STFC Early Career Researchers Conference 2015

Conference Booklet

STFCBatteries.org

Science & Technology Facilities Council

ESRN ENERGY STORAGE RESEARCH NETWORK

Early Career Researchers Conference - 2015

STFCBatteries.org

Chair: Dr. Shane Beattie

Session 1

Time	Dur.	Type	Speaker		Title
10:30	30"	Registration			Tea and coffee
11:00	30"	Plenary	Prof. Bill David	-	Electrons, hydrogen and ammonia
11:30	20"		Dr. Christopher Egan	-	X-ray methods for 3D chemical imaging
11:50	20"		Sam Cooper	-	Transport in SOFC electrodes: Diffusion at many length scales
12:10	15"	Tea / Coffee			
12:25	20"		Dr. Juan Paz-Garcia	-	Combining lab-scale and synchrotron radiation X-ray tomography to study micromechanics of lithium-ion batteries
12:45	20"		Dr. Billy Wu	-	Multi-scale imaging of dendrite formation in 3D printed zinc-air batteries
13:05	20"		Donal Finegan	-	In-operando fast tomography of Li-ion batteries during operation and failure
13:25	1h	Lunch			

Chair: Dr. Billy Wu

Session 2

Time	Dur.	Type	Speaker		Title
14:25	10"		Dr. Paul Shearing	-	STFCBatteries
14:35	20"		Matthew Worsdale	-	The potential of Ta:SnO2 and H:SnO2 as catalyst support for Low Temperature Fuel Cells
14:55	20"		Dr. Ehsan Ahmad	-	Optimising Oxygen Reduction Catalyst Morphologies from First Principles
15:15	20"		Tobias Binninger	-	Fundamental DFT Study of Electronic Interactions between Catalyst Metal Nanoparticles and Metal Oxide Support
15:35	20"		Michael Parkes	-	Ab initio Modeling of Yttria Stabilised Zirconia for Solid Oxide Fuel Cells
15:55	15"	Tea / Coffee			
16:10	20"		Rhodri Jervis	-	Development of a PdIr/C Anode catalyst for Alkaline Anion Exchange Membrane Fuel Cells
16:30	20"		Cheng Li	-	Surface segregation in Sr doped LaNbO4 and its effect on proton transportation
16:50	20"		Vidal Bharath	-	Characterisation of Thin Film Alkaline Anion-Exchange Membrane (AAEM) Fuel Cells Using a Quartz Crystal Microbalance (QCM) and Crystal Admittance Spectroscopy
17:10	30"	Plenary	Dr. Kevin Fahey	-	4D X-ray Microscopy and Modern Correlative Workflows in Electrochemical Research
17:40	1h	Poster Session			Tea, coffee and warm beverages will be provided by UCell Fuel cells during this time
19:00	30"	Drinks Reception			
19:30		Dinner			

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Chair: Dr. Juan Paz-Garcia

Time			Speaker		Title
9:45	30"	Plenary	Dr. Ralph Clague	-	Fuel Cells in 2015: SWOT Analysis
10:15	20"		Wasim Sarwar	-	High fidelity, multi-dimensional supercapacitor thermal modeling
10:35	20"		Dr. Celine Merlet		Development of a new simulation method to model diffusion and NMR spectra in porous carbons
10:55	20"		Dr. Ana Belen Jorge Sobrido	-	Carbon Nitrides: New Electroactive Materials for Energy Applications
11:15	15"	Tea / Coffee			
11:30	20"		James Robinson	-	Investigating the Effect of Thermal Gradients on Stress in Solid Oxide Fuel Cell Anodes Using Combined Synchrotron Radiation and Thermal Imaging
11:50	20"		Dr. Na Ni	-	TEM investigation of Cr poisoning of LSCF cathodes
12:10	20"		Marta Gandiglio	-	SOFCOM: the first biogas fed SOFC trigeneration plant with carbon capture and use
12:30	20"		Dr. Andrea Lanzini	-	Solid Oxide Fuel Cell Anode Degradation by the Effect of Fuel Contaminants

Session 3

Time			Speaker		Title
12:50	1h	Lunch			

Chair: Rhodri Jervis

Time			Speaker		Title
13:50	20"		Dr. Christopher Eames	-	Next-Generation Electrode and Electrolyte Materials for Li-, Na-, and Mg-ion Batteries
14:10	20"		Dr. Thomas Miller	-	Graphitic carbon nitrides as anode materials for Li-ion batteries
14:30	20"		Ian Hunt	-	A comparison of the effect of different cooling techniques on Lithium-ion battery degradation
14:50	15"	Tea / Coffee			
15:05	20"		Dr. Sylvia Britto	-	(De)lithiation Mechanism of Vanadium Sulfide, a Promising Battery Material
15:25	20"		Harini Hewa Dewage	-	Study of loss mechanisms in a Regenerative Hydrogen Vanadium Fuel Cell
15:45	20"		Iain Aldous	-	The Influence of Tetraalkylammonium Cation Chain Length on Gold and Glassy Carbon Electrode Interfaces for Alkali Metal-Oxygen Batteries
16:05	20"		Dr. Shane Beattie	-	Identification of failure mechanisms in Si electrodes for Li-ion batteries

Session 4

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List of Delegates

Dr	Ehsan	Ahmad	Imperial College London
Mr	Iain	Aldous	University of Liverpool
Miss	Laura	Allerston	University of Birmingham
Mr	Alistair	Barnes	Swansea University
Dr	Shane	Beattie	Warwick University
Mr	Vidal	Bharath	UCL
Mr	Tobias	Binninger	Paul Scherrer Institut
Mr	Moshiel	Biton	Imperial College London
Dr	Sylvia	Britto	University of Cambridge
Mr	Leon	Brown	UCL
Miss	Rowena	Brugge	Imperial College London
Mr	Tom	Bryden	University of Southampton
Dr	Ralph	Clague	Imperial College London
Mr	Sam	Cooper	Imperial College London
Prof	Bill	David	STFC & Oxford
Dr	Christopher	Eames	University of Bath
Dr	Christopher	Egan	University of Manchester
Dr	Kevin	Fahey	Carl Zeiss X-ray Microscopy
Mr	Donal	Finegan	UCL
Mr	Tom	Galloway	University of Liverpool
Miss	Marta	Gandiglio	Politecnico di Torino
Dr	Dawn	Geatches	STFC
Dr	Carol	Glover	Swansea University
Mr	Krishnakumar	Gopalakrishnan	Imperial College London
Mr	Kent	Griffith	University of Cambridge
Mr	David	Halat	University of Cambridge
Miss	Jennifer	Heath	University of Bath
Mr	Tom	Heenan	UCL
Dr	A. K. Ola	Hekselman	University of Oxford
Ms.	Harini	Hewa Dewage	Imperial College London
Mr	Ian	Hunt	Imperial College London
Dr	Hazel	Hunter	STFC
Ms.	Dina	Ibrahim Abou El Amaiem	UCL
Miss	Aimee	Jackson	University of Birmingham
Mr	Rhodri	Jervis	UCL
Dr	Ana Belen	Jorge Sobrido	UCL

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Miss	Chloe	Knox	UCL
Dr	Denis	Kramer	University of Southampton
Mr	Peter	Lander	ZEISS Company
Dr	Andrea	Lanzini	Politecnico di Torino
Mr	Cheng	Li	Imperial College London
Mr	Alvin	Lim	UCL
Mr	Joshua	Makepeace	University of Oxford
Mr	Jordan	Marinaccio	Swansea University
Ms.	Nina	Meddings	University of Southampton
Mr	Yu	Merla	Imperial College London
Dr	Celine	Merlet	University of Cambridge
Dr	Thomas	Miller	UCL
Dr	Na	Ni	Imperial College London
Mr	Mathew	Niania	Imperial College London
Mr	Michael	Parkes	Imperial College London
Dr	Juan Manuel	Paz-Garcia	Lund University
Miss	Peter	Robbs	University of Birmingham
Mr	James	Robinson	UCL
Mr	Wasim	Sarwar	Imperial College London
Dr	Paul	Shearing	UCL
Mr	Duke	Shih	Imperial College London
Miss	Emily	Smith	University of Surrey
Mr	Christopher	Sole	University of Liverpool
Mr	Luke	Sperrin	University of Cambridge
Mr	Dami	Taiwo	UCL
Mr	Bernhard	Tjaden	UCL
Dr	Florent	Tonus	Imperial College London
Mr	Amangeldi	Torayev	University of Cambridge
Ms.	Celeste	van den Bosch	Imperial College London
Mr	James	Walker	University of Birmingham
Mr	Chi Ho	Wong	Imperial College London
Mr	Stephen	Wood	University of Bath
Dr	Thomas	Wood	ISIS, STFC
Mr	Matthew	Worsdale	University of Southampton
Dr	Billy	Wu	Imperial College London
Miss	Assiya	Yermukhambetova	UCL

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Speakers and Abstracts

Prof. Bill David (University of Oxford, ISIS) Plenary Speaker

Electrons, hydrogen and ammonia

Dr Christopher Egan (University of Manchester)

X-ray methods for 3D chemical imaging

I will present techniques that combine X-ray based characterisation methods (e.g. powder diffraction, fluorescence and absorption spectroscopy) with computed tomography to obtain 3D images of materials and structures with chemical specificity. Using these methods each voxel of a 3D image contains some kind of chemical information whether that be an objects 3D crystalline structure via X-ray powder diffraction or its elemental content via X-ray absorption spectroscopy. This research is directed at developing these techniques using both synchrotron radiation and laboratory X-ray sources as well as using state-of-the-art X-ray detectors. Example applications will be presented covering a wide range of materials including functional materials and light alloys as well as potential applications to studying batteries and fuel cells.

Sam Cooper (Imperial College London)

Transport in SOFC electrodes: Diffusion at many lengthscales

Extrusion techniques can be used to produce microtubular SOFCs with a wide range of hierarchical microstructures. It is believed that by controlling the pore structure of the thicker supporting electrode, the transport properties can be optimised. X-ray micro-tomography has been used to image the finger-like voids in a microtubular anode. These structures are on the order of 10 microns in diameter; however, smaller characteristic lengthscales can be imaged using FIB/SEM, which reveals the packing of the sintered particles, as well as the pore structure within the particles. Quantifying the tortuosity factor at each of these lengthscales offers insight into the effect of tailoring the pores. The tortuosity factor of is used to account for the apparent reduction in species diffusion caused by the geometry of the network. It affects both the electrical transport in the solid phases as well as gas diffusion in the pores. This work explores a range of approaches to quantification in these complex, hierarchical structures.

Dr. Juan Paz-Garcia (University of Lund)

Combining lab-scale and synchrotron radiation X-ray tomography to study micromechanics of lithium-ion batteries

Nowadays, intense research is devoted to develop new generations of advanced lithium-ion batteries with high energy-density. For example, alloying Silicon anodes are promising electrodes with theoretical energy density up to ~ 4200 mAh/g against the ~ 375 mAh/g of graphite, which is still the most used anode material in commercial batteries. Silicon electrodes, however, have the drawback of

exhibiting drastic volume changes during the lithiation/delithiation processes (~ 310 % against the ~ 10 % of graphite). Volume changes within a battery's constrained case involve mechanical strains on the fundamental components of the material, which eventually causes the battery to fail.X-ray micro computed tomography techniques are suitable for the study of the coupled chemical and mechanical phenomena, as they allow the visualization of evolution of the microstructure properties of lithium-ion batteries during cycles of charge/discharge. High-resolution synchrotron radiation is typically preferable to lab-scale tomographs. Herein, we present and compare results from both synchrotron radiation (TOMCAT—PSI, Swiss Light Source) and laboratory tomograph (Xradia MicroXCT-520) for the study of silicon – lithium batteries. At the current case, a scan in synchrotron radiation lasts ~ 100 times faster than in lab tomograph for comparable resolution. The former's superior acquisition speed allows the in situ and in operandi visualization of batteries, under the assumption that the scanning time is short compared with the (dis)charging time. However, for very fast and very slow (dis)charging times, which may be needed depending on the stability of the battery and the objectives of the study, the use of the lab-tomograph is more convenient.

Dr. Billy Wu (Imperial College London)

Combining lab-scale and synchrotron radiation X-ray tomography to study micromechanics of lithium-ion batteries

A major challenge in the development of reversible zinc-air batteries is the suppression of dendrite formation. Using in-situ x-ray radiography we show how these dendrites grow and how the morphology changes in real time. 3D computed tomography scans then allows us to characterise the structures, pulling out metrics of interest. We then combine this with high resolution FIBSEM imaging to resolve smaller features to further allude to the structure of the dendrites, creating a multi-length scale imaging framework. Our study has shown that these dendrites grow with a narrow base, which upon dissolution, cause detachment of the dendrite leading to capacity loss. Continuous cycling leads to reattachment of previously detached dendrites causing large dendritic structures and short circuiting between electrodes. Using direct metal laser sintering (additive manufacturing) we then create imperishable scaffold structures with low tortuosity and functionally graded properties, onto which we electrodeposit zinc. This scaffold supports the zinc and acts as an integrated current collector. The 3D printed scaffolds have 2 levels of controllable porosity. Macroscopic controlled by the laser path, and microscopic controlled by the powder and laser scan parameters. We show that this approach can help to suppress the formation of zinc dendrites in zinc air batteries and improve power rate performance.

Donal Finegan (UCL)

In-operando fast tomography of Li-ion batteries during operation and failure

Lithium-ion batteries are recognised as being an integral technology in the process of achieving a clean and sustainable energy future. The safety of Li-ion batteries is of upmost importance particularly as the advancement of electric and hybrid electric vehicles require high energy density batteries to operate under a wide range of conditions. The thermal response of a cell is one of the most important characteristics to understand when assessing the safety of a cell design but little is understood about the dynamic mechanisms associated with thermally induced failures. X-ray tomography has become a widely used technique for 3D structural analyses of electrochemical materials using either lab based tomography or synchrotron tomography. Two of the major advances in tomography techniques in recent years are the reduction in tomogram acquisition time and the increased spatial resolution. In this study, high frequency tomography imaging of commercial lithium-ion batteries (18650 LG NMC

cells) during operation and failure was performed in beam-line ID15A at the European Synchrotron Radiation Facility (ESRF). Tomograms were captured at a rate of up to 2.5 Hz allowing us to study some of the most rapid failure mechanisms including those associated with thermal runaway. Simultaneous thermal imaging and X-ray tomography allowed structural and thermal dynamics to be linked with time. The evolution of gas pockets, electrode layer delamination and cracking are apparent from the results. Post-mortem tomography analyses of 18650 batteries after thermal runaway reveal a large degree of structural degradation containing features which may be indicative of temperatures reached (>1000 °C) during failure inside the cells. This analysis has provided unprecedented insights into the structural and thermal dynamics leading up to and during thermal runaway and failure of commercial lithium-ion batteries.

Matthew Worsdale (University of Southampton)

The potential of Ta:SnO2 and H:SnO2 as catalyst support for Low Temperature Fuel Cells

Metal oxides are one of the most promising family of durable catalyst support materials. SnO2 can only corrode above 1.4V in a strong acid. Although the conductivity of the defect-free wide-band gap (3.6eV) semi-conductor is very small compared to carbon, electrical conductivity on par with carbon blacks has been achieved experimentally. We evaluate the potential of extrinsic n-type dopants to increase conductivity, investigating the influence of Ta on the thermodynamic stability and electronic properties of Ta:SnO2 through DFT calculations. TaO2 also favours the rutile structure. This allows investigation of the full range of Ta concentrations in the rutile host. A cluster expansion (generalised Ising Model) is used to find low energy configurations (distributions of Ta:Sn atoms over the lattice).We find that alloys are substantially stabilised thermodynamically by lattice distortions, which indicates that the system is Jahn-Teller active (JT). As a consequence, the Ta donor state localises at Ta centres and freezes out. Our results suggest that Ta-doping in itself is not a feasible approach to increasing conductivity and highlight a more general conflict between thermodynamic stability and high conductivity.The influence of possible Hydrogen impurities has been investigated by analysing the resultant band structure of substitutional and interstitial (OH groups) Hydrogen defects. It is found that interstitial H can, depending on the placement in the lattice, brings about a large downward shift of the Conduction-Band-Minimum. This raises the possibility of activating Ta-induced deep donor levels via H impurities.

Dr. Ehsan Ahmed (Imperial College London0

Optimising Oxygen Reduction Catalyst Morphologies from First Principles

Catalytic activity of perovskites for oxygen reduction (ORR) was recently correlated with bulk d-electron occupancy of the transition metal. We expand on the resultant model, which successfully reproduces the high activity of $LaMnO_3$ relative to other perovskites, by addressing catalyst surface morphology as an important aspect of the optimal ORR catalyst. The nature of reaction sites on low index surfaces of orthorhombic (Pnma) $LaMnO_3$ is established from First Principles. The adsorption of O_2 is markedly influenced by local geometry and strong electron correlation. Only one of the six reactions sites that result from experimentally confirmed symmetry-breaking Jahn-Teller distortions is found to bind O_2 with an intermediate binding energy while facilitating the formation of superoxide, an important ORR intermediate in alkaline media. As demonstrated here for $LaMnO_3$, rational design of the catalyst morphology to promote specific active sites is a highly effective optimization strategy for advanced functional ORR catalysts.

Tobias Binninger (Paul Scherrer Institut)

Fundamental DFT Study of Electronic Interactions between Catalyst Metal Nanoparticles and Metal Oxide Support

In heterogeneous catalysis, it is well known that the support material can have a strong influence on the catalytic activity of the Pt nanoparticles (strong metal-support interactions, SMSI) [1]. In the last decade, the topic of metal-support interactions has gained increased interest also in the field of electrocatalysis due to an increased research focus on non-carbon supports like conductive metal oxides. Experiments have revealed an influence of the metal oxide type and the metal oxide surface stoichiometry on the stability and the activity of the supported Pt particles [2,3]. So far, however, the precise theoretical understanding of the origin of these metal-support interactions remained deficient. We present results from a theoretical study of metal-support interactions using density functional theory (DFT). The investigated catalyst systems consisted of cuboctahedral Pt55 clusters supported on various SnO2-type supports: Undoped SnO2 slabs as well as Sb-doped and In-doped ones with both stoichiometric and reduced (110) surfaces were used in the study. We followed an approach to identify purely electronic interactions between the Pt clusters and the support oxide by excluding lattice relaxation effects in the calculation of the combined system of Pt cluster and support. We relate our results to a more fundamental understanding of electronic metal-support interactions in terms of thermodynamic equilibration of the electron systems in the support oxide and the Pt nanoparticles. The possible influence of the observed interactions on the catalytic activity towards ORR was quantified by calculating the changes in the binding energy of an oxygen adatom on the outer surface of the Pt nanoparticle. The resultant order of magnitude of the influence of electronic metal-support interactions on the catalytic ORR activity is in agreement with recent experimental findings for Pt nanoparticles supported on oxidized and on reduced SnO2 thin-film surfaces [3].

Michael Parkes (Imperial College London)

Ab initio Modeling of Yttria Stabilised Zirconia for Solid Oxide Fuel Cells

Solid Oxide Fuel cells convert chemical fuels such as methane, directly into electricity, heat, with higher efficiencies than many conventional combustion technologies. Here, we present work on developing improved atomistic models of yttria stabilised zirconia (YSZ), which is used as a catalyst support and electrolyte material in a solid oxide fuel cell. The catalyst, YSZ, and a gas phase meet at the anode triple phase boundary (TPB) in an SOFC. The anode is susceptible to poisoning through detrimental chemical reactions, and a long term aim for the field of SOFC catalysis is to understand these reactions and design improved catalysts.A detailed knowledge of the YSZ surface chemistry is inhibited by a poor understanding of the distribution and local atomistic structure of the dopant Y3+ ions and oxygen vacancies in the bulk crystal and at the surfaces. We perform a comprehensive search for low energy defect structures using a combined classical modeling and density functional theory (DFT) approach to identify the low energy defect structures of 3.25mol% YSZ, chosen as the limit of low dopant concentration. The findings from the bulk crystal are used to establish the low energy surface structures, where we demonstrate that a slab model, much larger than that used in previous DFT studies, is required to obtain a converged surface energy. We investigate the preference for yttrium to segregate to the surface, and finally establish the chemically active sites for water dissociation.

Rhodri Jervis (UCL)

Development of a PdIr/C Anode catalyst for Alkaline Anion Exchange Membrane Fuel Cells

With the high cost and limited availability of platinum, much effort has gone into the reduction of catalyst loadings in fuel cell electrodes. Platinum is the most effective catalyst for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) in acidic polymer electrolyte fuel cells (PEM), but the vastly improved kinetics of the ORR in an alkaline medium opens up the possibility of utilizing cheaper catalysts for alkaline anion exchange membrane fuel cells (AAEM).However, in the alkaline environment, the kinetics of the HOR are an order of magnitude slower on Pt than in acid (though Pt remains the most widely used catalyst in both media). Therefore, in order to take advantage of the more facile ORR kineticsin alkaline, anode catalyst development and cost reduction is required. Anode catalyst development is often overlooked but is necessary for commercial realization of AAEM fuel cells. Rotating diskelectrode (RDE) studies, along with preliminary in situ fuel cell testing, have shown a PdIr alloy catalyst to haveactivation properties for the HOR superior to Pt when in an alkaline medium. The catalyst has been characterized using TEM, XPS, LEIS and synchrotron EXAFS and XRD experiments and the durability compared with Pt/C over accelerated stress testing. The increased activity and reduced cost of PdIr/C could enable AAEM fuel cells to compete with the more established PEM technologies.

Cheng Li (Imperial College London)

Surface segregation in Sr doped LaNbO4 and its effect on proton transportation

Acceptor doped LaNbO4 has been proposed as novel proton conductors recently. However, in contrast to the well-established bulk transportation mechanism, the surface chemistry this material, which plays a key part in the proton incorporation process, is yet known. The low energy ion scattering (LEIS) technique is extremely sensitive to the outmost atomic layer of the surface and in the present work, we have applied this powerful tool to study the surface chemistry of 1 at% Sr doped LaNbO4. Figure 1 shows the LEIS spectrums of the outmost layer in Sr-LaNbO4 samples under various anneal conditions. The surface spectrum of the undoped LaNbO4 is also shown as reference. For the 600 °C annealed sample, no Sr peak was observed within the detection limit. A shoulder at lower energy was observed in the 800 °C annealed sample which might result from a slight enrichment of Sr on the surface. Such feature is clearly detected for the 1000 °C annealed sample: the Nb signal on the surface is much weaker and a strong Sr segregation on the outmost layer was observed. Depth profile (not shown) of the same sample suggests that the segregation layer is about 10 nm thick. Sr segregation was also observed on the unpolished as-sintered sample. Interestingly, the intensity of the Sr peak is weaker comparing with the 1000°C annealed one, although the sintering temperature is 1400 °C. It is worth emphasizing that the bulk contains only 1 at % of Sr on the A site, Sr segregation on the surface would thus result in a significant reduction in Sr content and thus oxygen vacancy in the bulk, which might affect the proton conduction process. Dopant segregation was observed on the outmost layer of the Sr doped LaNbO4 after annealing at temperatures above 800 °C. Effect of the segregation on the proton transportation and surface exchange is to be investigated.

Vidal Bharath (UCL)

Characterisation of Thin Film Alkaline Anion-Exchange Membrane (AAEM) Fuel Cells Using a Quartz Crystal Microbalance (QCM) and Crystal Admittance Spectroscopy

Fuel cells are seen as one of the major contributors in the fight against both climate change and the energy crisis. However, traditional proton exchange membrane (PEM) fuel cells which utilize expensive platinum catalysts have struggled to become cost competitive compared to contemporary electricity generation methods. This, amongst other reliability issues, has hindered the technology's otherwise imminent commercialisation. Alkaline anion exchange membrane (AAEM) fuel cells are a novel solid polymer electrolyte (SPE) version of the aqueous alkaline fuel cell (AFC). Implementation of a SPE in theory should reduce carbonate salt precipitation, which has deleterious performance effects and also alleviates issues pertaining to transport and the use of a hazardous electrolyte seen in the original AFC. The AAEM does however retain the AFC's more facile oxygen reduction kinetics at the cathode, compared to the PEM, and thus can utilizes lower cost non-precious metal catalysts.The AAEM, boasting the benefits of both the PEM and AFC, shows great promise as a viable cost effective option for low temperature application. However, AAEMs are not without technological challenges. As with the AFC, AAEMs form carbonates when operating in even very low levels of CO_2; however, the SPE ensures immobilization of the cationic groups and thus should eliminate salt precipitation. This work explores thin film AAEM carbonation, water uptake and swelling characteristics using a quartz crystal microbalance (QCM) and crystal admittance spectroscopy.

Dr. Kevin Fahey (Carl Zeiss X-ray Microscopy) Plenary Speaker

4D X-ray Microscopy and Modern Correlative Workflows in Electrochemical Research

Recent advances in laboratory X-ray microscopy (XRM) have enabled detailed 3D imaging into the sub-micron and nanoscale resolution domains. Increasingly, such non-destructive tomographic imaging methods have uniquely been utilized to answer questions about the evolution and failure of materials and devices via '4D' time-lapse experiments (3D + time). The ability to explore 3D microstructure evolution over time, and in situ, has led to an abundance of new research opportunities, especially within the energy materials arena. In the first half of this talk, we sample the global research efforts that investigate microstructure, evolution and failure of electrochemical devices via XRM, including Li ion battery and fuel cell (PEFC, SOFC) applications. While the unique merits of XRM characterization offers exciting new research thrusts, it is equally important to relate characterization across many length scales, dimensions and imaging modalities. Efficiently tying together multiple 'views' of an experiment via light, X-ray, electron or ion microscopy has become a major focus area within the microscopy community. The second half of this talk will describe how ZEISS is changing the landscape for correlated imaging. Specifically, we review the recent development of a modern correlative workflow environment (ZEISS Atlas 5) which acts as the nucleus for image correlation and advanced automated acquisition strategies across platforms. For example, this approach has enabled such workflows as taking 4D XRM data to target precise sub-surface regions of interest that are subsequently located by FIB-SEM tomography.

Dr. Ralph Clague (Intelligent Energy) Plenary Speaker

Fuel Cells in 2015: SWOT Analysis

Wasim Sarwar (Imperial College London)

High fidelity, multi-dimensional supercapacitor thermal modelling

Existing supercapacitor thermal models are capable of providing a bulk temperature, a cell center temperature inferred from this bulk temperature, and highly simplified three-dimensional distributions. The author has developed a high fidelity thermal model, which is capable of describing temperature distributions in both the radial and axial directions of large form factor cylindrical supercapacitor cells. Furthermore, the model consists of multiple 1D elements, and therefore is significantly less computationally expensive than true three-dimensional modeling.

Dr. Celine Merlet (University of Cambridge)

Development of a new simulation method to model diffusion and NMR spectra in porous carbons

This project focuses on the characterisation of the electrode/electrolyte interface in supercapacitors through the combination of in situ NMR techniques and lattice simulations. The idea is to bridge the gap between molecular simulations, which provide information about quantities such as energy landscapes and locally induced magnetic fields, and NMR experiments which correspond to averages over relatively long times and length scales compared to molecular simulations. In the case of supercapacitors, the active material for the electrodes consists in porous carbons with high surface areas to maximise ion adsorption, which is at the origin of energy storage in these systems. The carbon materials commonly used are disordered which renders the description of their structure and the electrode/electrolyte interface very difficult although this characterisation is an essential step in order to understand the relation between the structural properties of the materials and the obtained electrochemical performances. The technique presented in this work provides a tool to extract information about the spatial distribution of pore sizes from NMR spectra. Such information is difficult to obtain from other characterisation techniques. This new lattice model is expected to provide new insights into in situ NMR experiments performed on supercapacitors. Moreover, because of its versatility, the lattice model is a powerful tool to investigate a full range of materials, for which NMR parameters can be determined, including battery and fuel cell materials.

Dr. Ana Belen Jorge Sobrido (UCL)

Carbon Nitrides: New Electroactive Materials for Energy Applications

Due to their extraordinary compositional and structural flexibility along with their semiconducting and optoelectronic properties, polymeric/graphitic carbon nitride materials (gCNMs) have received significant interest in recent years for catalysis applications. gCNMs consist of s-triazine or heptazine (tri-s-triazine) units linked by bridging –NH- or –N= groups to form polymeric 2D structures with different degree of condensation. These structures differ from graphitic carbon or graphene in that the presence of N atoms and C-N bonds creates voids within the extended layered structure. These voids are lined with N lone pairs and / or N-H functional groups, being ideally suited for acid / base and host / guest chemistry. This includes intercalation reactions, charge storage, ionic diffusion, gas sorption

and support of catalytically or electrochemically active species. We have demonstrated that the band gap of gCNMs can be controlled by modifying the preparation experimental conditions via the extent of condensation, layer buckling and potentially charge transfer processes with guest ions. gCNMs are easily prepared by condensation of C, N-containing precursors at temperatures between 550 and 650 oC in N2 (g) flow. Alternative approaches to improve crystallinity, conductivity or porosity include the use of molten eutectic mixtures, anion doping or soft / hard templates, respectively. We have recently revealed that gCNMs exhibit excellent performance as catalyst support in direct methanol fuel cells and in water electrolysers. In this work, we present the potential of these materials as electrocatalysts / electrocatalyst supports in energy conversion devices.

James Robinson (UCL)

Investigating the Effect of Thermal Gradients on Stress in Solid Oxide Fuel Cell Anodes Using Combined Synchrotron Radiation and Thermal Imaging

Thermal gradients can arise within solid oxide fuel cells (SOFCs) due to start-up and shut-down, non-uniform gas distribution, fast cycling and operation under internal reforming conditions. These gradients can exacerbate degradation arising from the thermal expansion co-efficient mismatch between the metallic and ceramic phases. Here, the effects of operationally relevant thermal gradients on Ni / YSZ SOFC anode half cells are investigated using combined synchrotron X-ray diffraction and thermal imaging. The combination of these techniques has identified significant deviation from linear thermal expansion behaviour in a sample exposed to a one dimensional thermal gradient. Stress gradients are identified along isothermal regions due to the presence of a proximate thermal gradient, with compressive stress deviations of up to 75 MPa being observed across the sample at a constant temperature. Significant strain is also observed due to the presence of thermal gradients when compared to work carried out at isothermal conditions.

Dr. Na Ni (Imperial College London)

TEM investigation of Cr poisoning of LSCF cathodes

In this study, LSCF electrodes were deposited onto Ce0.9Gd0.1O1.95 electrolytes by screen printing. The LSCF electrodes were solution impregnated with chromium and heat treated at 900°C to simulate the Cr poisoning effect. The morphology change of LSCF after Cr poisoning and the behavior of Cr in the LSCF at the nona-scale were carefully investigated by advanced transmission electron microscopy (TEM) with a focus on the nanoanalysis using EDX and electron energy loss spectroscopy (EELS). The results are correlated with the change of the electrochemical property of the LSCF cathode measured by impedance spectroscopy for establishing a link between nano-scale structural/chemical changes and the Cr poisoning effect.

Marta Gandiglio (Politecnico di Torino)

SOFCOM: the first biogas fed SOFC trigeneration plant with carbon capture and use

The presented demonstration plant was developed in Turin in the framework of the EU project SOFCOM (www.sofcom.eu) and is the first SOFC based tri-generation plant, able to produce simultaneously power, heat and chemicals and to reduce emissions to the environment. The plant is placed in SMAT, the Turin waste water treatment plant, cleaning the water of over 2.5 million of

equivalent inhabitants. From the water cleaning line, sludges are produced and sent to four anaerobic digesters. Biogas is thus produced (55'000 Nm3/day) and currently sent to four internal combustion engines able to produce 5.6 MWe. In the framework of the SOFCOM project, a relatively tiny portion of the produced biogas is used to feed the demonstration plant. The biogas is passed through a chiller to remove moisture. Subsequently sulfur, halogens and siloxanes are removed in adsorption beds. Dry clean biogas (roughly 55-65% CH_4, 35-45% CO_2) is thus ready to feed a steam-reformer unit. The reformate gas feeds the 2 kWe SOFC module (operated at around 800 °C). The cathode off-gas is kept separated from the anode and used to pre-heat inlet fresh air. The anode outlet stream is treated in an oxy-combustor to yield an almost pure H_2O-CO_2 mixture that is eventually cooled down to 100-200 °C. Steam is condensed and separated in a dedicated condenser unit. The resulting pure CO_2 is thus pressurized and available for sequestration or other uses. Due to the limited size of the demo plant, the choice was to feed it to a photobioreactor with algae, where these are grown with waste water nutrients, sunlight and CO_2. A tubular photobioreactor has been chosen with a productivity of 20 g/day/m2 of dry algae. The outlet stream will be an algae purge that could be recirculated to the biogas digesters closing the system carbon cycle.

Dr. Andrea Lanzini (Politecnico di Torino)

Solid Oxide Fuel Cell Anode Degradation by the Effect of Fuel Contaminants

Lifetime and durability issues connected with Solid Oxide Fuel Cell (SOFC) technology are strongly related to the amount of contaminants that reach the stack. In this study the focus is on anode contaminants that are found in the fuel stream (e.g., biogas or syngas). The degradation of the anode performance in the presence of sulfur, chlorine and silicon based compounds is studied. Especially, organic silicon compounds (siloxanes) and their highly detrimental effects on the performance of SOFC Ni-YSZ anodes is investigated. The involved mechanism of degradation is clarified and quantified through several test runs and subsequent post-mortem analysis on tested samples. In particular, experiments on both Ni anode-supported single cells and 11-cell- stacks are performed, co-feeding D4-siloxane (octamethylcyclotetrasiloxane, $C_8H_{24}O_4Si_4$) as model compound for the organic silicon species which are generally found in sewage biogas. High degradation rates are observed already at ppb(v) level of contaminant in the fuel stream. Post-test analysis revealed that Si (as silica) is mostly deposited at the inlet of the fuel channel on both the interconnect and the anode side of the cell suggesting a relatively fast condensation-type process. Deposition of the Si was found on the interconnect and on the anode contact layer, throughout the anode support and the three phase boundary in the anode, correlating with the observed increase of polarization losses from the EIS analysis of tested cells.

Dr. Christopher Eames (University of Bath)

Next-Generation Electrode and Electrolyte Materials for Li-, Na-, and Mg-ion Batteries

The next generation of materials for batteries must have high safety, low cost, high energy density and high rates of charge and discharge. To meet all of these requirements, the development and understanding of the atomic-level properties of candidate materials are crucial first steps. In this presentation, we summarise recent work in the two major regions of the battery. 1) Solid electrolytes are a non-flammable alternative to the currently used liquid electrolytes, but their ionic conductivity is much lower. Working with experimental collaborators, the ionic conductivity of the Li_4SiO_4-Li_3PO_4 system has been improved by several orders of magnitude by forming mixed silicates/phosphates. 2) Graphene-based transition metal carbides (MXenes) are high capacity, extremely high rate capability anodes with kinetics so good they have even been suggested as suitable for supercapacitors. We

identify, using high throughput screening of all possible compositions, those chemistries that offer high capacity for lithium-ion and magnesium-ion batteries.

Dr. Thomas Miller (UCL)

Graphitic carbon nitrides as anode materials for Li-ion batteries

The graphite anodes commonly used in Lithium-ion Batteries (LIBs) are known to limit performance as they have a low number of electron transfer sites and slow electrode kinetics. As various C,N based materials have shown significantly improved performance over graphite in electrochemical applications there is interest in their use in LIBs. In this work we investigate graphitic carbon nitride materials (gCNMs) as an alternative anode material for LIBs. These materials, like graphite, are layered structures but are formed from s-triazine or heptazine (tri-s-triazine) rings, linked by -N= or -NH- units and are therefore built on heteronuclear C-N bonds containing a high N:C ratio (>1). The gCNMs were synthesised via thermolysis of simple C,N containing precursors, such as melamine, at temperatures between 500 and 650 °C, after which extensive structural characterisation was performed. The resulting distinctive yellow material (above) was processed into anodes after the addition of differing quantities of graphite (between 0 and 100% of active mass) to aid electrical conductivity, and electrochemical tests were performed. It was shown that gCNMs were indeed capable of intercalating Li+, even without the addition of conducting graphite, but performance was enhanced when graphite was present. This was shown to be due the semiconducting nature of the gCNM compounds. Although the composite electrodes were shown to have significantly higher capacities for Li+ than those made of only gCNM, the capacity commonly achieved in graphite-anode batteries cannot currently be increased through the addition of gCNMs.

Ian Hunt (Imperial College London)

A comparison of the effect of different cooling techniques on Lithium-ion battery degradation

Lithium-ion battery packs require thermal management in order to manage degradation and reduce the risk of safety issues such as thermal runaway. Different cooling methods can be used to cool batteries, including plate cooling, cell tab cooling and forced air convection1. This talk will explore the use of these cooling methods and the effect on degradation during charging and discharging. Many experiments use forced convection thermal boundary conditions1,2. In this case, three different thermal boundary conditions were used, all of which can be thought of as holding the cell at a set temperature. For each case the degradation rates were different, emphasising the importance of managing thermal boundary conditions, both in the lab and in real-world applications.

Dr. Sylvia Britto (University of Cambridge)

(De)lithiation Mechanism of Vanadium Sulfide, a Promising Battery Material

The low theoretical capacities of the conventional LiCoO2 cathode materials (120-150 mAh g-1) [1] and graphite anodes (372 mAh g-1) [2, 3] used in rechargeable Li ion batteries fuels an intense search for alternative electrode materials capable of higher electrical storage capacities. One way of achieving a larger specific capacity is to explore materials that are capable of undergoing a wider change in oxidation states thereby allowing for the accommodation of more than one Li ion per transition metal ion leading to higher capacities. We have found that VS4, which is found as the

mineral patronite [4], also described as V4+(S22-)2, has enormous potential as an electrode material in combination with graphite oxide, with preliminary electrochemical data indicating a remarkably high charge capacity close to 900 mAh/g. This material crystallizes in the monoclinic symmetry and is comprised of uncommon eight-coordinate V4+ ions coordinated to S22- dimers which are linked together as linear chains with alternating bonding (2.8 Å) and non-bonding contacts (3.1 Å) between the vanadium centers. The products of discharge/charge are nano-sized and therefore difficult to characterize by conventional crystallographic methods. Pair Distribution Function analysis combined with Solid State NMR and XANES indicate that the VS4 is partially reversible and undergoes a unique internal redox process during discharge in which electron transfer from the V to S leads to the breaking of sulfur dimers and formation of a tetrahedral intermediate.

Harini Hewa Dewage (Imperial College London)

Study of loss mechanisms in a Regenerative Hydrogen Vanadium Fuel Cell

Development of renewable energies such as solar and wind power have received a great deal of attention. However, in order to utilise efficiently the power generated, it is essential to introduce energy storage systems at the grid level scale. Redox flow batteries are excellent candidates for this purpose as they present many potential advantages such as: decoupling of power and energy; modularity (kilowatts to megawatts systems); site independence; long cycle life; and minimal maintenance. But there remains scope to reduce the cost and improve the performance of current systems, and in this context a novel regenerative fuel cell, utilising an aqueous vanadium electrolyte and hydrogen gas has recently been reported. The advantages offered by this approach are fast hydrogen kinetics, use of half of vanadium electrolyte in comparison to the conventional all vanadium flow battery and the absence of cross-contamination between the positive and negative half-cells.The first generation of this vanadium-hydrogen cell assembled with commercial MEAs demonstrated a maximum power density of 107 mW/cm2 in a 1M V(IV)/V(V) solution. In this work we report improved performance to achieve a maximum power density of 453 mW/cm2 through cell design modification. Half-cell measurements have been used to gain a better understanding of the loss mechanisms in the cathode and anode.

Iain Aldous (University of Liverpool)

The Influence of Tetraalkylammonium Cation Chain Length on Gold and Glassy Carbon Electrode Interfaces for Alkali Metal-Oxygen Batteries

The oxygen reduction and evolution (ORR/OER) reactions that govern alkali metal oxygen (M-O2) technology are heavily dependent on electrolyte composition.1-3 To fully understand these dependencies it is necessary to study the complex air cathode interface. The continued development of in situ surface enhanced Raman spectroscopy (SERS) can provide mechanistic detail of air cathode interfacial regions through the analysis of the species present at the interface. Fundamentally ascertaining the mechanism of ORR/OER in the absence and presence of alkali metal cations (M+) builds a picture of how changing the cation Lewis acidity affects ORR/OER. In the absence of M+ electrolytes commonly employ tetraalkylammonium salts (TAA+) as a conductive support and as such it is crucial to ascertain the effects this has on ORR/OER. Here the effects that TAA+ chain length has on the interface can begin to explain measured electrochemical differences. These observations suggest that longer alkyl chain lengths impede the analysis of M-O2 due to the dominance of longer chain TAA+ signals due to a reorientation of TAA+ at peak potentials of ORR.4 Along with other observations the formation of a tetrabutylammonium superoxide complex may hint that TAA+ may act as phase transfer catalysts within M-O2 batteries.

Dr. Shane Beattie (Warwick University, WMG)

Identification of failure mechanisms in Si electrodes for Li-ion batteries

Silicon based anodes are widely studied as a high capacity alternative to graphite for Lithium-ion batteries. Unfortunately, when silicon-based anodes are paired with a commercially relevant cathode the cell typically suffers from rapid capacity fade. Major failure mechanisms that contribute to rapid capacity fade will be identified using a careful study of cycling data from three-electrode cells, different upper voltage cut-off values, and ex-situ X-ray diffraction.