



# STFC Batteries Annual Meeting

14<sup>th</sup>-15<sup>th</sup> July 2016

Conference Booklet



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# STFC Batteries Annual Meeting

## 14<sup>th</sup>-15<sup>th</sup> July 2016

Welcome to the 4<sup>th</sup> annual STFC Batteries meeting at Cosener's House, Abingdon. The annual meeting is a great opportunity to bring together the best researchers in academia, industry and large facilities from the UK and beyond to discuss the latest developments in batteries and energy technologies. Over the two days we will have talks and discussion on the topics of Batteries, Facilities, Fuel Cells, Supercapacitors and Materials. We will also be hearing from recipients of the STFC Batteries Early Career award – funding allocated to promising young researchers to enable them to attend another university, book time on a large scale facility or collaborate with other institutions around the world.

We hope that you enjoy the conference and that a fruitful and enjoyable time is had by all.

*-Paul Shearing and Rhodri Jervis*



# The STFC Batteries Network

Electrochemical devices are already part of our day-to-day lives, particularly Li-ion batteries that have transformed modern life through their ubiquitous application in consumer electronics. In the future, these devices will play an increasing role in our lives, from batteries that will power our cars and buses to fuel cells that will provide grid independent electricity. The UK has played a crucial role in the discovery and development of these devices, and through continuing cutting edge research at universities, national labs and companies, remains at the forefront of electrochemical device research. Large scale user facilities, including synchrotron and neutron sources and high performance computing continue to play a pivotal role in this research and development

Since 2013, the STFC Global Challenge Network in Batteries and Electrochemical Energy Devices has helped to consolidate the UK research community active in this area, seed new research and collaborations, and through its advocacy has promoted the UK as a world leader in this field.

The Network provides a focal point for UK research in electrochemical devices, with a particular focus on the application of large-scale facilities. In Phase 2, we will continue to advocate and enable cutting edge research in electrochemical energy devices using large scale facilities, by on-going networking activities and by the allocation of funding for research and researcher mobility.





Day 1: July 14th								
Start	End	Duration	Speaker		Talk Title			
10:00	10:30	00:30	Registration Open					
10:30	10:35	00:05	Welcome Day 1					
Chair: Paul Shearing								
10:35	11:00	00:25	Session 1a	1.1	Prof Peter Hall	Materials Issues in the Safe Operation of Grid Connected Batteries - How to Prevent Birmingham Being Destroyed in a Lithium Fire	Batteries	
11:00	11:25	00:25		1.2	Dr Melanie Loveridge			Hybrid Active Materials for High Capacity Anodes for Li-ion Batteries
11:25	11:50	00:25		1.3	Dr Ainara Aguadero			Revealing the Optimum Li-Mobility in Garnet Electrolytes
11:50	12:05	00:15	Coffee					
Chair: Ryan Bayliss								
12:05	12:30	00:25	Session 1b	1.4	Dr David Prendergast	First-Principles Exploration Beyond Li-Ion		Batteries
12:30	12:55	00:25		1.5	Dr Stefan Freunberger	Electrolytes in Post Li-Ion Batteries: Materials, Reactions and Mechanisms		
12:55	13:20	00:25		1.6	Dr James Frith	Li-O <sub>2</sub> Batteries With Redox Mediators		
13:20	14:20	01:00	Lunch					
Chair: Emma Kendrick								
14:20	14:45	00:25	Session 2a	2.1	Prof Charles Monroe	Extraction of Material Properties from Lock-in Thermography of Pouch Cells	Batteries	
14:45	15:10	00:25		2.2	Dr Juliette Billaud	Pushing Further the Limit of Operando Techniques to Probe Battery Materials		
15:10	15:35	00:25		2.3	Prof William Mustain	Understanding the Behaviour of Metal Oxide Anode Materials in Lithium-Ion Batteries		
15:35	15:45	00:10	Coffee					
15:45	16:10	00:25	Session 2b	2.4	Dr Benjamin Morgan	Sparse Cyclic Excitations in the Solid Lithium-Ion Electrolyte LLZO		Batteries
16:10	16:35	00:25		2.5	Dr Kimberly See	Solvation Structures of Mg Cations in the MACC Electrolyte		
16:35	16:50	00:15	Coffee					
Chair: Peter Lee								
16:50	17:15	00:25	Session 3	3.1	Prof Chiu Tang	Synchrotron Powder Diffraction Beamline (I11) for Battery Research	Facilities	
17:15	17:40	00:25		3.2	Dr Christoph Rau	Tomographic Imaging of Battery Dynamics with Synchrotron Radiation		
17:40	18:05	00:25		3.3	Dr Michael Drakopoulos	Update on Recent Progress at the DIAD Beamline		
18:05	18:10	00:05	Close and Thanks					
18:10	19:40	01:30	Drinks reception					
19:40	21:10	01:30	Dinner Followed by drinks					

Day 2: July 15th							
08:55 09:00 00:05 Welcome Day 2							
Chair: Denis Kramer							
09:00	09:25	00:25	Session 4a	4.1	Dr Veronica Celorrio	XAS for Electrocatalysis	Fuel Cells
09:25	09:50	00:25		4.2	Dr Antonio Bertei	Electrochemical Simulation of Solid Oxide Fuel Cell Electrodes: an Integrated Approach to Address the Microstructure-Performance	
09:50	10:15	00:25		4.3	Prof Peter Slater	Oxanion Doping In Solid Oxide Fuel Cell Materials	
10:15 10:30 00:15 Coffee							
Chair: Dan Brett							
10:30	10:55	00:25	Session 4b	4.4	Prof John Varcoe	High Performance Radiation-Grafted Anion-Exchange Polymer Electrolytes	Fuel Cells
10:55	11:20	00:25		4.5	Dr Richard Dawson	Alkaline Fuel Cells – to the Moon and Back	
11:20	11:45	00:25		4.6	Dr Jeff Gostick	Modelling Multiphase Transport in Fuel Cells: The Power of Pore-Scale Approaches	
11:45 12:45 01:00 Lunch							
Chair: Dale Brownson							
12:45	13:10	00:25	Session 5	5.1	Prof Craig Banks	Electrochemical Explorations of Graphene and Related Materials	Carbon
13:10	13:35	00:25		5.2	Dr Anthony Rennie	Electrochemical Stability in Ionic Liquid based EDLCs	
13:35	14:00	00:25		5.3	Dr Ryan Wang	Porous Carbon Materials: Heterogeneous Catalysis and Beyond	
14:00	14:25	00:25		5.4	Dr Billy Wu	3D Printed Structural Pseudocapacitors	
14:25 14:40 00:15 Coffee							
Chair: Rhodri Jervis							
14:40	15:00	00:20	Session 6	6.1	Donal Finegan	Li-Ion Battery Failure: X-ray Microscopy Across Multiple Time and Length Scales	Early Career
15:00	15:20	00:20		6.2	Marco Amores Segura	Fast Microwave-Assisted Synthesis and Lithium-Ion Diffusion Studies of Lithium Stuffed Garnets	
15:20	15:40	00:20		6.3	Kent Griffith	Synchrotron X-rays for the In Situ Investigation of High-Rate Battery Materials	
15:40	16:00	00:20		6.4	Kenneth Inglis	Structure and Sodium Dynamics Investigation of Sodium Strontium Silicate by Solid-State NMR	
16:00	16:20	00:20		6.5	Moshiel Biton	Contrast Improvement Applied to Lithium Ion Battery Electrode Materials Enabling High Resolution 3D Imaging and Quantification	
16:20 16:25 00:05 Close and Thanks							

# Materials Issues in the Safe Operation of Grid Connected Batteries - How to Prevent Birmingham Being Destroyed in a Lithium Fire

*Peter Hall<sup>a\*</sup>, Steve Jubb<sup>a</sup>, David Stone<sup>b</sup> Dan Gladwyn<sup>b</sup> Martin Foster<sup>b</sup>*

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One reason why Li-ion batteries are regarded as being expensive, or not cost effective, is that battery systems are deliberately over engineered to guarantee safety or battery lifetime. For example, traction batteries typically use half of the available energy stored in them. Of course customers should expect safe operation and a lifetime long enough for economic pay back but battery designers are over cautious because quite simply there is not enough known about how to monitor the state of health and state of charge of batteries with sufficient accuracy. Traction batteries are considered as useless when they have lost 20% of their capacity.

Safe operation of battery systems is ensured through the Battery Management System (BMS), software that can monitor such features as cell voltage, temperature, state of charge and cycle number. The BMS can control charge and discharge rate, control the cooling system and rebalance the batteries to restore uniform state of charge.



**Figure 1. The 20 Ah Toshiba SCiB cells installed in the UoS 2MW/1 MWh battery**

The University of Sheffield (UoS) has constructed a 2MW/1MWh LTO battery connected to the 11.5kV grid in Willenhall near Birmingham. It comprises over 8500x20Ah Toshiba SCiB units, or 21,120 individual cells. As the power to energy ratio suggests this is designed for power deliver rather than bulk energy storage and is aimed at voltage/frequency support in the Enhanced Frequency Response (EFR) and the Short Term Operating Reserve markets. It is often claimed that Li-ion batteries operate over 90% efficiency. It is quite clear from our initial tests that the actual efficiency is much less than this evidenced by heat loss at high C rates. Also during operation certain cells need more balancing than others, indicating that they are aging faster. These cells can be removed from the stack and tested using a variety of non-invasive analytical techniques to understand the aging mechanism. Interestingly, the BMS restricts maximum charge discharge rates that are much smaller than the individual cells are capable of and we are uncertain about the state of charge values delivered by the BMS.

Operating batteries to respond to the EFR market means going from zero to full output or input within ~20ms. This is not the way in which batteries ought to be run to ensure maximal lifetime or safety and this is an ideal opportunity to examine which (and how) different cells or units age faster than others. Experimental techniques include impedance measurement, calorimetry and in situ x-ray analysis.

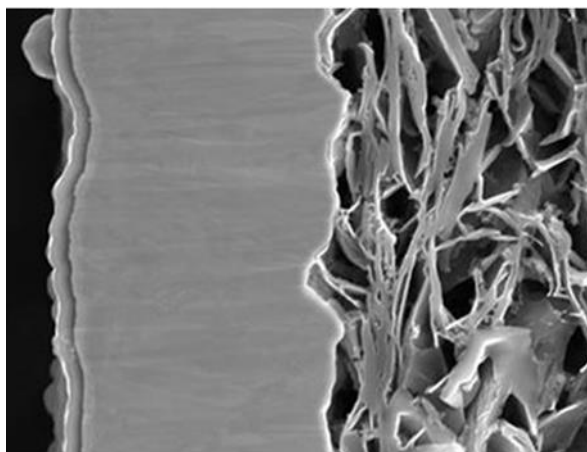
# Hybrid Active Materials for High Capacity Anodes for Li-ion Batteries

*M. J. Loveridge*

University of Warwick

One of the strategies to overcome the capacity limitation of graphite anodes (372mAh/g) is to hybridize the C with a metallic element, capable of accommodating more Li per unit mass. A major challenge here is controlling the hybridization process such that the resulting electrode architecture can be regulated e.g. for tuning the interfacial electrochemical activity that spans the nm to the  $\mu\text{m}$  scale. The effective use of bulk high capacity Group IV elements such as Si or Sn has been hindered by the pulverization of the particles following excessive volume expansion.

To circumvent this and generally improve the electrochemical behaviour, this study proposes to generate hybrid, hierarchical electrodes with a superior conductive matrix effectual over short and long-range orders.



**Figure 2 Few-layer graphene-PAA film on Cu**

Various Si-based graphene composite hybrids have provided enhanced electrochemical performance in Li-ion cells. However, these candidates still yield low initial coulombic efficiency and electrical disconnections. A more robust electrode structure is required to solve these problems along with appropriate binder and electrolyte chemistry.

This study compares (i) Si-Few-layer graphene (FLG) composite with (ii) a Si-Sn hybrid and seeks to establish:

- Whether a more stable electrochemical cycling and rate performance can be achieved using metal-carbon or bimetallic hybrid systems as anodes.
- Both co-materials were for their capacity contribution (as well as conductivity properties) but how reversible and stable is the electrochemical cycling of graphene?
- How does the electrode expansion and deterioration manifest itself in the hybrid systems compared with electrodes based on Si only as the Li host?

# Revealing the optimum Li-mobility in garnet electrolytes

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“Li-stuffed” garnet electrolytes can deliver the adequate Li-conductivity, safety and cycle life required for the commercialisation of high-energy density batteries (i.e. high voltage Li-ion and Li-metal based batteries). However, these garnet electrolytes, if they are not processed properly, suffer from severe moisture-sensitivity that leads to *drastic degradation of their transport and microstructural properties* – a problem that has not been universally recognised in the field and that is impeding the achievement of the optimum performance of garnet electrolytes in Li-batteries. This is partially due to the Li-H Exchange taking place during the atmospheric degradation process that not only leads to a decrease in the Li transport number but also to the formation of insulating secondary phases (i.e.  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ) in the grain boundaries and interfaces. In fact, the integration of garnet electrolytes in Li battery devices has been delayed due to the high interfacial resistances at the lithium metal anode side which limits the performance to low current density cycling<sup>1</sup>. Again, this high interfacial resistance has been related to the formation of a  $\text{Li}_2\text{CO}_3$  layer between the garnet and the Li-metal when not enough care is taken with the control of moisture during processing of the ceramics<sup>2</sup>.

We have developed a unique setup that allows a strict control of the moisture during the processing and characterization of the garnets. The synthesis and processing of  $\text{Li}_{7-nx}\text{A}_x\times_{(n-1)x}\text{La}_3\text{Zr}_2\text{O}_{12}$  (A= Ga(III), Ge(IV),  $\times$  = lithium vacancy,  $\text{V}_{\text{Li}}$ ) garnets have been performed in a Ar-filled glove box with a high temperature furnace coupled to it. This has result in a *three-fold enhancement in the total lithium-ion conductivity, up to 1.3 mS/cm at 24 °C<sup>3</sup> and the performance of garnets with highly controlled microstructure with densities up to 98%*. The intrinsic Li-mobility in garnets has been characterised by means of impedance spectroscopy and <sup>6</sup>Li-isotopic labelling. The effect of the moisture-degradation on the charge carriers concentration and mobilities has also been analysed using a controlled exchange in  $\text{D}_2\text{O}$ . To achieve this, a focussed-ion beam, secondary ion spectrometer has been used to detect all elements and their isotopes and yields the distribution of species in three dimensions on a nanoscale resolution, allowing the evaluation of the independent contributions of each isotope (<sup>6</sup>Li<sup>+</sup>, <sup>7</sup>Li<sup>+</sup>, H<sup>+</sup>, D<sup>+</sup>) to the conduction process.

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<sup>1</sup> S. Ohta, et al., J. Power Sources, 2013, 238, 53

<sup>2</sup> L. Cheng, et al., PCCP, 2014, 16, 18294

<sup>3</sup> C. Bernuy-Lopez, et al. Chem. Mater., 2014, 26, 3610

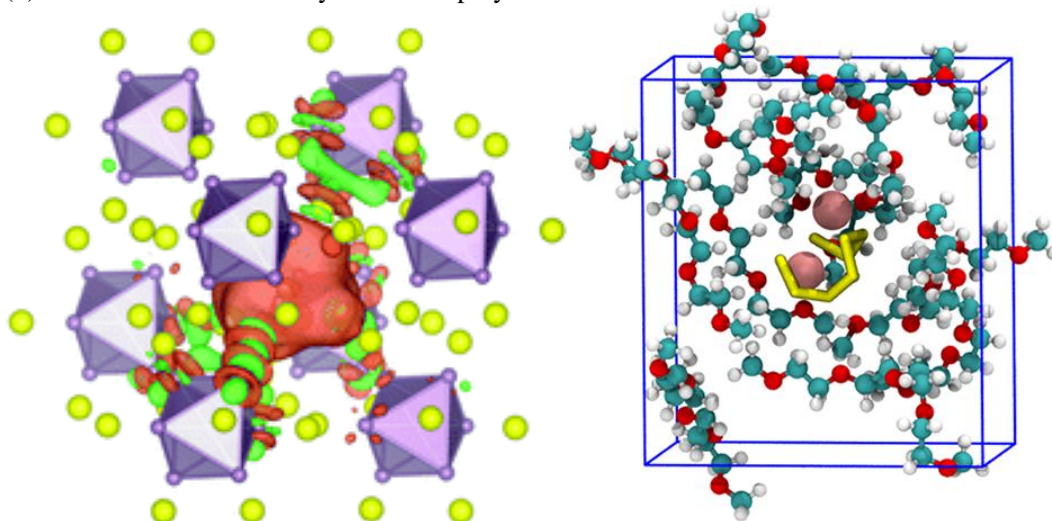


# First-principles exploration beyond Li-ion

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The Molecular Foundry, Berkeley Lab

The increased desire to expand the electrification of existing and emerging economies in both mobile electronics and automotive applications has established the need to move beyond the current practical, and even theoretical, limitations of Li-ion batteries in terms energy and power density, cycle life and safety. Current avenues of research are exploring various options in this beyond Li-ion space. Here we will discuss two directions, based on magnesium and lithium-sulfur electrochemistry. Our approach is to establish an atomistic understanding of these systems using first-principles approaches, such as density functional theory, and to validate our models by direct simulation of characterization – specifically near-edge X-ray absorption spectroscopy measurements made at synchrotrons. Advances in supercomputing power and computational methodology permit studies of simplified models of interfacial systems with nanoscale dimensions. In tandem, in situ and operando studies of similar systems at X-ray light sources provide a fertile ground to validate such simulations and to support claims about specific chemical and electrochemical mechanisms relevant to battery function. In this short presentation, we will explore two topics: (1) details of Mg-ion insertion into the original Mg-battery cathode – Chevrel phase  $\text{Mo}_6\text{S}_8$ <sup>1-3</sup> and (2) the solvation and stability of lithium polysulfides in ethers.<sup>4-7</sup>



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- [4] The X-ray absorption spectra of dissolved polysulfides in lithium-sulfur batteries from first-principles. Tod A. Pascal, Kevin Hamilton Wujcik, Juan J. Velasco-Velez, Cheng-Hao Wu, Alexander Andrew Teran, Mukes Kapilashrami, Jordi Cabana, Jinghua Guo, Miquel Salmeron, Nitash P. Balsara, and David G. Prendergast, *J. Phys. Chem. Lett.*, 5, 1547 (2014).
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- [6] Characterization of Polysulfide Radicals Present in an Ether-Based Electrolyte of a Lithium-Sulfur Battery During Initial Discharge Using In Situ X-Ray Absorption Spectroscopy Experiments and First-Principles Calculations. K. H. Wujcik, T. A. Pascal, C. D. Pemmaraju, D. Devaux, W. C. Stolte, N. P. Balsara, D. Prendergast, *Adv. Ener. Mat.* 5, 1500285 (2015).
- [7] Polysulfide-Blocking Microporous Polymer Membrane Tailored for Hybrid Li-Sulfur Flow Batteries Changyi Li, Ashleigh L. Ward, Sean E. Doris, Tod A. Pascal, David Prendergast, and Brett A. Helms, *Nano Lett.* 15, 5724 (2015).

# Electrolytes in Post Li-Ion Batteries: Materials, Reactions and Mechanisms

*Stefan A. Freunberger<sup>\*</sup>, Nika Mahne, Lukas Schafzahl,*

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Li-ion batteries will continue to be the dominant electrochemical energy storage device for years to come. However, society needs energy storage that outperforms current Li-ion batteries in terms of energy density, power density, safety, material sustainability, long-term stability, and cost. Major directions involve improved intercalation materials (*e.g.*, multi electron and high voltage materials) and new concepts for anodes (*e.g.*, based on conversion reaction or alloying) and cathodes (*e.g.*, Li-O<sub>2</sub>, Li-S) as well as attempts to improve the energy that supercapacitors. The overriding factors for eventual success are improved energy storage metrics under the constraint of material sustainability and cost. All these new battery chemistries have their particular problems but they have one challenge in common: massive requirements onto the electrolyte.

We will discuss recent results of our major research directions that largely focus on electrolytes: alkaline-O<sub>2</sub> cathodes, Na-ion batteries.

Concerning metal-O<sub>2</sub> batteries it remains the central goal in the field to repeatedly achieve high discharge capacity, *i.e.*, nearly complete pore filling, and to be able to recharge the cell fully at high rate [1]. True reversibility of the cathode reaction in the Li-O<sub>2</sub> cell requires a set of quantities to obey the stoichiometry and to match each other during discharge and subsequent charge. Typically these measures deviate more or less significantly from the ideal due to parasitic reactions, which are not entirely understood. Hitherto known processes cannot explain all deviations of the mass balance over even a single cycle, let alone extended cycling. Only better knowledge of parasitic reactions will allow inhibiting them and reaching towards fully reversible cell reactions. We will discuss our recent insights into parasitic reactions that have so far been overlooked and their detection via newly developed methods. This allows for strategies to suppress a major contribution to irreversibilities [2].

Understanding the properties of the solid electrolyte interface (SEI) in alkaline ion batteries is important for improving SEI related phenomena including irreversible capacity, interfacial resistance, cycle life and safety. While there has been extensive work on the SEI in Li batteries there is comparatively little knowledge for Na batteries. Recently, the SEI on Na electrodes was found to be much more instable than on Li electrodes. This holds also particularly true for the metal electrodes. Since new battery chemistries are typically assessed in half cells with metal counter electrodes this raises questions about the reliability of Na-ion half-cell experiments as well as with other low voltage anodes [3]. We will present results on a new electrolyte that forms a stable and resilient SEI on sodium metal and thereby enables more reliable sodium ion half-cells and full cells as demonstrated for Na plating/stripping, hard carbon anodes and vanadium phosphate cathodes [4].

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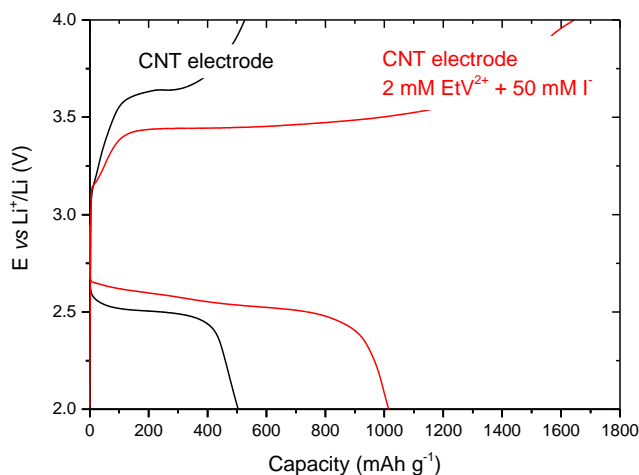
[4] L. Schafzahl et al., submitted.

# Li-O<sub>2</sub> batteries with redox mediators

*James Frith<sup>\*</sup>, Nuria Garcia-Araez, John Owen*

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Li-O<sub>2</sub> cells have the potential to become the next generation of energy storage devices as they have a theoretical specific energy of around 5 times that of current Li-ion cells. Currently, the main factor that limits the commercialization of Li-O<sub>2</sub> batteries is the sluggish reaction kinetics for the charge and discharge reactions, which leads to electrode passivation, problems of degradation side reactions, low capacities and fast capacity fading, poor round trip efficiency, etc. Mediators have been demonstrated to be a powerful tool to facilitate charge and discharge reactions in Li-O<sub>2</sub> batteries leading to outstanding improvements in battery performance [1] and suppression of degradation reactions [2]. This talk will describe a mechanistic study of the effect of mediators in Li-O<sub>2</sub> batteries, supported by a range of techniques such as electrochemical measurements, mass spectrometry, X-ray diffraction and Raman. A systematic study of the effect of cobalt complexes will be presented [3], as well as the development of batteries incorporating two mediators: ethyl viologen for the oxygen reduction reaction and iodide for the oxygen evolution reaction (figure 1).



**Figure 3.** Galvanostatic cycling data of Li-O<sub>2</sub> cells at 200 mA g<sup>-1</sup> in 1 M LiTFSI, Pyr14TFSI:diglyme (1:1 volume ratio) with (red) and without (black) mediators.

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# Extraction of material properties from lock-in thermography of pouch cells

*Howie Chu and Charles Monroe\**

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The large-format prismatic 15 Ah and 20 Ah lithium-ion pouch cells produced by A123 Systems exhibit significant in-plane temperature variation during steady operation. Spatial nonuniformity of temperature within a battery can potentially impact its voltage response. Over long times, a spatially varying thermal history can impact state of health in complicated ways. ‘Lock-in thermography’ (LIT) is an experimental technique wherein measurements of a battery’s surface-temperature distribution and its voltage response are measured synchronously [1]. Our work aims to develop models that can be validated against LIT data and ultimately used for battery simulation under different control schemes.

We have performed LIT on A123 pouch cells, measuring the responses of initially equilibrated batteries to repeated square-wave current excitations; this excitation profile allows periodic steady operating states at up to 5C to be observed without significantly perturbing the average state of charge. In parallel we have created a streamlined multiphysics finite-element model, which relies on a simplified version of the Fuller-Doyle-Newman theory. Our model operates very efficiently, allowing model parameters to be determined by directly fitting the entire experimental LIT data sets. This parameterization technique has proved successful for A123 cells and also holds promise for future efforts aimed at state-of-health ‘fingerprinting’.

## References

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# Pushing further the limit of operando techniques to probe battery materials

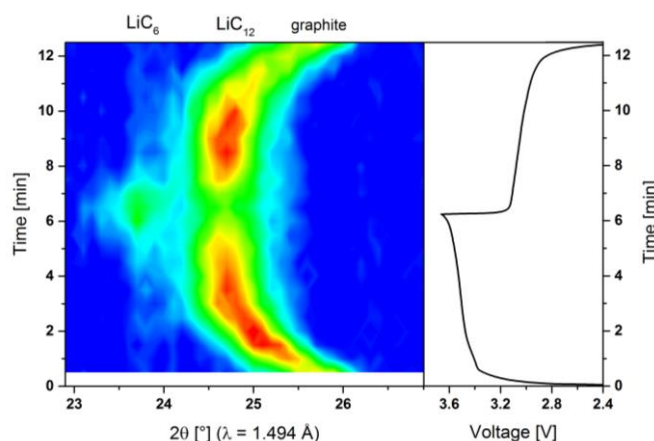
*Lucien Boulet-Roblin, Joanna Conder, Juliette Billaud<sup>\*</sup>, Claire Villevieille*

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The Li-ion chemistry is thus far the most advanced chemistry employed in battery technology. To date, Li-ion batteries dominate the market of the electronics and portables devices. However, in the field of electric and hybrid vehicles further improvements are required in terms of performance, safety, and cost. Advanced Li-ion batteries and the novel systems (Li-S and Na-ion) utilize less understood electroactive materials, showing new reaction mechanisms during electrochemical cycling and the understanding of which requires new characterization tools and techniques.

Development of a reliable electrochemical cells is thus of a prime importance when studying battery materials in operando mode during cycling. This is never an easy task, since the design of such cells has to be adequate to the technique of a choice and meet all its necessary requirements.

Herein we present different cell designs developed in our laboratory and used for operando studies. Having overcome many obstacles, our operando cells are able to sustain more than 100 cycles and simultaneously to perform structural studies such as X-ray and neutron diffraction. For the latter one, we also tested and adapted a new set-up called stroboscopic mode. It allows operando study of the batteries that are cycling at very high rates (e.g. 10C) with a neutron patterns collected each 1 s along 200 cycles and more.



**Figure 4.** Operando neutron powder diffraction measurements using stroboscopic mode (cell cycled at 9C rate) performed in a full-cell LiFePO<sub>4</sub> vs. graphite. Evolution of the main peak of the graphite (002) along charge and discharge

We will also discuss other example such as Li<sub>2</sub>MnO<sub>3</sub>. It is known that the optimal cycling condition of this active material requires the activation at elevated temperature. Therefore, we modified our X-ray diffraction cell to be able to cycle it at temperatures higher than 25°C and thus to study the activation mechanisms of Li<sub>2</sub>MnO<sub>3</sub>. These and other examples based on different operando techniques used to characterize Li-ion, Na-ion, and Li-S batteries will be presented during the talk.

*Acknowledgment: The authors would like to express their gratitude to Dr. Denis Sheptyakov from HRPT, SINQ, PSI beamline and fruitful help/discussions regarding neutron experiments. Mr. Hermann Kaiser and Christoph Junker are acknowledged for their help in all technical aspects of this study and the development of the cells. SAFT, SNF and SCCER Heat and Storage are thanked for financial support.*



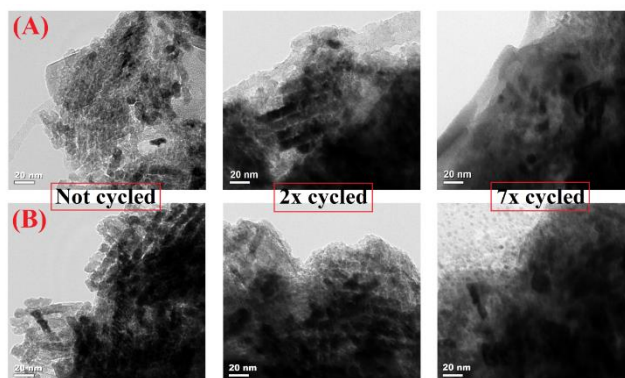
# Understanding the Behaviour of Metal Oxide Anode Materials in Lithium-Ion Batteries

*William E. Mustain*

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Transition metal oxides have been widely discussed as possible alternatives to graphite at the lithium ion battery anode for emerging high capacity applications such as (hybrid) electric vehicles and grid-scale energy storage. However, metal oxide-based anodes have struggled to show acceptable capacity retention characteristics over prolonged cycling, particularly at higher discharge rates and realistic active material loading. Storing charge with metal oxides is more complicated than graphite because they do not intercalate lithium during charge/discharge, but rather rely on chemical transformations that may lack chemical and structural reversibility, limiting cycle life and capacity retention. Understanding the chemical and structural transformation of metal oxides during charge/discharge will be important for future anode improvements.

This talk will primarily focus on techniques to probe metal oxide anode structure and performance, including identical-location transmission electron microscopy (IL-TEM), which allows individual particles to be imaged during electrochemical testing. Application of IL-TEM to understand the structural evolution of an ordered mesoporous NiO anode is shown Figure 1. Material properties that impact reaction reversibility (and hence capacity retention, i.e. nanostructure and electronic conductivity) as well as strategies for improving material stability over 100's of cycles will also be discussed over multiple metal oxide chemistries [1-3].



**Figure 5. Identical-location TEM image showing the structural evolution of an ordered-mesoporous NiO anode during cycling. Note the agglomerated structures and noticeable dark areas, which are phase separated Ni nanoparticles.**

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# Sparse Cyclic Excitations in the Solid Lithium-Ion Electrolyte LLZO

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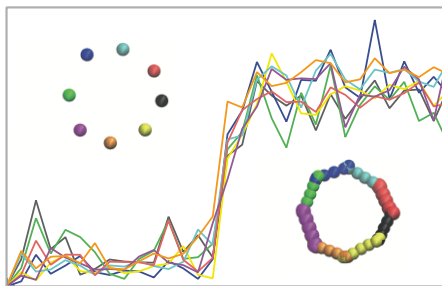
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Lithium-stuffed garnets,  $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$  are a promising family of solid lithium-ion electrolytes, and have been proposed as replacements for conventional liquid polymer electrolytes in next-generation lithium-ion batteries.<sup>1</sup> Within this material family, the lattice cation identities {A,B} and lithium content can both be varied, and differences in lithium-ion conductivity of  $\times 10^3$  have been achieved by changing the chemical composition. The most studied member of this family,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO), exhibits two phases with strikingly different ionic conductivities: a cubic phase, favoured at high temperature, or stabilized by doping, with  $\sigma \approx 10^{-4} \text{ S cm}^{-1}$ , and a tetragonal phase formed at low temperatures in stoichiometric samples, with  $\sigma \approx 10^{-6} \text{ S cm}^{-1}$ . This large difference in ionic conductivities is somewhat surprising, because the pathways available for lithium-ion conduction are topologically identical in both phases, and is not understood.

We have performed long-timescale molecular dynamics using an atomistic potential developed from first-principles calculations on the cubic and tetragonal phases of LLZO. This method makes long simulations computationally tractable while avoiding empirical parameterisation, and allows good statistical sampling of the lithium transport behaviour.

Applying two techniques from the supercooled liquid community, we identify displacive excitations of groups of ions, which have quantitatively different behaviour between the two phases. In tetragonal LLZO, these excitations are temporally and spatially sparse, with lithium moving preferentially around closed loops. This qualitative difference is explained as a consequence of lithium ordering in the tetragonal phase, and provides a mechanism for the much lower ionic conductivity of tetragonal versus cubic LLZO.<sup>2</sup>



**Figure 6. A highly concerted cyclic diffusion process in tetragonal LLZO.**

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# Solvation Structures of Mg Cations in the MACC Electrolyte

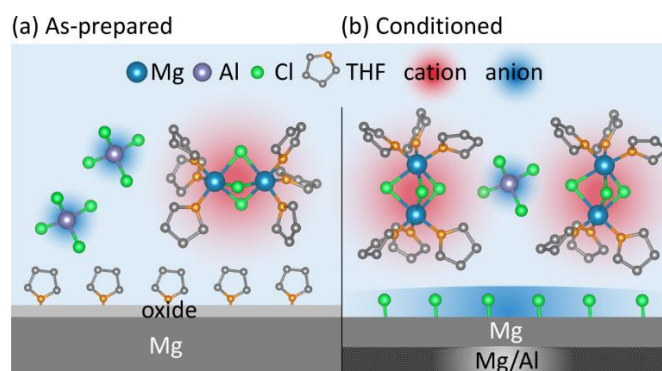
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Mg batteries are an attractive alternative to Li-based energy storage devices due to the high volumetric capacity afforded by Mg metal anodes. Electrodeposition of Mg metal results in smooth morphologies without the dendrites that plague electrodeposition of Li, thereby providing a route to a viable metal battery. The development of Mg batteries is strongly dependent on understanding the electrolyte component and charge transfer processes at the electrode interface during deposition. To this end, we have studied a promising electrolyte based on the magnesium aluminum chloride complex (MACC) which is composed of stable chloride salts and supports nearly 100% Coulombic efficiencies for Mg electrodeposition and stripping with high anodic stability. Interestingly, efficient Mg electrodeposition and stripping behavior is only achieved after the electrolyte is electrolytically conditioned.[1] This talk will detail the changes that occur in electrolyte speciation upon conditioning.

Due to the complex nature of speciation in the multicomponent MACC electrolyte, a combination of characterization techniques was used to determine the solvation structure of both Mg and Al. Raman spectroscopy, surface enhanced Raman spectroscopy, <sup>27</sup>Al NMR, <sup>35</sup>Cl NMR, and pair distribution function analysis together enabled the characterization of Mg complexes in the active electrolyte. Relative changes in speciation between the as-prepared and conditioned electrolyte suggest that free Cl<sup>-</sup> in solution plays a vital role in supporting efficient Mg electrodeposition and stripping behavior.[2]



**Figure 7. Schematic representing the speciation of Mg<sup>2+</sup> and Al<sup>3+</sup> in the magnesium aluminum chloride complex (MACC) electrolyte in the (a) as-prepared state resulting in poor Mg electrodeposition and stripping behavior and the (b) conditioned state resulting in efficient Mg electrodeposition and stripping.**

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# Synchrotron Powder Diffraction Beamline (I11) for Battery Research

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The high brightness beamline (I11) at Diamond Light Source is a dedicated synchrotron powder diffraction instrument which has been in user operation for a number of years. In the first experimental hutch (EH1), the high-precision diffractometer is equipped with multi-analysing crystals (MAC) detectors [1,2] which are routinely used for detailed structural investigations of new materials such as Li-ion cathode compounds. The diffraction instrument also has a fast position-sensitive detector (PSD) for in situ experiments [3] including studies of structural-electrochemistry relationships using in operando battery cells [4]. Recently, a second hutch (EH2) has been built for long duration experiments (LDEs) of natural, engineering or processing systems which require weeks to months of periodically monitoring “slow” changes. It is of particular benefit to research areas where important information on the development of phases over time cannot be obtained via ex-situ methods. Also applicable is battery research to study long-term changes of structural-chemistry due to charge/discharge over many cycles. The new facility houses the necessary hardware and equipment for multiple experiments including modified coin cells and electrochemical cyclers. These experiments are mounted on sample tables equipped with adjustable linear drives to periodically move battery cells in and out of the beam, and diffraction data are collected using a large area detector. Together with the hardware details, results from our battery research will be presented to demonstrate the capability of the beamline, including preliminary data from LDEs.

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# Tomographic Imaging of Battery Dynamics with Synchrotron Radiation

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# Update on Recent Progress at the DIAD Beamline

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# XAS for Electrocatalysis

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Efficiency in fuel cells is strongly linked to the performance of the electrocatalysts for the oxygen reduction reaction (ORR) at the cathode side, being Pt-based alloys the benchmark materials [1]. Transition metal oxides have been reported as active materials for ORR in alkaline media [2]. Although a number of high profile studies have proposed various descriptors for rationalizing the reactivity of TMOs in this context, a generally accepted understanding to rationally drive catalyst optimization has not yet emerged [3]. We probed that the ORR catalytic activity of transition metal oxides can be tuned by modifying the position of surface states. Our investigation reveals that by altering the redox surface states position, the ORR onset potential can be displaced.

$\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$  nanoparticles were synthesized via an ionic liquid method. Surface composition studies by XPS show that A-site segregation to the surface is favoured by the presence of  $\text{La}^{3+}$  ions. Mn oxidation state was investigated by ex-situ EXAFS analysis. The electrochemistry study of these oxides on an Ar-saturated solution, provide conclusive evidence of the position of the redox states, shifting to more negative potentials with the increase in the Mn oxidation state. The RRDE studies in the presence of  $\text{O}_2$  reveal that the onset potential for ORR closely matches with the position of the redox surface states. These observations provide the clearest indication that oxygen bond breaking requires changes of oxidation state within a range close to the reversible oxygen potential. Further probe is gained by in-situ EXAFS experiments.

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# Electrochemical Simulation of Solid Oxide Fuel Cell Electrodes: an Integrated Approach to Address the Microstructure-Performance Correlation

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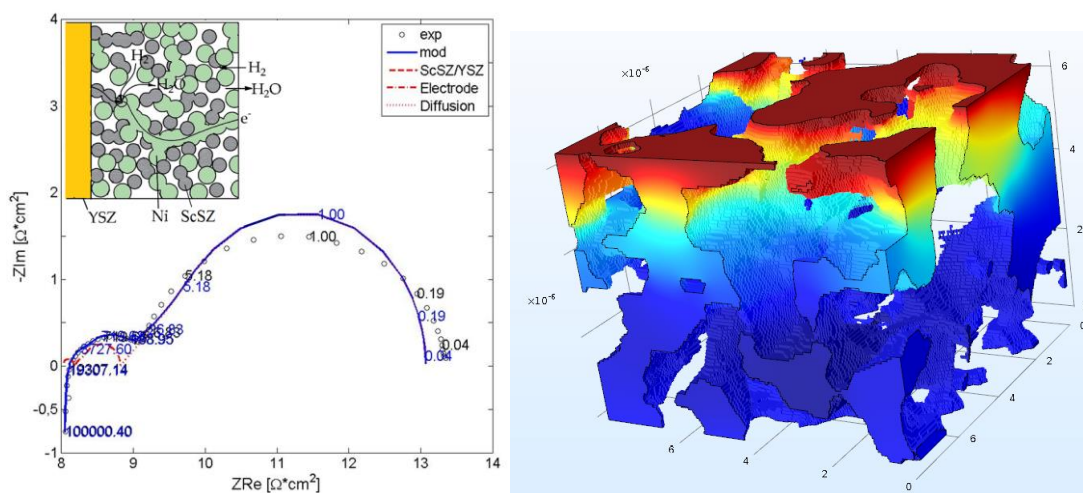
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Understanding the complex interplay between electrode microstructure and electrochemical performance is one of the key aspects for the optimization of Solid Oxide Fuel Cells (SOFC). Physically-based modelling, at different levels of sophistication, can provide a valuable insight in order to help the interpretation of experimental data and provide design indications to improve electrode stability and performance.

In this contribution we summarize the different modelling approaches used in our group, ranging from physically-based equivalent circuits, continuum conservation models and 3D models solved within the reconstructed electrode microstructure. When necessary, these models are coupled with percolation theory, packing algorithms and tomographic techniques. Special focus is given to the application of the models to interpret impedance spectra and their thorough validation under different conditions. Examples include the application of the models to electrodes with different microstructures, the study of the degradation mechanisms of Ni-infiltrated anodes as well as impedance simulations in real microstructures (Figure 1).

Results reveal that coupling physically-based modelling, impedance spectroscopy and 3D tomography is a promising approach to gain a fundamental understanding of the phenomena occurring at different length scales in SOFC electrodes, allowing for interpreting and planning experiments as well as to design more stable and more efficient electrodes.



**Figure 8.** Examples of physically-based impedance simulation and 3D modelling of gas transport

# Oxyanion Doping In Solid Oxide Fuel Cell Materials

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Perovskite systems have attracted considerable attention as electrolytes and electrodes for use in solid oxide fuel cells [1]. Traditionally doping strategies to optimize the conductivities for such materials have entailed doping with aliovalent cations of similar size, e.g.  $\text{BaCeO}_3$ , doped with Y on the Ce site. Prior work on cuprate materials related to high temperature perovskite superconductors, however, showed that the perovskite structure could incorporate significant levels of oxyanions (carbonate, nitrate, borate, sulphate, phosphate) [2]. The B, C, N, S, P of the oxyanion is incorporated onto the perovskite B cation site, with the oxide ions of the oxyanion occupying 3 (carbonate, nitrate, borate) or 4 (sulphate, phosphate) of the available 6 anion positions around this site.

Recently we have been examining the use of such oxyanion doping to modify the conductivity of fuel cell electrolyte and electrode materials, and the results from such studies will be presented, with a particular focus on the latter electrode systems [3]. We will also show that other structure-types will accommodate these oxyanions, highlighting that some “oxide” materials previously reported in the literature are in fact oxide carbonates.

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# High Performance Radiation-Grafted Anion-Exchange Polymer Electrolytes

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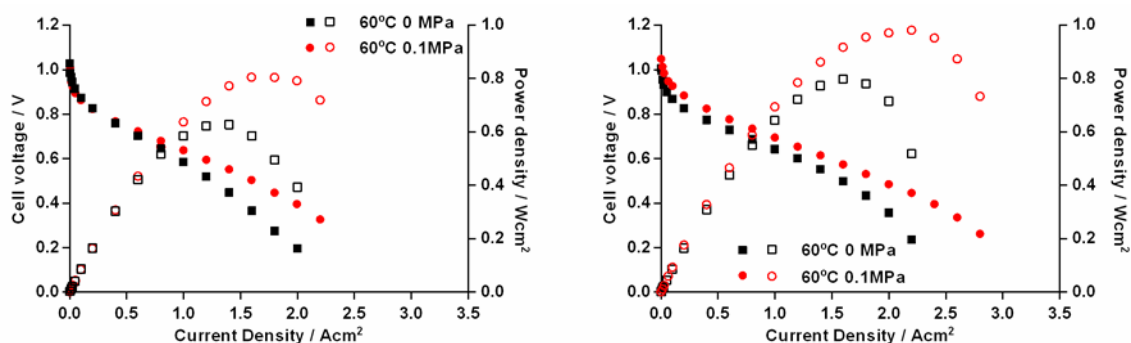
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This presentation will describe the latest research at the University of Surrey and the development of anion-exchange membranes (AEM) and ionomers (AEI) for use in alkali membrane fuel cells and electrolyzers.<sup>1</sup> These anion-exchange polymer electrolytes are produced using the post-irradiation grafted method (PIG). Poly(ethylene-co-tetrafluoroethylene), ETFE, materials can be used as substrates for radiation-grafted AEMs and AEIs.<sup>2</sup>



**Figure 9.** H<sub>2</sub>/O<sub>2</sub> alkaline membrane fuel cell performances at 60°C for a ETFE-based radiation-grafted AEMs (left = 100 μm thick and right = 50 μm thick AEM) with CCM-based MEAs (PtRu/C anode and Pt/C cathode - both with Wuhan University polysulfone-based AEI). Gas line back-pressures given in legends.

Recent achievements and advancements in this technology include: Synthesis of AEMs with benzyl-type heterocyclic chemistries that are more stable to alkali than those containing the benzyltrimethylammonium benchmark; Synthesis protocols that require reduced radiation doses, reduced amounts of monomer and reduced amounts of non-aqueous solvents; Synthesis of thinner PIG-based AEMs; The ability to produce PIG-AEMs based on low density polyethylene (LDPE) rather than ETFE; Synthesis of an interesting class of PIG-based solid-state AEI powders; AEMs with high hydroxide conductivities and high performances in H<sub>2</sub>/O<sub>2</sub> fuel cells.

This research was funded by the Engineering and Physical Sciences Research Council of the UK (grants EP/M005933/1, EP/M014371/1, EP/M022749/1). We also acknowledge the groups of Prof Andrew Herring (Colorado School of Mines, USA, hydroxide conductivities and SAXS data), Prof Lin Zhuang (Wuhan University, P. R. China, fuel cell test data), and Prof William David FRS (University of Oxford and Rutherford Appleton Laboratory, SANS data) for providing the indicated data.

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# Alkaline fuel cells – to the moon and back

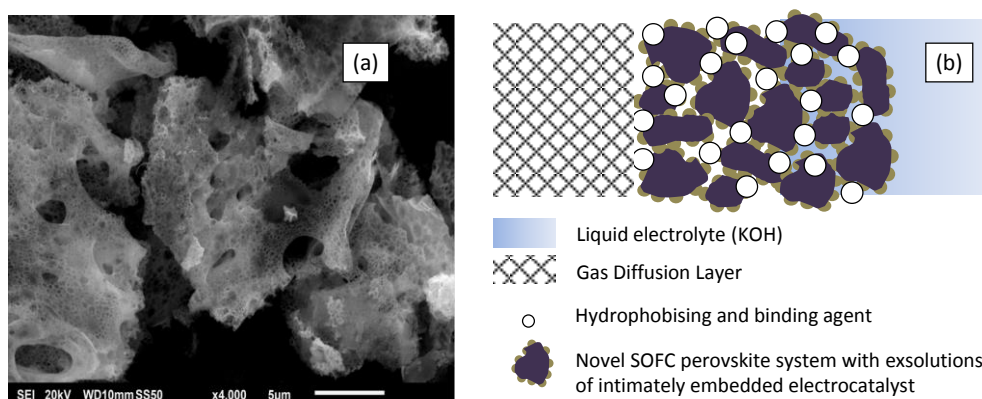
*Richard Dawson<sup>a\*</sup>, Anant Patel<sup>a</sup>, Anushree Khandale<sup>b</sup>  
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Alkaline fuel cells have a long history dating back the turn of the 20<sup>th</sup> century. In the 1940s and 50s Francis Bacon, one of the ‘fathers’ of practical fuel cell devices, developed the first useful fuel cell systems using potassium hydroxide electrolyte based cells. These were demonstrated as a small power units and most famously as a 15 kW unit in an Allis Chalmers tractor. The ‘Bacon’ cell patents were sold to Pratt & Whitney who developed the systems further for space applications taking astronauts to the moon and later, under the ownership of UTC, on repeated visits to space in the orbiter vehicles where they provided reliable power and potable water. In the more recent past interest had waned in AFCs whilst research in other fuel cell types boomed, however, partly with the development of alkaline membrane cells there has been a resurgence in the last 10-15 years. This is witnessed in the increasing number of related publications in the field and commercially by the success of UK based AFC Energy Plc, the world’s largest developer of alkaline fuel cell technology.



**Figure 1: (a) SEM image of lanthanum calcium titanate material with Ni exsolutions. (b) general AFC electrode structure.**

Setting the historical context we will present the current state-of-the-art in alkaline fuel cells, the advantages, the challenges and possible futures. As an example particular reference will be made to a recent EPSRC Supergen funded project that was undertaken as a collaboration between Lancaster University, St Andrews University and AFC Energy Plc. This explored the initial feasibility of using novel A-site deficient titanate materials with exsolutions of candidate electrocatalysts as building block for new alkaline electrodes. Figure 1a shows and SEM image of part of an electrode structure (general configuration shown in Figure 1b) using an example material with a Ni exsolution in the active layer of the cell.

# Modelling multiphase transport in fuel cells: The power of pore-scale approaches

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Incomplete understanding of multiphase transport phenomena in porous fuel cell electrodes has been a major roadblock to commercialization. Roughly speaking, if mass transfer rates could be doubled then stack size, platinum usage, and overall cost could be halved. One of the ever-present challenges has been the failure of traditional tools, both modelling and experimental, to effectively study fuel cell components, which differ in important ways from conventional (i.e. geological) porous materials. Fuel cell electrodes, encompassing the catalyst layer, gas diffusion layer and microporous layer, are thin, nanoporous, anisotropic, spatially heterogeneous, fibrous, multi-layered and hierarchical, mixed wettability, and highly porous. The transport phenomena inside fuel cells is equally challenging, with highly coupled, non-isothermal, multicomponent, multiphase conditions all impacting overall performance. The experimental difficulty of determining relevant transport parameters for these complex conditions, and the fundamental limitations of the widely used volume-average modelling for these atypical materials, combine to undermine the accuracy of the fuel cells models. The past decade, however, has seen tremendous efforts and significant progress on this front, and this talk will present an overview of the current situation and understanding. Particular emphasis will be placed on advances in pore scale approaches, including Lattice-Boltzmann simulations on X-ray tomography images, interpretation of effective transport properties in finite sized materials, pore network modelling of capillary behaviour in fibrous media, and multi-physics modelling of fuel cell performance using pore scale approaches to avoid the volume-average assumption altogether.

# Electrochemical Explorations of Graphene and Related Materials

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Graphene, a planar monolayer of carbon atoms that are densely packed into a 2D honeycomb lattice, has become one of the most intensively explored carbon allotropes in materials science due to its reported unique electronic and mechanical properties. One area that graphene has significantly influenced is in the field of electrochemistry where it is potentially represents the world's thinnest electrode material and has been applied in many areas, such as in sensing and energy storage/conversion.

This talk will explore recent work from my group on graphene and related 2D materials starting with fundamental insights into graphene's electrochemistry through to understanding related 2D materials and the implications into energy storage/generation.

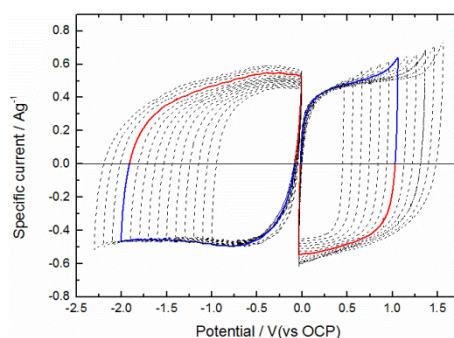
# Electrochemical Stability in Ionic Liquid based EDLCs

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Electrochemical double layer capacitors (EDLCs) exhibit relatively high power densities and can withstand hundreds of thousands of full charge-discharge cycles, but are limited by energy densities that are typically a tenth of that provided by Li-ion batteries. Operating at higher potentials can increase energy density, however the electrochemical stability window (ESW) of the electrolyte restricts operating potential. Ionic liquids have been widely investigated for use in EDLCs as they can operate at a higher potential than conventional electrolytes. Two of the more popular ionic liquids applied in EDLCs are *N*-butyl-*N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ([Pyr<sub>1,4</sub>][Tf<sub>2</sub>N]) and 1,3-ethyl methyl imidazolium tetrafluoroborate ([EMIm][BF<sub>4</sub>]) and have demonstrated stable operation at operating potentials of 3.7V[1] and 3.4V[2] respectively. Determining reliable operating potentials for new electrolytes is complicated by the influence of electrode characteristics on electrolyte decomposition. In order to identify suitable operating potentials, a few techniques based on cyclic voltammetry have been proposed [2,3]. These methods are applied to different combinations of ionic liquid (including [Pyr<sub>1,4</sub>][Tf<sub>2</sub>N] and [EMIm][BF<sub>4</sub>]) and activated carbon materials, and the results discussed with respect to the influence of a number of factors (such as particle size distribution, porosity, surface functionalities, binder material). Figure 1 illustrates typical cyclic voltammograms used in the determination of operating potentials; increasingly wide potentials are cycled through and the quantities of anodic and cathodic charge passed during each cycle are used to define a suitable operating potential. The quantities of charge passed at various potentials are also useful in the identification of suitable electrode mass loadings for EDLC cells. The influence of unsuitable mass loadings is also explored with respect to cell performance and electrochemical stability.



**Figure 10. Determination of a suitable operating potential for EDLCs using [Pyr<sub>1,4</sub>][Tf<sub>2</sub>N] and microporous carbon ( $S_{\text{BET}} = 2,200\text{m}^2\text{g}^{-1}$ ) using cyclic voltammetry. (Scan rate =  $5\text{mVs}^{-1}$ )**

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# Porous carbon materials: heterogeneous catalysis and beyond

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Porous carbon is among one of the most important supporting materials for heterogeneous catalysis. In general, it offers high surface area, controllable pore size and tuneable surface behaviours. Those advantages can also play an important role in electrochemistry. However, the experiences gained in the catalysis field may not be easily translated to the electrochemistry field, due to the technical barriers in the translation of scientific languages. In this presentation, I will start with the design of a type of hollow carbon spheres and compare their behaviours in heterogeneous catalysis and electrocatalysis. Hopefully this could help establish a good knowledge transfer between the two fields.

The hollow porous carbon spheres are developed via silica hard templating. Chemical vapour deposition is used to deposit and carbonize ferrocene into the silica template. The silica template is then removed by HF, which *in situ* generated via decomposition of PTFE, giving hollow mesoporous carbon with up to 1,700 m<sup>2</sup>/g of specific surface area. Loaded with Ru nanoparticles at 1 nm, the catalysts converted 85% of 5-hydroxymethylfurfural into 2,5-dimethylfuran, an alternative fuel with an octane number of 119.

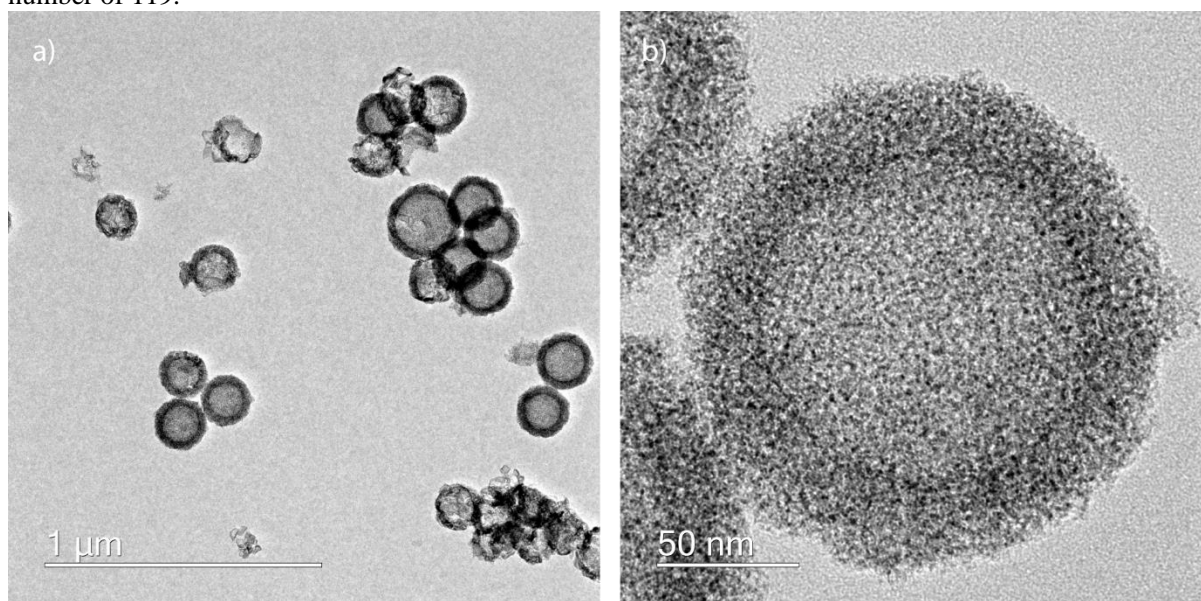


Figure 11. TEM images of Ru loading on hollow graphitic spheres

The hollow porous carbon spheres can be further graphitized into graphitic carbon under the assistance of Fe. High graphitic domain in the materials will boost the electron conductivity and thus make them suitable for electrocatalysis such as oxygen reduction reaction. In this case, Pt nanoparticles are loading into the pores of the carbon spheres and the catalyst showed excellent stability in ORR.

In both case, pore confinement was found to be the most important advantage of the porous carbon spheres. The bottleneck type of pores prevents the growth and aggregation of the metal nanoparticles. High surface area help the dispersion of the metal nanoparticles and over 20wt% of metal loading could be achieved. Both reactions take place at the gas, liquid and solid interface and the mass transfer will play an important role.



# 3D printed structural pseudocapacitors

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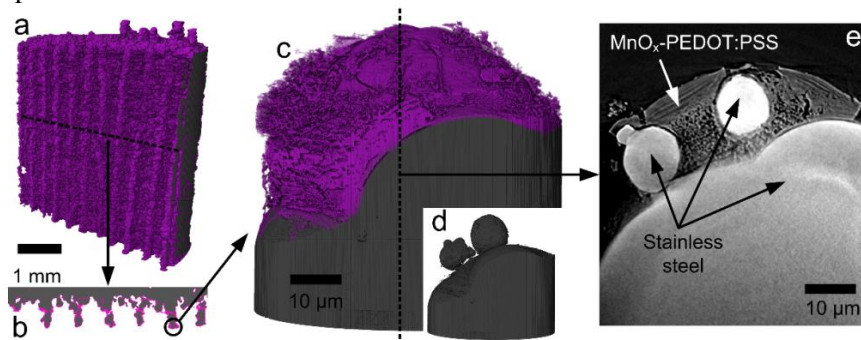
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Pseudocapacitors are energy storage devices which offer energy and power densities greater than supercapacitors and lithium-ion batteries respectively, however their mainstream adoption has been limited by poor lifetime and low areal capacitance. Of the pseudocapacitive materials, manganese oxides have received broad interest due to their relatively high gravimetric capacitances and low cost, however poor electronic conductivity results in low areal capacitance and thus impractical devices. To mitigate this, authors have combined manganese oxides with conductive additives in order to achieve higher mass loadings with high power rate capability. Of the conductive additives, doped polymers such as PEDOT:PSS are attractive as they are not only highly conductive but also exhibit pseudocapacitive behaviour, however the volume expansion observed upon charging/discharging results in limited electrode lifetime due to irreversible microstructural changes.

Here we present a novel 3D printed pseudocapacitor, suitable for structural energy storage applications which exhibits improved performance and lifetime over traditional planar electrodes. Using direct metal laser sintering, we create intelligently designed scaffolds of stainless steel onto which we perform a co-deposition of manganese oxides (electrochemical deposition) and doped conducting polymer (electrophoretic deposition) to create a composite electrode with hierarchical porosity. Raman and x-ray photoelectron spectroscopy are used to confirm the presence of the manganese oxides and conducting polymers via the co-deposition process. Using a combination of scanning electron microscopy, multi-scale x-ray computed tomography and electrochemical tests, we then show new insights into how microstructural evolution relates to observed performance increases and decreases over the device lifetime. Through the creation of porous 3D printed scaffolds, we show that this approach can improve durability via mechanical confinement of the active material, minimising the detrimental effects of the volume expansion such as electrode delamination. High resolution x-ray computed tomography was then used to demonstrate how microstructural features such as the lamella like electrode structure and evolution of cracks in the electrode can explain the initial observed performance increase upon cycling due to an increase in accessible surface area.

The figure below shows the reconstructed x-ray image of the 3D printed metal scaffold (grey) and co-deposited pseudocapacitive material (purple) with an orthogonal slice shown indicating the distribution of active material. The orthogonal slice of the high-resolution x-ray tomography image shows the lamella like structure, porous under-layer and cracks in the active material which contributes to changes in the electrochemical performance of the device.



**Figure 12. Reconstructions of x-ray CT data of the 3D printed scaffold with deposited active material**



# Li-ion battery failure: X-ray microscopy across multiple time and length scales

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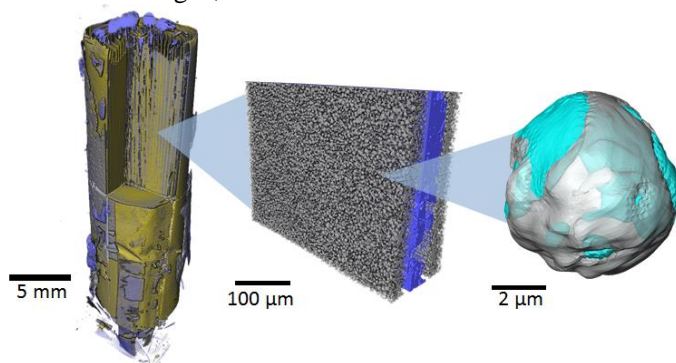
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Li-ion batteries are recognised as being an integral technology in the process of achieving a clean and sustainable energy future. The safety of Li-ion batteries is of upmost importance, particularly as the advancement of electric and hybrid electric 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; however, there is limited understanding of the dynamic mechanisms associated with thermally induced failures.

X-ray tomography has become a widely used technique for 3D structural analyses of electrochemical materials. In this study, high frequency tomography imaging of commercial Li-ion batteries during operation and failure was performed in beam-line ID15A at The European Synchrotron (ESRF). Radiographs were captured at a rate of up to 20,000 frames per second (fps), allowing us to study some of the most rapid failure mechanisms including those associated with thermal runaway [1]. The failure mechanism of cells is inextricably linked to their mechanical design; here, through application of a range of thermal, mechanical and electrical abuse scenarios, we reveal key degradation mechanisms as well as the influence of mechanical designs, and avoidable risks within commercial cells.



**Fig. 13. X-ray microscopy across multiple length scales.**

Multi-scale *post-mortem* tomography analyses of failed battery materials (Fig. 1) reveal a large degree of microstructural degradation, from the cell scale down to the particle scale. Features which may be indicative of temperatures reached, and reaction pathways during failure are identified inside the cells. This combined *operando* and multi-scale approach has provided new insights into the structural and thermal behaviour of cells leading up to and during thermal runaway and failure.

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# Fast microwave-assisted synthesis and lithium-ion diffusion studies of lithium stuffed garnets

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Lithium-stuffed garnets attract huge attention due to their outstanding potential as solid-state electrolytes for lithium batteries.[1] However, there exists a persistent challenge in the reliable synthesis of these complex functional oxides together with a lack of complete understanding of the lithium-ion diffusion mechanisms in these important materials. Addressing these issues is critical to realizing the application of garnet materials as electrolytes in all solid-state lithium-ion batteries. We have synthesised a cubic phase garnet of nominal composition  $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_{2.92}\text{Zr}_2\text{O}_{12}$  through a microwave-assisted solid-state route for the first time, reducing considerably the reaction times and heating temperatures. Lithium-ion diffusion behaviour has been investigated by electrochemical impedance spectroscopy (EIS) and state-of-art muon spin relaxation ( $\mu$ -SR) spectroscopy, displaying activation energies of  $0.55 \pm 0.03$  eV and  $0.19 \pm 0.01$  eV respectively.[2]

This difference arises from the high inter-grain resistance, which contributes to the total resistance in EIS measurements. In contrast,  $\mu$ -SR acts as a local probe providing insights on the order of the lattice, giving an estimated value of  $4.62 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for the lithium diffusion coefficient. These results demonstrate the potential of this lithium-stuffed garnet as a solid-state electrolyte for all solid state lithium-ion batteries, an area of growing interest in the energy storage community.

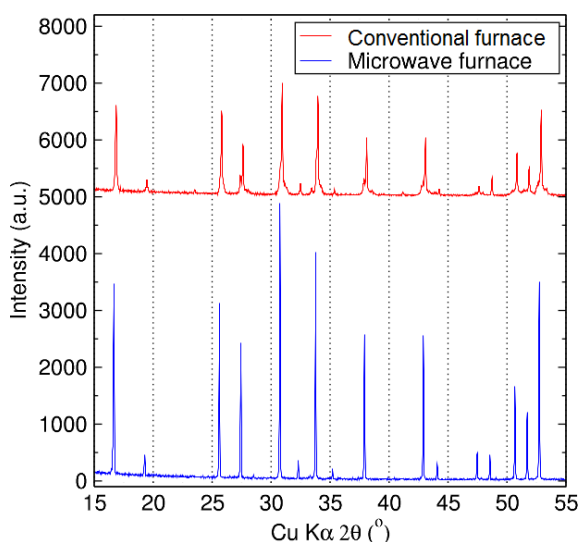


Figure 1. PXRD pattern of the as-synthesized  $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_{2.92}\text{Zr}_2\text{O}_{12}$  garnet by microwave-assisted vs conventional solid-state approach. Both samples were heated during 6 hours at 700 °C and a further 6 hours at 950 °C

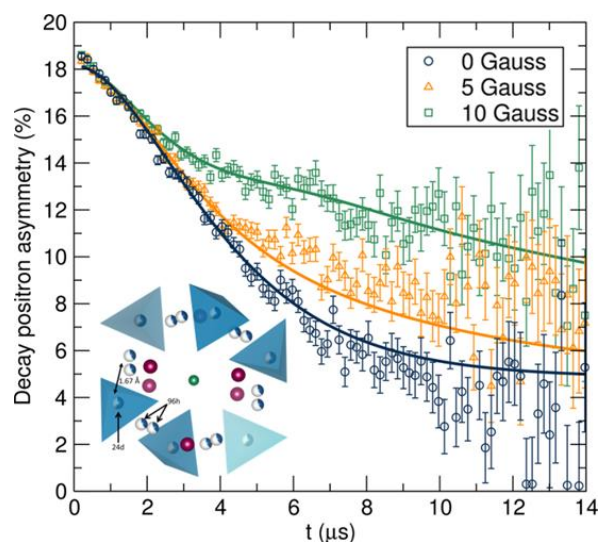


Figure 2.  $\mu$ -SR raw data collected at room temperature at zero field (circles) and applied fields of 5G (triangles) and 10G (squares), fit using the Keren function for the  $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_{2.92}\text{Zr}_2\text{O}_{12}$  garnet.

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# Synchrotron X-rays for the *In Situ* Investigation of High-Rate Battery Materials

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Energy storage materials with both high capacity and high charge/discharge rate enable applications that require long life, high power, and rapid recharge. Electric double-layer capacitors offer high power and conventional battery electrodes offer relatively high capacity but the combined properties require advanced materials. While nanostructures have dominated this emerging field, there are well-known issues regarding cost, stability, scalability, and safety of nanoparticles for battery applications. Recently, complex oxide structures from facile solid state synthetic methods have shown promising rate, capacity, and stability for reversible lithium intercalation. Complex structure types with low symmetry, large unit cells, site disorder, superstructure, order-disorder transitions, local second-order Jahn-Teller distortions, and mobile lithium atoms create severe challenges and interesting opportunities for experimental and computational investigations. Herein, we discuss the structure and properties i.) crystallographic shear compounds (e.g.  $\text{TiNb}_2\text{O}_7$ ) and ii.) tungsten bronze-type phases (e.g.  $\text{T-Nb}_2\text{O}_5$ ). Electrochemical results are interpreted with insights from *in situ* X-ray absorption and *in situ* X-ray diffraction. *In situ* techniques at synchrotron sources allow efficient and rapid acquisition of chemical and crystallographic changes during charge/discharge. The high photon flux that a synchrotron provides is critical for the study of high-rate materials and metastable intermediates, where fine temporal resolution is required.

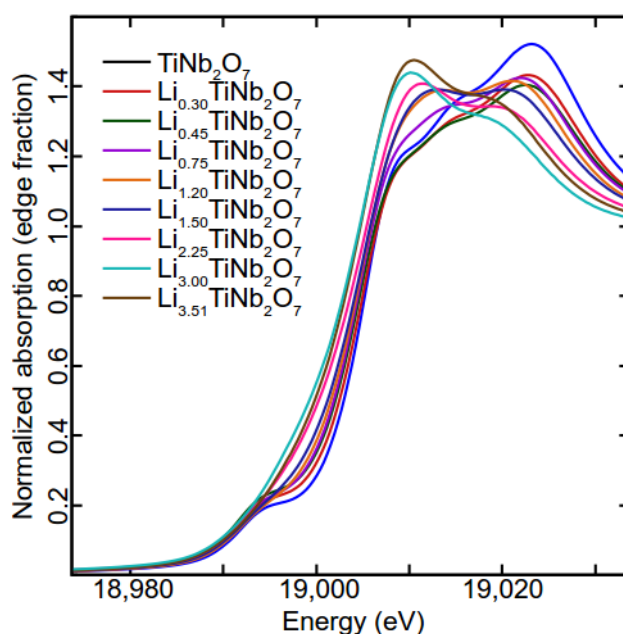


Figure 14. Nb K-edge X-ray Absorption Spectra of  $\text{Li}_x\text{TiNb}_2\text{O}_7$

# Structure and Sodium Dynamics Investigation of Sodium Strontium Silicate by Solid-State NMR

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Initial reports of Na-doped strontium silicate  $\text{SrSiO}_3$  (i.e.  $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ ) by Singh and Goodenough<sup>1</sup> caused high debate in terms of its structure, chemical composition, ionic conductivity and the nature of the charge carrier. In efforts to replicate these results, Bayliss *et al.*<sup>2</sup> proposed that there was no Na-doping and the material was not single phase. It was suggested that material is a biphasic solid solution of  $\text{SrSiO}_3$  and an amorphous Na containing disilicate glass  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , with the latter being responsible for the high conductivity observed in the original study; confirmed with consequent studies.<sup>3–7</sup> However, the overall conductivity of the material was still up for discussion as the associated activation energy for mobility of the charge carrier ranged by a factor of 3.<sup>1,4,6</sup> These differences were assumed to arise from varying thermal histories and devitrification processes of  $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$  and the complex polymorphism of the glass  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  when crystallising to  $\text{Na}_2\text{Si}_2\text{O}_5$ .<sup>8</sup>

We present here the structural and  $\text{Na}^+$  ion dynamics investigation of  $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$  and after its devitrification.<sup>7</sup> Using  $^{23}\text{Na}$ ,  $^{29}\text{Si}$  and  $^{17}\text{O}$  MAS NMR, we confirm the absence of Na-doping in  $\text{SrSiO}_3$  and re-establish that the material is a biphasic solid solution consisting of  $\text{SrSiO}_3$  and  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  as the single Na-containing phase – in agreement with the proposed structure by Bayliss *et al.*<sup>2</sup>  $\text{Na}^+$  ion dynamics of  $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$  probed by  $^{23}\text{Na}$  spin-lattice relaxation rates  $T_{1(\rho)}^{-1}$  were seen to have activation energies in good agreement with ac impedance spectroscopy data, while the devitrified sample showed insulative properties as expected from molecular dynamics simulation.<sup>9</sup>

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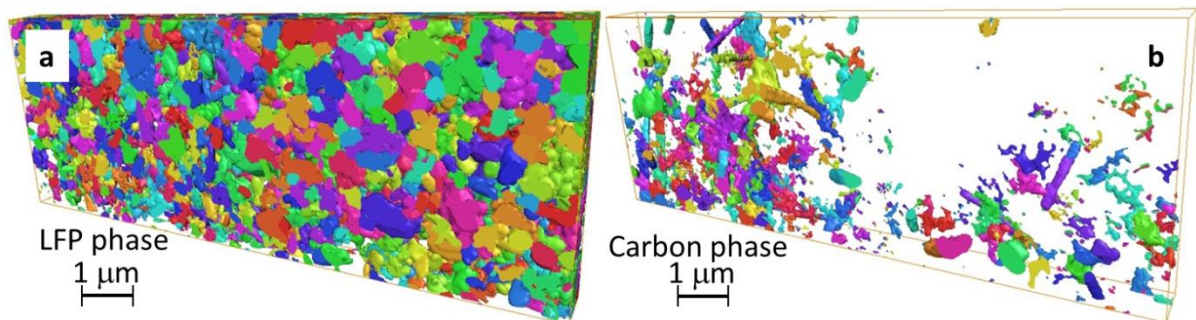
# Contrast improvement applied to lithium ion battery electrode materials enabling high resolution 3D imaging and quantification

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The authors present for the first time a new methodology of contrast enhancement for multi modal 3D imaging, including novel advanced quantification, on a commercial Lithium Iron Phosphate (LFP)  $\text{LiFePO}_4$  cathode. The aim of this work is to improve the quality of the 3D imaging of challenging battery materials by developing methods to increase contrast between otherwise previously poorly differentiated phases. This is necessary to enable capture of the real geometry of electrode microstructures, which allows measurement of a wide range of microstructural properties such as pore/particle size distributions, surface area, tortuosity and porosity. These properties play vital roles in determining the performance of battery electrodes. In this study we present a novel method of sample preparation with a new type of epoxy impregnation, brominated (Br) epoxy, which is introduced here for the first time for this purpose and found suitable for multi modal imaging, for both focused ion beam scanning electron microscope (FIB-SEM) tomography and X-ray micro tomography. The Br epoxy improves image contrast, which enables higher FIB-SEM resolution (3D imaging), which is amongst the highest ever reported for composite LFP cathodes using FIB-SEM. In turn it means that the particles are well defined and the size distribution of each phase can be analysed accurately from the complex 3D electrode microstructure using advanced quantification algorithms.



**Figure 15. High resolution 3D image of (a) LFP particle size distribution (b) Carbon particle size distribution (each colour represent a different particle size) STFC AM 2016**