studies as it offers a wider range of infrared throughput extending to the region where lithium superoxide (LiO₂) and peroxide (Li₂O₂) can be detected. We will report on the electrochemistry of dioxygen in aprotic electrolytes relevant to Li-O₂ batteries; the reaction products and intermediates probed using our in situ ATR-SEIRAS technique, and its implications.

In-situ Electrochemical Characterisation of Iron Sulfide-Electrolyte Interface under Anoxic Conditions

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Iron sulfide Greigite $\text{Fe}_3\text{S}_4$ has been recently used as a cathode in Polymer Electrolyte Membrane (PEM) water electrolyzers as an alternative to the expensive platinum to facilitate efficient hydrogen evolution reaction.\(^1\) It has also been used as a cathode material for rechargeable magnesium batteries\(^2\) and an anode material for lithium ion batteries\(^3\). However to realise its potential for applications in PEM water electrolyzers and batteries, \textit{in situ} surface characterisation is needed.

The motivation for the use of Greigite in this work stems from the similarity of its cubic structure to $\text{Fe}_3\text{S}_4$ active sites of iron sulfur proteins (ferredoxins). Owing to this structural similarity, Greigite has been suggested as a $\text{CO}_2$ reduction catalyst in Origin of Life theories, producing key molecules for biochemical evolution.\(^4\) Additionally, magnetotactic bacteria produce Greigite and exploit its ferromagnetic property to achieve directional sensing around the Earth’s magnetic field.\(^5\) However these reactions occur under anoxic conditions and the surface structure of Greigite under anoxic conditions is not well studied.

Surface structure is of importance in catalysis and thus an experimental study on the stability of Greigite in aqueous media with or without an applied potential is of significance to PEM water electrolysis technology, geochemistry, biomineralogy and Origin of Life sciences.

We have developed in situ ATR-FTIR and XAS electrochemical cells to characterise and monitor changes to Greigite in anoxic aqueous environments, with and without an external potential. We show that greigite transforms into a core-shell structure, with oxyhydroxide and oxide layers as its shell.

References:
The Effect of Applied Electric Field on Structure of Lipid Bilayers

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The basis of a biological cell membrane is a bilayer of lipid molecules, in which are embedded proteins that carry out functions such as signalling and controlling the transport of ions and molecules across the membrane. Many lipids are found in nature and the composition of the membrane depends on the type of cell (e.g. mammalian or bacterial) and on its function (e.g. plasma membrane, mitochondrial membrane), yet little is known about the reasons for this variety. Indeed, the importance of lipids in protein function has only recently begun to be recognised. Both lipids and proteins experience strong electric fields as a result of charge asymmetry across the membrane and/or ion gradients. Electrochemistry provides the ideal means to mimic this electric field: the electric field at the electrode/electrolyte interface can be controlled continuously to a magnitude comparable with that found in nature, simply through applying a potential at the working electrode. By depositing a lipid bilayer on an electrode surface, we can not only measure its electrical barrier properties but we can follow structural changes in the lipid bilayer as the electric field is varied, using reflectometry, vibrational spectroscopy and scanning probe microscopy.

Here we present a study of the effect of lipid structure on organisation and packing within a bilayer, which in turn influence both barrier properties and response to an applied electric field. Polarisation Modulated Infrared Reflection Absorption Infrared Spectroscopy has been used to investigate lipid bilayers supported on a Au(111) surface under potential control. This technique allows the acquisition of spectra in the presence of solvent without relying on potential modulation. Using the peak positions and full width half maxima (fwhm) of the peaks arising from C-H stretching vibrations, we have determined how lipid structure influences packing within the ensemble. Using the peak areas, we have measured changes in orientation of the hydrocarbon chains as the applied field is varied. In the carbonyl and phosphate stretching regions of the spectra, we have analysed the shape of the absorptions to determine levels of hydration in the interfacial and headgroup regions of molecules. In a previous study, we observed differences in response to applied field between different common phospholipids and these differences were attributed to the different packing arrangements of the molecules, as a result of their different shapes and capacities for inter-molecular hydrogen bonding. In the present study, we have found that molecules of similar shape may respond differently to the applied field, which means that the ability of molecules to hydrogen-bond directly with each other is a major factor in determining lipid bilayer properties.

Using Spectroelectrochemistry to Probe Surface Reaction Pathways in Heterogeneous Catalysis

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The combination of electrochemical methods with in situ molecular spectroscopy can provide valuable information about physical and chemical processes at electrode-electrolyte interfaces. In particular, infrared and Raman spectroscopies have been shown to yield unique mechanistic insights into organic redox reactions at electrodes through the fingerprinting of surface adsorbates and intermediates via identification of characteristic vibrational modes. In addition to acquiring spectra as a function of applied electrode potential and time, simultaneous cyclic voltammetry can yield further information about the surface cleanliness and the occupation of specific atomic sites and crystallographic facets by organic species. One spectroelectrochemical approach that has received considerable attention is electrochemical surface-enhanced infrared absorption spectroscopy (SEIRAS), in which a thin film of metal nanoparticles is deposited on top of an internal reflection element and plasmon enhancement phenomena at the metal surface provide a means to monitor species specifically at the electrode-electrolyte interface.

Here we demonstrate the application of electrochemical SEIRAS to studying heterogeneous catalysis at platinum nanoparticles. By applying hydrogen evolution potentials to the platinum surface, we simulate the conditions of catalytic hydrogenation, enabling organic reaction pathways in aqueous media to be probed. This methodology is exemplified by two case studies relevant to heterogeneous catalysis in the fine chemicals industry, namely the hydrogenation of the α-keto ester ethyl pyruvate and the α,β-unsaturated aldehyde, cinnamaldehyde. In both cases a decarbonylation side reaction is shown to occur, yielding adsorbed CO, the generation of which is shown to be highly sensitive to surface potential. Furthermore, assessment of decarbonylation kinetics via time-series measurements reveals a strong dependence on the history of the platinum surface.
XAS Spectroelectrochemistry to Follow Metallic Nanoparticle Deposition at a Liquid/Liquid Interface

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The interface between two immiscible electrolyte solutions (ITIES) has been harnessed as a site for the electrodeposition of nanoparticles for a number of years 1 to overcome some of the main difficulties when studying nucleation. By confining the reaction to the ITIES and using an element specific spectroscopic technique it becomes possible to identify the transient, low concentration nuclei with significant contrast when compared to the bulk phase.

In our work we have focused on the combination of electrochemistry and X-ray absorption spectroscopy (XAS) to follow the onset of nanoparticle nucleation. To date we have focused on the interfacial deposition of Au and Pd. In following the reduction of Au(III) using XAS and X-ray fluorescence (Figure 1) we have been able to observe the presence of Au(I) as a stable intermediate. 2 The stability of this species is significant in the chemical synthesis of metallic nanoparticles. 3 By examining the reduction of Pd(II) we have gained insight into the nanoparticle growth process. The manipulation of reactant concentration or interfacial potential results in either spontaneous growth or the formation of a metastable pre-nucleation state resulting in fluctuations in size and oxidation state prior to the onset of stable growth. 4

References

Equivalent Circuit Fitting with Non-Linear Elements

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A novel analysis tool for EIS data was developed, that can determine the higher order derivatives of an electrochemical process, by using the combined 1st, 2nd and 3rd harmonic responses. This method can be executed with the same ease as the classical Equivalent Circuit Analysis. It can be applied on most Electrochemical Equivalent circuits, accounting for series and parallel elements in a rigorous manner, such as in the Randles circuit, on the full frequency range.

Electrochemical objects generally have a non-linear IV relation, therefore the amplitude must be kept small for the classical EIS linear analysis to be valid. Although non-linear EIS has been applied on several occasions, its use has been limited due to the complexity of the analysis. Especially if other equivalent circuit elements need to be included, such as series resistors and parallel capacitors, the rigorous analysis is a laborious exercise. That job is made easy by the application of this tool.

There are several advantages of the non-linear analysis. Higher amplitudes may be applied without causing measurement artefacts, resulting in impedance results with a better signal/noise ratio. Also extra information is obtained, from the 2nd and 3rd order impedance derivatives. For Butler-Volmer type reactions, these can be used to determine transfercoefficients/ Tafel-slopes and rate constants. For semiconductors the saturation current and exponential coefficient can be obtained.
Cryo-spectroelectrochemistry of Temperature Sensitive Copper-Oxygen Complexes

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Peroxo, bis(μ-oxo) and superoxo-copper complexes have been invoked as the active motif for the mechanistic performance of several kinds of enzymes\(^1\) such as Tyrosinase (Ty) and Particulate Methane Monoxygenase (pMMO), the latter being currently of great interest since it is able to active the strong C-H bond of Methane and convert it into Methanol. Despite the vast amount of spectroscopic data of the different small molecular models of the nature occurring active intermediates collected over decades\(^2\) little is known about their electrochemical properties as well as the optical and electronic features of the species evolved after the electron transfer takes place, probably as a consequence of the usual thermal sensitivity of these copper-oxygen complexes.

Herein we present the electrochemical and spectroelectrochemical study of a dinuclear bis(μ-hydroxoro) Cu(II) complex (I) which after oxidation produces a mixed-valence Cu(III)-(OH)\(_2\)-Cu(II) compound thought to play a pivotal role in the catalytic performance of pMMO. Low-temperature spectroelectrochemistry has allowed us to establish unambiguously its UV-vis spectroscopic signature and discern it from that one coming from degradation products as evidenced in the same experiment at r.t. In addition, an EPR study confirms the presence of a Cu(III)Cu(II) unit in the oxidized complex. Our studies have led to the development of methods to carry out electrochemical and spectroelectrochemical measurements at very low temperature (~ 80 °C or even lower if required) paving the way for the consideration of other Cu-O\(_2\) species.

![Figure 1. UV-vis spectroelectrochemistry of 1 at T = 233 K.](image)

References
Current and Future Electrochemistry Capabilities at the ISIS Neutron Scattering Facility

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The study of electrochemical systems at ISIS in the recent past has been successfully exploited by a relatively small community and has predominantly made use of neutron reflectometry. However, the ISIS second target station and its growing instrument suite have the potential to provide new opportunities in neutron reflection, small angle neutron scattering (SANS) and neutron imaging. Extra SANS capacity is now available on Larmor and soon on Zoom that will enable the development of new sample environment equipment for electrochemistry. Imaging will also become available on IMAT in early 2017 which will enable structures to be studied with a minimum resolution of 50\mu m, potentially in real time.

The currently planned upgrade to the reflectometry suite, which will be delivered over the next few years, is anticipated to decrease either the measurement time or required sample size by up to an order of magnitude. This will mean that measuring \sim 1\ cm^2 sample areas will become routine or the study of dynamics on larger samples using timescales of \sim 5\ s will become possible. Recent developments in data acquisition and synchronisation have enabled much greater flexibility in the post experiment analysis of data collected in parallel with the neutron measurement. The impact of these changes, the increase in performance and their possible applications will be discussed along with potential new sample environment ideas. In addition, the possibilities for SANS will be presented and the potential of IMAT for imaging reviewed.
The Effect of Ultrasound on Acid Copper Electroplating Additive - Sulphopropyl Sulphonate

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Keywords: Electroplating Copper; Sulphopropyl Sulphonate, Mercaptopropane Sulphonic Acid, Ultrasound, Sonication, Electrolysis.

Several workers [1,2] have shown that the application of ultrasound during electrochemical metal deposition can have beneficial effects. Many metal deposition electrolytes contain a range of additives to modify the deposit in terms of its mechanical properties, aesthetic quality and grain structure. If ultrasound is to be employed in such electrolytes it is therefore very important to understand the effect of acoustic cavitation on such additives. One such additive – SPS is often used as a brightener to improve the appearance of the deposit. The primary decomposition product of SPS is proposed to be a copper thiolate complex [3,4,6]. The thiolate appears to be mercaptopropane sulphonate (MPS). The SPS decomposition product is formed through an electrochemical oxidation reaction in the presence of Cu(II)/Cu(0).

The effects of three different ultrasonic frequencies on the decomposition of sulphopropyl sulphonate (SPS) in acid copper electroplating chemistry was studied using Cyclic Voltammometric Stripping (CVS), High Pressure Liquid Chromatography (HPLC) with UV/VIS spectroscopy detection and Hull Cell test. Ultrasound was applied during electrolytic copper deposition at 20 kHz, 40 kHz and 850 kHz frequencies at a constant temperature (20 °C) and ultrasonic energy density (18 W/litre). The HPLC analysis of standard acid copper deposition (without ultrasound) showed a depletion of SPS and the formation of copper thiolate/MPS byproduct [3,5,6] whilst CVS analysis indicated a depletion of SPS but no detectable evidence of electrochemical oxidation byproduct formation. HPLC analysis of the electrolytes that had been subjected to 20 kHz and 40 kHz ultrasonic irradiation showed higher concentration peaks of Copper thiolate/MPS byproducts suggesting that 20 kHz and 40 kHz ultrasound accelerate the depletion of SPS and formation of Copper thiolate/MPS complex. CVS analysis of sonicated electrolytes also showed clear shifts in the oxidation curve caused by the formed thiolate/MPS byproducts in the presence of ultrasound. HPLC and CVS data also suggested that the increase in decomposition byproducts affected by electrochemical sonication were in the order 20 kHz > 40 kHz > 850 kHz. Similarly the acceleration effect of formation of Copper thiolate/MPS complex of ultrasound is suggested to be in the order 20 kHz > 40 kHz > 850 kHz. Hull cell tests on acid copper electrolytes that had been electrolysed in the presence and absence of ultrasound showed little or no difference in hull cell appearance post electrolysis. This suggests that although low frequency ultrasound accelerates the formation of the Copper thiolate/MPS byproducts in the electrolyte the copper deposit quality is unaffected, as the byproducts also act as brightener/accelerator species.

A pulse reverse plating technique using an anionic surfactant has been developed to produce cobalt and nickel matrix nanocomposites. Electrodeposited Co-SiC nanocomposites produced with 50nm mean diameter of SiC in a previous study [1] have been produced again using different cathodic pulse time (t_c). Microstructural characterization (see fig. 1a) has been used to study the contribution to the coating hardness from the simultaneous effects of grain size refinement and dispersion strengthening. Ni-SiC coatings with good particle dispersion have also been produced using the same technique with gluconate and sulphamate baths. Different electroplating parameters were used to give control the SiC nano particle content throughout the metal matrix.

Results indicate that grain size refinement and dispersion effects are both controlling the hardness of the Co-SiC. The electroplated Ni-SiC produced from gluconate baths exhibited oxide layers through the metal matrix. Ni-SiC nanocomposites coatings produced from sulphamate baths showed sound coatings with particles well dispersed throughout the matrix, as shown in Fig. 1b.

References

The Effect of Organic Additives in Electrodeposition of Co from Deep Eutectic Solvents

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Metal electrodeposition using ionic liquid electrolytes and deep eutectic solvents is now well known for electrolytic deposition of metals such as nickel\textsuperscript{1} and cobalt. It has previously been shown that deep-eutectic solvents (DES), which are mixtures of quaternary ammonium salts with either hydrogen bond donors or metal salts, can be used for metal deposition.\textsuperscript{2} A range of organic/ inorganic additives have traditionally been added to electroplating solutions to improve brightness and encourage levelling. A limited number of studies have shown that some brighteners function in ionic liquids. In this study the effect of 4 additives; nicotinic acid (NA), methyl nicotinate (MN), 5,5 dimethyl hydantoin (DMH) and boric acid (BH), have been measured on the electrodeposition of cobalt in the 1choline chloride (ChCl): 2 ethylene glycol (EG) based deep eutectic solvent (DES). In general the addition of these additives causes the deposition potential of Co to be shifted to more negative over-potentials. The surface morphology was significantly changed by the addition of each of the additives, suggesting that they function by modifying the double layer. The nucleation and growth mechanism of Co deposition was found to change in the presence of these additives. Flat, shiny and high uniform cobalt layers were obtained with the additives whereas in their absence the deposit was black and dull (see Figure 1). The additives significantly increased the hardness of the cobalt deposit and this was shown to be related to the crystal structure of the deposit which was determined using XRD.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Scanning electron micrograph shows the bulk electrodeposition of 0.4 mol dm\textsuperscript{-3} CoCl\textsubscript{2}-6H\textsubscript{2}O in Ethaline at 90 \textdegree C on a Cu substrate.}
\end{figure}

Super-efficient Deposition using Powder Pulse Plating

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Electrodeposition is commonly used for the deposition of metallic and composite coatings. It is useful as it can coat complex structures and can be used for the deposition of alloys. There are a few disadvantages; it is relatively slow to build up thick coatings and in some cases the current efficiency can be low.

In this study a fundamentally different method for carrying out electrodeposition is demonstrated by using specifically designed 3D printed cells. Here instead of dissolving metal from the anode and depositing it on the cathode a powder of the coating metal is put in contact with the cathode and pulse plating sequentially dissolves metal from the powder and then deposits it between the powder grains. By this method super-efficient deposition (efficiency >100%) can be achieved and thick layers can quickly be deposited.

This can in principle be carried out in any media but in this study ionic liquids were used to increase the current efficiency of the process. The method is demonstrated using both zinc and copper. It is shown that using these media certain crystal planes can be promoted and ordered deposits are obtained. In addition the same technique was used to deposit composite materials by stirring with a mixture of metal powder with ceramic powders, such as alumina, silicon carbide. The morphology of the surfaces was characterized using SEM, X-ray diffraction, and 3D optical microscopy techniques.
Effect of Electrode Potential on the Acid/base Properties of Graphene Nanoflakes

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Graphene nanoflakes (GNF) with average diameter of 30 nm and edge-terminated with carboxylic acid (COOH) functionalities have recently been synthesised[1]. The small size of the flakes and the high concentration of the acidic edge groups lead to different bonding environments, such as armchair and zigzag edge, as well as varying degrees of electrostatic and hydrogen-bonding interactions between groups. Consequently, deprotonation of GNF has been observed to occur over a wide pH range[2].

In addition to solution pH, electrode potential may also provide a way to control the degree of protonation of acidic surface groups. For example, potential-induced ionisation of COOH-terminated self-assembled monolayers on Au electrodes has been reported by several groups ([3] and references therein). However, both a decrease and an increase in the monolayer acidity have been observed as the potential is made more negative.

Here, we report on the effect of electrode potential on the acid/base properties of GNF using a spectroelectrochemical technique. The working electrode – boron-doped diamond (BDD) modified with GNF complexed with Ca$^{2+}$ – was placed in contact with a diamond ATR element and a series of potential steps were applied. The influence of solution pH, electrolyte concentration and identity of ions were explored. The strength of electrostatic interaction of Ca$^{2+}$ with carboxylates could not be overcome by the range of potentials used in this study. Instead, free carboxylic acid groups were observed to undergo potential-induced protonation/deprotonation and shifts in the C=O frequency.

REFERENCES

Forgotten Applications of the Rotating Ring-Disk Electrode

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In the five decades since a robust theory for the Rotating Ring-Disk Electrode (RRDE) was developed by Albery and Bruckenstein, the RRDE has become a mature tool for elucidating electrochemical reaction mechanisms. A survey of publications from the past decade reveals that the most popular use of the RRDE is to characterize the mechanism and efficiency of oxygen reduction reaction (ORR) electrocatalysts via relatively straightforward “generator/collector” experiments. In stark contrast, however, the early decades of RRDE research witnessed other more exotic uses of the ring-disk geometry that are not as widely known today. Examples include diffusion layer titrations, hydrodynamically modulated voltammetry, split ring-disk electrodes, and several spectroscopic variants such as the rotating optical disc-ring electrode. Many of these methods are technically demanding, both in terms of the underlying mathematical treatment and the engineering needed to assemble the experimental apparatus. This paper will provide a rapid review of several of these lesser known RRDE applications.

The Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via ‘Nano-Impacts’

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The kinetics of the hydrogen oxidation reaction (HOR) on Pt nanoparticles (PtNPs) is investigated via both experiment and simulation. This reaction system is selected as a paradigmatic example of an inner sphere reaction and is of both fundamental and commercial interest. The study of the hydrogen oxidation reaction is implemented both on ensembles of PtNPs and at individual PtNPs. The adsorption rate constant for the hydrogen oxidation reaction on individual PtNPs is measured to be $0.020 \pm 0.008 \text{ m s}^{-1}$. It is further found that the kinetics for HOR on PtNPs detected from an ensemble of PtNPs is significantly underestimated, emphasizing the importance of applying the nano-impact technique to correctly understand electrocatalytic reactions on nanoparticles. Physical insights into the differences between single nanoparticle and ensemble behaviour are drawn.

References
“COMSOL Multiphysics® for Electrochemists”

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Within the investigation of an electrochemical system, contemporary electrochemists frequently exploit numerical simulation as an essential technique. COMSOL Multiphysics is an increasingly popular choice of commercial software for researchers who solve equations describing electrochemical phenomena. The software uses the finite element method to combine commonly studied physical effects with novel, user-defined equations, on any geometry. Interfacial electrochemistry is readily combined with other physical effects such as fluid flow and heat transfer.

This talk will address COMSOL’s outlook on use of electrochemical simulation by modern researchers, and the advantages of the COMSOL Multiphysics software as a tool in electrochemistry. We also aim to identify some relevant limitations, and areas of overlap with other methods.

We will review some prior applications of the software in electroanalysis and electrochemical sensing, as well as applied fields of electrochemistry such as corrosion, electroplating, batteries, and fuel cells. This talk aims to introduce physical principles central to electrochemical simulation, and to assist those electrochemists already familiar with these principles to understand the capability, contents, and relevance of the COMSOL Multiphysics software. We will also discuss conditions for independent reproducibility of prior COMSOL Multiphysics results in the literature.
Deposition of Pt Nanoclusters on Au and their Catalytic Activity Toward Formic Acid Oxidation

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Spontaneous deposition (SD) [1] and the surface limited redox replacement (SLRR) [2] of an underpotentially deposited sacrificial metal layer are two methods utilised to control submonolayer deposition of Pt on Au. In this work we compared the deposition of Pt nanoclusters via two methods and studied their catalytic activity toward formic acid oxidation (FAO).

Pt deposition via SD was systemically studied as a function of time of [PtCl₄]²⁻ complex adsorption and the number of deposition cycles. The results showed that the coverage of Pt on Au surface obtained from a single deposition cycle is independent of time of the [PtCl₄]²⁻ complex adsorption. The fraction of Au surface covered with Pt decreases with the number of successive SD cycles until it becomes constant after 5 SD cycles. Further application of SD cycles results in the steady growth of Pt nanoclusters height. SLRR was used to form 2D nanoclusters controlled by the coverage of Pb underpotential sub-monolayer. The results showed that with the increased coverage of Pt nanoclusters activity toward FAO decreases and approaches that of bulk Pt. The electrocatalytic activity of low coverage Pt nanoclusters (~ 20%) deposited via SD and SLRR showed differences that can be attributed to their size distribution on Au. The higher FAO activity of low coverage nanoclusters was attributed to the promotion of the FAO direct pathway as confirmed by CO electro-oxidation measurements.

![Graph](image)

Figure 1. Forward potential scan in 0.5 M HCOOH + 0.1 M H₂SO₄, 50mVs⁻¹, on Pt clusters formed by SD and SLRR on Au.

References:

Mineral Processing Using Deep Eutectic Solvents

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Hydrometallurgy is a cornerstone of primary and secondary metal recovery. It involves utilizing large volumes of aqueous solutions with reactive chemical reagents to solubilize minerals followed by extraction and recovery process. Metals can be recovered using: precipitation, cementation, electrowinning and ion exchange. However, this process risks negative impacts on the environment through the discharge of these heavy metals and toxic reagents into the water course as well as emitting toxic gases. Deep eutectic solvents (DESs) may provide an alternative to conventional hydrometallurgy that uses environmentally benign components and avoids the production of large volume/low concentration aqueous wastes.

In this study it is shown that deep eutectic solvents can be used to solubilise a range of sulfide based minerals through novel redox chemistry. Iron, copper, tin and lead minerals are shown to be electroactive and pure metals can be efficiently recovered by this method. It is shown that metals can be solubilised through both oxidative and reductive routes in a DES called Ethaline, a mixture of choline chloride and ethylene glycol. The redox chemistry is demonstrated using cyclic voltammetry and chronocoulometry. The dissolving species can be identified using Electrochemical Quartz Crystal Microbalance (EQCM) and uv-vis spectroscopy. This study also uses a novel 3D optical microscopy method to monitor and quantify the dissolution rates of pyrite in-situ. It is shown that a minimal amount of solvent is necessary for this process which is effectively run in a slurry using the ionic liquid as an electrolyte. Novel redox chemistry to be exploited by ensuring that the medium is largely non-aqueous enable.
Machine Learning for the Analysis of Single-Molecule Charge Transport Data

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Charge transport measurements in single-molecule electrode junctions have become relatively straightforward nowadays and a number of experimental platforms are available, including scanning probe microscopy, mechanical break junctions and chip-based nanoelectrodes. The target molecule typically features two 'anchor' groups that in some cases allow for well-defined and strong binding to the respective electrode surfaces. However, even for the same type of molecule, say an α,ω-alkanedithiol, each molecule seems to behave 'a little bit' differently, for example due to differences in the binding configuration or in the dynamics of the junction. Accordingly, the molecular signature in the charge transport data can vary, but is usually not known a priori. A large number of individual measurements are then needed to capture the full conductance distribution of the molecular junction. Automated data acquisition methodologies can be advantageous and we have recently demonstrated an approach that integrates recording of up to 100,000 data traces with STM imaging.[1]

Analyzing such large data sets can be very challenging and often relies on an assumption of the expected signal shape - for example, the presence of a plateau feature in the current-distance trace while the electrode/molecule/electrode junction is intact. The analysis also tends to focus on the most abundant event class. Sub-populations or 'rare events' in the data are easily overlooked, despite the fact that they can shed valuable insight into the processes taking place at the nanoscale. Clearly, a classification methodology is needed, that does not make any assumptions regarding expected signal shape, is able to detect and quantify sub-populations in the data and requires as little user intervention as possible (i.e. is unsupervised).

We have now developed and extensively tested such a classification methodology.[2] It is based on Machine Learning strategies, which we believe can change the way single-molecule data are assessed, analyzed and ultimately interpreted. In this contribution, we will explain the fundamental working principle as well as some applications.

Electrochemical Investigation In Gaseous Plasma Media

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ABSTRACT

Cyclic voltammetry is an extremely useful tool in the study of redox reactions at an electrode/electrolyte interface, commonly carried out in a liquid phase electrolyte. The technique, however, is hampered by a restricted potential window (typically 4.5 to 6 V): defined by the oxidation and reduction potentials of the solvent itself. Removal of this solvent effect allows investigation into redox chemistry outside the confines of the potential window and improved (diffusional) mass transport effects. We propose a gas phase electrolyte, specifically a plasma, as a method to surpass this restriction and to study novel chemistry at the solid/gas interface.

Thermal and non-thermal plasmas open avenues for the detection of gaseous species in the environment. Both have been explored as a medium within which analytical electrochemical techniques can be performed at the solid/gas interface with work focusing on development of an electrochemical setup and detection of radical species in a flame plasma electrolyte [1-3]. It is hoped that the electrochemical information obtained in a plasma will increase our understanding of ionisation phenomena and lead to a novel sensing technology.

REFERENCES


The Application of Electrochemistry in the Nuclear Industry: Development of the ELENDES Process from Laboratory to Pilot Scale

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Large amounts of infrastructure from the UK civil nuclear programme are to be decommissioned over the next 50+ years. During the decommissioning process it is often desirable to remove surface contamination in order to reduce hazard to workers and simplify further processing operations (e.g., providing man access for cutting and size reduction operations). Wet decontamination procedures are commonly employed for this purpose, which generate large volumes of liquid effluent. Management and disposal of effluent is a limiting factor in deployment of wet decontamination processes. The use of aggressive chemical decontamination agents such as chloride containing solutions or organic acids is severely restricted by the incompatibility of existing effluent treatment routes and downstream process pipework to solutions other than nitric acid. If aggressive decontaminations reagents could be used then it will speed up decommissioning and reduce decommissioning costs.

To overcome these limitations, C-Tech Innovation Ltd and National Nuclear Laboratory (NNL) cooperated to develop the ELENDES process (Electrochemical Enhancement of Nuclear Decontamination Solutions) which allows the removal of chlorides and organic species from aggressive decontamination agents down to sub ppm levels prior to disposal down conventional nuclear effluent treatment and pipework. The process was taken from a laboratory feasibility study to a fully integrated pilot scale, see Figure 1 below and has successfully undergone trials with ‘active’ solutions.

This talk will describe the market for the technology, the basic electrochemistry, results from the work, the plant design, some of the challenges of introducing electrochemistry into the nuclear industry and other potential nuclear applications for electrochemistry.
Scaling Up of Aluminium Electroplating Processes from Ionic Liquids and Deep Eutectic Solvents

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To date all existing Al coating technologies have either suffered from major technical limitations and/or been very expensive and although ionic liquids and deep eutectic solvents have been successfully used for electrodepositing aluminium coatings in several R&D projects at the lab-scale, the scale-up of these process to industrial scale has, until now, never been attained. Many issues have been encountered for upscaling of IL-based aluminium electrodeposition, particularly the moisture sensitivity of the electrolytes, and overcoming these challenges removes the final technological barriers to obtaining high-tech coatings in a productive and cost-efficient way. These new processes will replace conventional more harmful/hazardous techniques such as pack cementation and electroplating from Cadmium cyanide or Chromium VI electrolytes.

Figure 1: Pilot automated IL electroplating system developed during the Scail-up project.

The primary objective of the ALPCAR project was to scale up an aluminium plating process, based on a promising new generation of Deep Eutectic Solvents and develop a process demonstrator for an Al plating line using these new electrolytes. The primary application being targeted within the proposed project is a replacement for Cadmium within the aerospace industry.

The main objective of the SCAIL-UP project is to develop a radically new manufacturing industrial green process based on the electrodeposition of aluminium from ionic liquids and post-processing of the pure aluminium coatings to obtain high-tech engineered metallic materials for the automotive and aerospace sectors.
Extraction and Electrocatalytic Polymerisation of Thiophene from Oil using Ionic Liquids

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Deep desulfurization of diesel fuel has attracted significant attention due to the stringent regulations imposed on sulfur emissions from internal combustion engines. Eutectic based ionic liquids have been used to extract thiophene from decane which is a model diesel fuel. Thermodynamic analysis is presented for the liquid-liquid extraction and it is shown that solubility is governed by the energy required to create a cavity in the ionic liquid. Equimolar ratio and 2:1 of ferric chloride: 1-butyl-3-methylimidazolium chloride (Bmim)Cl were utilised to enable thiophene to be both chemically and electrochemically polymerised respectively after extraction from a decane layer. To optimise the performance of the Lewis acidic Fe-based imidazolium halide in thiophene removal, different reaction conditions were tested. The mass of polythiophene produced was determined using an electrochemical quartz crystal microbalance. The use of a 2 FeCl\textsubscript{3}: 1 (Bmim)Cl mixture enabled in excess of 90\% of the thiophene to be extracted from a decane layer and polymerised to polythiophene at 25 °C in 10 min.

Multiple catalytic electrochemical polymerisation of thiophene from decane into IL mixture a) before, b) after polythiophene formation, at 50 mVs\textsuperscript{-1} and 30 °C.
Supported bi-metallic catalysts have been a hot topic in recent years due to their excellent catalytic properties towards several chemical and electrochemical reactions. The electrochemical formation of supported bi-metallic nano-systems presents many advantages over other methodologies due to the ease with which one can control the size and shape of the resulting deposits by simply changing the applied potential.

The objective of the present work was the study of the electrodeposition of Rh over Ag substrates from salts containing chloride (Na$_3$RhCl$_6$) and sulphate (Rh$_2$(SO$_4$_)$_3$). In order to characterize the deposition process, different electrochemical techniques, such as chronoamperometry and cyclic voltammetry, were employed. Additionally, the observed stability of the Rh deposits was explained by using computational modelling with DFT calculations.

Experimentally it was observed that the system containing chloride anions shows a mechanism for the deposition of Rh consisting of two distinct stages. A deposition consistent with a 2D process is observed at low overpotentials, suggesting a stabilization effect of the chlorides on the fresh Rh deposits, while a 3D process takes place at higher overpotentials. In the case of a sulphate rich media, Rh deposition follows a 3D mechanism throughout the whole potential region explored. The observed stabilization process was later confirmed by means of first-principles atomistic thermodynamics using DFT calculated energies[1]. The theoretical calculations allowed for the explanation of what was observed experimentally.

References

Poster Presentation Abstracts
Electrochemical Techniques and Tools

Electrochem 2016
Poster Presentations
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- Electrochemical Characterisation of Thin Metal Films and Bilayers for Application in the PCB Industry
  Emma J. R. Palin, University of Leicester, UK.

- Nanoporous Plasmonic Materials
  Vinicius Cruz San Martin, University of Bristol, UK.

- The Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via ‘Nano-Impacts’
  Chuhong Lin, Oxford University, UK.

- Application of the Combined Electrochemical Quartz Crystal Microbalance and Probe Beam Deflection Technique for Characterization of Ag-Bi Alloy Films
  Marian Perera, University of Leicester, UK.
Electrochemical Characterisation of Thin Metal Films and Bilayers for Application in the PCB Industry

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The fabrication and assembly of printed circuit boards (PCBs) involves the layering of metals onto an insulating substrate prior to the addition of electronic components. The interfaces between these metal layers are often subject to metal-metal interdiffusion, formation of brittle intermetallics and corrosion, compromising the integrity of the PCB-component solder joints. We have recently developed environmentally sustainable, non-toxic methodologies for application of metal PCB finishes using Deep Eutectic Solvents (DESs) as a novel solvent medium.

Here we focus on the characterisation of metal-metal interfaces in DES media quantifying interfacial structure, layer thickness and morphology using a range of electrochemical and microscopy techniques, including chronoamperometry, cyclic voltammetry (CV) and novel simultaneous thickness electrochemical potential (STEP) measurements. We have developed the STEP methodology specifically for high ionic strength media, specifically DESs.

Deposition of Ag, Cu and Sn layers has been carried out in a range of different configurations onto Au substrates and characteristic STEP traces are presented for each upon galvanostatic stripping. The STEP methodology facilitates the identification and quantification of each metal layer by galvanostatic dissolution. The characteristic features of the STEP measurements are discussed including the shape and potential of the dissolution trace. The degree of mixing between the layers is determined from $E$ vs. $t$ traces, along with the layer composition and thickness for systems in which layers remain discrete.

The morphology of metal layers was characterised by atomic force microscopy (AFM). It was observed that the stripping STEP traces for Cu and Ag bilayers was identical irrespective of the orientation of the bilayer with respect to the solid-liquid interface. Additionally, STEP data for Au-Cu interfaces showed evidence of intermetallic formation and interdiffusion. Rapid interdiffusion was also observed at the interface between Au-Sn.

In summary, we present the results of the application of STEP (galvanostatic stripping) methodology in DES media which provides insight into the thickness, composition and interfacial mixing between adjacent metal layers used in PCB fabrication.

Nanoporous Plasmonic Materials

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The localised interactions between the electromagnetic field of light with the oscillation of surface charge are called surface plasmons (SP). Plasmonic materials are materials of interest for applications in optics, magneto-optic storage, photovoltaics and for single biological molecule detection. One of the main drivers for the development of plasmonic materials has been a massive signal enhancement that can be achieved in surface-enhanced Raman spectroscopy (SERS) on metallic structures with dimensions much smaller than the wavelength of light. SERS is a technique that can provide highly resolved vibrational information about molecules adsorbed on nanostructured surfaces and nanoparticles. Development of new highly active electrodes for SERS has a great potential to improve sensors and help understand molecular interactions.2,3

Silver and gold are commonly used materials for SERS due to local enhancement of the electromagnetic field caused by the resonance between the incident light and SP oscillations.4 The SERS electrodes are often made by assembly of nanoparticles or by roughening of planar surfaces. Recent work has shown that nanoporous electrodes have a great potential as active SERS electrodes3. Here in this work development of nanoporous gold (NPG) and silver (NPS) electrodes using electrochemical methods will be presented. NPG electrodes were formed by electrochemically controlled de-alloying, i.e. by selective dissolution of Ag, of electrodeposited AgAu alloys electrodeposited from thioulsulphate solution. Silver is a metal that has many advantages over gold with the SERS enhancement of 100-1,000 times.3 NPS electrodes were formed by electrodeposition of epitaxial Ag ultra-thin films on NPG. Examination of the SERS activity of the developed electrodes was done by using the micro-Raman scattering with different laser excitations (UV/vis/IR) and chemical markers, such as organic dyes. Developed NPG and NPS electrodes will be compared to the electrodes formed by conventional Au and Ag oxidation-reduction roughening.

References:

The Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via ‘Nano-Impacts’

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The kinetics of the hydrogen oxidation reaction (HOR) on Pt nanoparticles (PtNPs) is investigated via both experiment and simulation. This reaction system is selected as a paradigmatic example of an inner sphere reaction and is of both fundamental and commercial interest. The study of the hydrogen oxidation reaction is implemented both on ensembles of PtNPs and at individual PtNPs. The adsorption rate constant for the hydrogen oxidation reaction on individual PtNPs is measured to be $0.020 \pm 0.008 \text{ m s}^{-1}$. It is further found that the kinetics for HOR on PtNPs detected from an ensemble of PtNPs is significantly underestimated, emphasizing the importance of applying the nano-impact technique to correctly understand electrocatalytic reactions on nanoparticles. Physical insights into the differences between single nanoparticle and ensemble behaviour are drawn.

References
Application of the Combined Electrochemical Quartz Crystal Microbalance and Probe Beam Deflection Technique for Characterization of Ag-Bi Alloy Films

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Electrodeposited silver coatings are widely used in a range of engineering and electronic applications, but their performance may be limited by their hardness, wear, tarnishing or friction coefficient. One way to alleviate these problems is alloying, to produce intermetallic compounds; relatively modest amounts of the alloying element may have highly beneficial effects. In the case of silver, formation of Ag-Bi alloys can produce coatings with enhanced hardness and wear resistance [1]. Changes in grain structure of the alloy (cf. pure silver) also result in decreased porosity and thence better resistance to corrosion [2]. Bismuth alloys are also used in the manufacture of bearings, where alloy formation can result in self-lubrication properties. While the technological advantages of alloy formation are widely exploited, a concern is that they are commonly deposited from electrolytes (e.g. containing strong alkali or cyanide [3]) that present environmental issues.

Here we explore the possibility of Ag-Bi alloy deposition from an environmentally benign medium, the deep eutectic solvent Ethaline (choline chloride: ethylene glycol in 1:2 stoichiometric ratio). We report observations of the deposition of metal films and their subsequent dissolution under potentiodynamic control using the combined electrochemical quartz crystal microbalance (EQCM) / probe beam deflection (PBD) technique. Here, electrochemistry (E) provides control of the interfacial reactions and gives an overall measure of rate (via current, i), the acoustic wave (QCM) response yields the deposited mass (Δm, via Δf) at the interface and the optical signal (PBD) provides information on chemistry of the reactants and products (via refractive index gradient). The spatial separation of the probe beam and the electrode surface means that there is a delay between the responses, associated with the diffusion of solution species across the intervening solution; a convolution algorithm is used to project the responses onto the same location, i.e. effectively to synchronise them for direct comparison [4].

In a voltammetric experiment involving an Ethaline solution containing AgCl and BiCl₃, the difference in metal system formal potentials results in sequential deposition of the components. There is initial deposition of a single component film, followed by co-deposition of the two metals; the relative contributions of these were varied via potential range and scan rate. In the reverse potential sweep, the temporal variation in the product(s) of subsequent dissolution were used to explore the rate of interdiffusion of the alloy components. Interestingly, the optical signal is sensitive to aspects of solution complexation chemistry to which the electrochemical and acoustic wave responses are insensitive. In Ethaline, this relates to metal/chloride coordination chemistry and the local availability of ligand at high metal dissolution rates. The EQCM/PBD observations are supported by rotating disc electrode measurements that provide insight into passivation and dissolution rate. These data are used to deduce mechanistic details of film deposition and alloy component interdiffusion.

References
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