Warwick Battery Days (WBD 2024)
University of Warwick
20-21 June 2024

Programme

Day 1

9:00 am – 10:00 am: Registration and morning coffee
10:00 am – 10:10 am: Welcome and Opening Remarks
10:10 am – 10:50 am: David Greenwood (Keynote)
10:50 am – 12:05 am: Session 1 – Chair: Louis Piper
    10:50 am – 11:20 am: Paul R. Shearing
    11:20 am – 11:50 am: Matteo Bianchini
    11:50 am – 12:05 am: Raj Pandya
12:05 pm – 1:00 pm: Lunch & poster set-up
1:00 pm – 1:40 pm: Saiful Islam (Keynote)
1:40 pm – 3:00 pm: Session 2 – Chair: Matteo Bianchini
    1:40 pm – 2:10 pm: Rhodri Jervis
    2:10 pm – 2:40 pm: Siân Dutton
    2:40 pm – 3:00 pm: Ferran Brosa Planella
3:00 pm – 3:30 pm: Coffee break / posters
3:30 pm – 4:30 pm: Session 3 – Chair: Ioan-Bogdan Magdau
    3:30 pm – 4:00 pm: Chris-Kriton Skylaris
    4:00 pm – 4:15 pm: Huseyin Sener Sen
    4:15 pm – 4:30 pm: Paolo Melgari
4:30 pm – 6:00 pm: Poster session
6 pm – 7 pm: free time
7 pm – 9 pm: Conference dinner (ticketed event)

Day 2

9:00 am – 10:00 am: Registration and morning coffee
10:00 am – 10:40 am: Emma Kendrick (Keynote)
10:40 am – 12:00 pm: Session 4 – Industry Talks – Chair: Chris-Kriton Skylaris
    10:40 am – 11:00 am: Felix Hanke (Dassault Systèmes BIOVIA),
    11:00 am – 11:20 pm: Alice Merryweather (illumion),
    11:20 am – 11:40 pm: Jacob Gavartin (Schrodinger),
    11:40 am – 12:00 pm: Rowena Brugge (Nyobolt)
12:00 pm – 1:00 pm: Lunch
1:00 pm – 3:00 pm: Session 5 – Chair: Ivana Hasa
    1:00 pm – 1:15 pm: Mark Phipps (TA Instruments/ Waters)
    1:15 pm – 1:45 pm: Peter Slater
    1:45 pm – 2:15 pm: Pooja Goddard
    2:15 pm – 2:30 pm: Masoud Jabbari
    2:30 pm – 2:50 pm: Ioan-Bogdan Magdau
    2:50 pm – 3:00 pm: Poster prizes
3:00 pm – 3:30 pm: Coffee break
3:30 pm – 4:30 pm: Session 6 – Chair: Bora Karasulu
    3:30 pm – 3:50 pm: Ieuan Seymour
    3:50 pm – 4:10 pm: Ivana Hasa
    4:10 pm – 4:30 pm: Alex Robertson
4:30 pm – 4:45 pm: Closing remarks

*All talks will take place in the Tiered Lecture Theatre

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ABSTRACTS

Day 1 – Thursday, 20th June

Keynote 1:

Future battery needs of the automotive industry, and the UK R&D infrastructure needed to support it

Dave Greenwood
University of Warwick / WMG

Abstract to be communicated

Session 1:

Understanding battery materials using advanced X-ray and correlative imaging methods

Paul R. Shearing
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The Li-ion battery was one of the transformative technologies of the 20th century and promises to have wider impact in the 21st century with the rapid uptake of electric vehicles and the deployment of grid scale energy storage. Energy storage is critical to achieve ambitious targets for Net Zero where electrochemical technologies are expected to be a cornerstone of decarbonisation efforts in a range of sectors.

To support the acceleration of energy storage technologies, the past decade has seen the rapid development and proliferation of three-dimensional X-ray imaging tools applied to Li-ion batteries. This provides a framework to improve the understanding of electrode morphology and its influence on transport processes, electrochemistry and mechanical behaviour. Moreover, through the application of image-based modelling tools, it has become possible to simulate a range of phenomena using a computational framework derived directly from tomographic images.

The non-destructive, and multi-scale characteristics of X-ray imaging tools provide benefits to quantify hierarchical complexity from the particle to the electrode and device level, where the portfolio of techniques available includes absorption and phase contrast CT to understand multi-scale morphology, XRD-CT to reconcile chemical, crystallographic and morphological behaviour and Bragg Coherent Diffraction Imaging to access sub-particle behaviour. Meanwhile complementary neutron, electron and ion beam imaging techniques can also leverage the benefits of the alternative contrast modes possible.

Here, we will review this progress and reflect on recent developments using multi-modal methods to understand the performance of advanced batteries. In concert, the portfolio of imaging and modelling tools provides a platform to explore the performance, degradation and failure of Li-ion batteries and to accelerate the development of post Li-ion chemistries.

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P2-type sodium layered oxides doped with redox-inactive elements and halide solid electrolytes for Na-ion and Na-solid state batteries

Matteo Bianchini
University of Bayreuth

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Among sodium-based cathodes, layered oxides (NaxTMO2, TM = transition metal) are one of the most attractive candidates. P2 and O3 are two of the most studied structures in the NaxTMO2 system. Regarding Na+ conductivity, P2 is believed to be preferable over O3 as it provides open prismatic pathways with a lower energy barrier for Na diffusion.[1] However, a drawback for P2 materials is that they are typically synthesized with low Na content, often close to x = 2/3, and can rarely reach beyond 3/4, which is not ideal when building full cells.[2] The other major issue of P2 is the P2–O2 phase transition taking place at high voltage during electrochemical cycling, which is not well reversible and limits its cycling stability and capacity retention.[3,4]

The aim of our work on the cathode is twofold: i) to improve the Na inventory available for P2 materials, and ii) improve the cycling stability by doping inactive elements in the pristine materials without excessively compromising specific discharge capacity. In this contribution, we focus on a family of Li doped P2 materials with nominal compositions of Na5/6LiyNi5/12-3y/2Mn7/12+y/2O2 (y = 2/18, 3/18, 4/18, 5/18). We report on the characterizations of the crystal structures of these materials, as well as the temperature-resolved in situ XRD during their solid-state synthesis. These studies provide guidance for further synthesis of desired phases and compositions of the P2 materials[5].

Electrochemically, this family of materials show an increasing trend of polarized hysteresis in the first charge and discharge cycle, which suggests the capacity contribution from oxygen redox. We coupled semi-simultaneous operando x-ray absorption near edge structure (XANES) and operando XRD to understand the structural evolution and redox behavior during this process. In particular, we observed that Li in the TM site mitigates phase transitions at high voltage, with a threshold between 0.15 and 0.18 Li per formula unit (f.u.). An increasing Li amount facilitates the activation of the O-redox starting at lower voltages and mitigates the P2-O2 phase transition. The cycling stability and rate performances of these materials were investigated in half cells. The 0.15 and 0.18 f.u. Li stoichiometric compositions prove to deliver the best balance of cycling stability and capacity. Finally, we applied the best materials against home-made hard carbons in exploration of their performances in full cells.

Furthermore, given the strong interest nowadays towards solid-state batteries, we will report on recent developments in our group with respect to novel halide-based solid electrolytes (SE) based on modifications of the well-known NaAlCl4 [6] . Given the high electrochemical stability at high potential, the aim is to employ such materials in catholyte composites together with the above-mentioned P2 cathode active materials. We will report on our initial work in this respect.

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Femto and picosecond charge dynamics in battery cathodes

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In this talk I will showcase some of our preliminary results on using ultrafast pump probe spectroscopies to access battery-relevant femtosecond electronic dynamics in model LixMn2O4 cathodes. I will start by highlighting the relevance of ultrafast dynamics in these systems before discussing how we can adapt pump probe methods, designed for looking at photoactive materials, for batteries. I will summarise by showcasing early data using these techniques in conjunction with THz pump probe, 2D IR and XFEL probes to reveal information on the primary polaronic excitations in cathodes and their transport properties.

Keynote 2:

From Lithium-Rich Cathodes to Thiophosphate Solid Electrolytes: Insights into Battery Materials on the Atomic Scale

Saiful Islam
University of Oxford

Further breakthroughs in high energy density lithium-ion batteries require advances in new compositions and underpinning materials science. Indeed, a greater fundamental understanding into battery materials require atomic-scale characterisation of their ion transport, electronic and local structural behavior, which are important for optimizing performance. In this context, combined modelling-experimental work has been a powerful approach for investigating these properties. This presentation will describe such studies in two principal areas: (i) investigating redox processes and nanostructures of Li-rich layered oxide and disordered rocksalt oxyfluoride compounds as promising high capacity battery cathodes; here, the atomic-scale mechanisms governing redox behaviour in Li-rich structures are not fully understood (ii) cation doping and ion transport mechanisms in solid electrolytes for solid-state batteries including oxyhalide and thiophosphate based materials. Microscopic effects are considered, and the results are used to rationalise macroscopic behaviour to guide future work on optimising battery performance.

Session 2:

Advanced X-ray CT and image analysis techniques for understanding cracking in NMC811 Polycrystalline particles

Rhodri Jervis
University College London

Co-authors: Huw Parks, Matthew Jones, Aaron Wade, Alice Llewellyn, Chun Tan, Hamish Reid, Ralf Zieche, Thomas Heenan, Shashidhara Marathe, Christoph Rau, Paul Shearing, Rhodri Jervis

High-nickel content layered cathodes (Ni>80%) of the form LiNixMnyCozO2 (NMC) undergo considerable anisotropic lattice changes during cycling (lithiation and delithiation) which has been attributed to the creation of microcracks in polycrystalline agglomerate cathode particles. This cracking behaviour has long been suspected to cause significant degradation; however, the pre-existence of particle cracks and defects from manufacturing and calendaring of the electrodes can make it difficult to assess the contribution of the electrochemical history alone in causing cracks[1]. In a bid to reduce this, so-called single-crystal materials have been proposed to be more resistant to degradation[2] due to their resilience to cracking[3] and lower surface exposure to electrolyte, which can cause parasitic reactions and drive oxygen loss[4].

Assessing the origins of cracking and its evolution with battery ageing is complex due to the small and internal nature of the cracks, often requiring either destructive imaging techniques or small sample sizes in non-realistic environments to facilitate non-destructive imaging by methods such as X-ray CT. We have previously used electrodes with optimised tab geometries for in-situ and operando X-ray CT and related characterisation methods[5, 6], which allows for a pseudo- in-situ nano-CT study of electrochemically induced cracking in NMC811 particles with minimal pre-existing damage[7]. We show that even on the first cycle, significant intergranular cracks can develop in the polycrystalline materials.

Here, we extend this methodology to assess the progression of first cycle cracking throughout the charge and discharge range on a large volume of the same electrode within a realistic pouch cell environment[8]. Automated image processing and analysis allows us to follow around 7,000 particles through multiple SoC, revealing the diversity of cracking behaviour within working, commercially relevant, Li ion battery electrodes, including a statistically relevant quantification of the extent of crack closure behaviour.

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The role of the Fe metal impurity in the electrochemical properties of MgFeB2O5

Sian Dutton
University of Cambridge

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We investigate the magnesium-iron pyroborate MgFeB2O5 as a potential cathode material for rechargeable magnesium-ion batteries. Synchrotron Powder X-ray diffraction and Mössbauer spectroscopy confirm its successful synthesis and iron stabilization in the high-spin Fe(II) state. Initial electrochemical testing against a lithium metal anode yields a first charge
capacity near the theoretical value (147.45 mAh/g), suggesting MgFeB2O5 as a promising cathode candidate. However, multimodal analyses including Scanning Electron Microscopy Energy Dispersive X-ray analysis, operando X-ray Absorption Near Edge Spectroscopy, and magnetic measurements reveal the absence of any Fe redox reactions. Instead, we propose that the source of the observed capacity is the dissolution of a small (4-7 wt%) Fe metal impurity. These findings highlight the need for diverse characterization techniques in evaluating the performance of new Mg cathode materials, as promising initial cycling may be due to competing side reactions rather than Mg (de)intercalation.

Continuum models for lithium-ion batteries: a mathematical approach

Ferran Planella Brosa
University of Warwick

In order to optimise battery design and management, we need models than can provide fast and accurate predictions of the battery behaviour. However, many of the existing are posed in an ad hoc way, making them challenging to extend and prone to inconsistencies. This presentation will explore how we can leverage advanced mathematical techniques to derive and implement better models for battery design, control and characterisation.

Session 3:

Large-scale quantum atomistic and multiscale simulations of batteries

Chris-Kriton Skylaris
University of Southampton

Co-authors: Arihant Bhandari, Jacek Dziedzic, Michael Mercer, John Owen, Denis Kramer

We are developing new software tools with unique capabilities for large-scale atomistic electrochemical simulations under operational conditions. The aim is to not only capture all the essential chemistry and physics of devices such as batteries, but also to provide the parameters needed for bridging atomistic with larger scale simulations. Our developments are within the ONETEP program [1], which is based on a linear-scaling reformulation of density functional theory (DFT) that allows atomistic simulations of several orders of magnitude more atoms than conventional DFT approaches, so that we can study more complex models. In this talk, I will outline our developments so far, which include methods for metallic systems, solvent and electrolyte models [2], and a grand-canonical approach which allows simulations at fixed voltage with respect to a computational reference electrode [3-4]. Also, I will describe our ongoing development of new DFTB approaches within the linear-scaling framework of ONETEP which will enable simulations at longer timescales to allow study of problems such as the chemistry taking place during SEI formation. Finally, I will summarise recent applications of these tools to the process of lithium metal deposition on anodes and its competition with Li dendrite formation [5], one of the major mechanisms of battery degradation.

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Atomistic Simulations of Interfaces within All-Solid-State Batteries: A special case of Lithium Thiophosphates

Huseyin Sener Sen
University of Warwick

Co-authors: Bora Karasulu
[1] Department of Chemistry, University of Warwick

All solid state batteries employs non-combustible solid electrolytes that promise safe energy storage. They also offer the utilization of metallic lithium as anode to achieve highest energy density. However, the creation of an electrolyte possessing both high ionic conductivity, while maintaining thermodynamic stability towards lithium, is a significant challenge. To resolve this issue, we proposed a route where we discover novel solid state electrolytes with high ionic conductivity and stability against Li anode using ab-initio random structure search and test them using atomistic modelling and experimental characterization. For this purpose, we screened the Li-P-S ternary phase space using high-throughput crystal structure predictions. Here, we introduce highly conductive solid solutions that lie along the Li_3P-Li_2S tie line as the most promising phases. The solid solutions are synthesized using ball milling technique. Structural properties and Li-ion mobility of the resulting materials are systematically characterized through X-ray and neutron diffraction, solid-state NMR, and EIS. As anticipated by structural predictions, the solid solutions exhibit a fluorite structure (Li_2S) with P substituting for S and additional Li^+ ions occupying octahedral voids to facilitate ionic transport. Structural stability, diffusivity, and activation barriers for Li^+ transport are assessed via quantum-chemical calculations. The new solid electrolytes demonstrate ionic conductivities comparable to established materials (such as $Li_7P_3S_{11}$), while their composition ensures thermodynamic stability against Li metal anodes. Simulations with machine learning potentials and ab initio molecular dynamics investigating the electrode-electrolyte interfaces further confirm the predictions of high stability and ionic conductivity. The results indicate that these ternaries might be the cheap electrolytes with high ionic conductivity and stability against Li anode that the industry is looking for.

Performance Enhancement of Nickel Manganese Cobalt Oxide Cathodic Material by Advanced Coatings

Paolo Melgari
University of Warwick

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Batteries as any electronic devices are affected by parasitic (physical and chemical) phenomena at bulk and interfaces. The phenomena lead to degradation in performance, impose operation restrictions and potentially make devices unsafe.

Lithium-metal-based batteries show promise to meet EV market requirements. However, electrode manufacturing design is required to mitigate cathode/electrolyte interfacial side reactions which can lead to passivating layer formation, thus increasing cell resistance, unwanted additional overvoltage, and ultimately capacity loss.

Within this work we have evaluated Spray Drying (SD) and Atomic Layer Deposition (ALD) coating processes to engineer the cathode/ electrolyte interface and mitigate the interfacial degradation. SD has been used to synthesise battery electrode materials at scale. ALD is a SemiConductor (SC) industry technique to deposit stoichiometrically-fixed, defect-free and nanometric-thick materials. As such, the application of ALD to coat powders in the battery community is currently under development.

Cathodic materials such as NMC (Nickel Manganese Cobalt Oxides) have been investigated, as the need to improve capacity retention is strong for high-content nickel cathodes.

Indeed, ALD utilised to coat NMC powder provides a nanometre- thick layer of a dielectric but ionic conductive metal oxide, and the aluminium oxide shell - nickel material core structure has been investigated here. In parallel, SD has been used to create an NMC powder decorated structure starting from preformed metal oxide particles and the cathode material.

Morphological and chemical characterisation of the products have been crucial to develop the coating processes. Electrochemical tests probed the engineered cathode/ electrolyte interface in multiple cell configurations and helped the design of SSB. The SSB cells were assembled using thin lithium metal anode, sulphur-based electrolyte, and surface-engineered NMC supported by aluminium foil.

Day 2 – Friday, 21st June

Keynote 3:

Sustainable Battery Design

Emma Kendrick

University of Birmingham

To create better and more sustainable battery chemistries, it is important to consider all aspects of the battery cycle. This includes factors such as raw materials and their supply chain, manufacturing processes of materials, electrodes and cells, performance properties, and recycling or end-of-life processes.

This presentation will discuss the importance of both critical and non-critical materials in batteries and their use in different battery chemistries. Lithium-ion batteries often contain high value elements such as cobalt or nickel which means that the current recycling processes are more viable, however for lower value materials such as lithium iron phosphate or the sodium-ion cathode materials lower cost recovery processes are required. If the materials can be recovered easily with low-cost processes routes and in a form that can be directly re-used in a battery, direct recycling, the economics should be more favourable than returning to the elements to either their metallic or precursor salt as is done in pyrometallurgical and hydrometallurgical routes.

When developing new battery technologies, there's a chance to design in recycling from the start, rather than retrospectively, as is currently the case for lithium-ion batteries. Additionally, this presentation will explore design principles for creating a more sustainable battery technology, such as optimizing materials processing, electrode design, and properties that promote long-lasting performance and increased recovery efficiencies.

Session 4:

Automated workflows for battery material performance and degradation

Felix Hanke

Dassault Systèmes BIOVIA, Cambridge (UK)

Materials modelling delivers value by enabling predictions for processes and properties that are intractable or very expensive to investigate experimentally. Automated and validated workflows facilitate this for molecular simulation experts and democratized users such as engineers or laboratory based battery engineers. Here I will outline how molecular level simulations fit into the Dassault Systèmes multiscale simulation framework to link molecular dynamics simulations (MD) to cell level performance. The same MD is an essential ingredient in a distributed and autonomous Materials Acceleration Platform, which links multiple different experiments, molecular simulations, materials databases, all coupled to an AI-driven optimization mechanism to optimize an electrolyte for performance. I will also outline our general approach toward simulating molecular level degradation by rigorously coupling electronic structure and molecular dynamics simulations. These simulations show how the solid electrolyte interphase forms on a molecular level over long time scales.

Charge photometry: visualising single-particle state-of-charge and morphology changes

Alice J. Merryweather
Illumion Ltd.

Co-authors: C. Schnedermann, C. Xu, Z. Lun, Q. Jacquet, A. Mahadevegowda, S. Oswald, A. Rao, C.P. Grey

Key to advancing lithium-ion battery technology is our ability to follow and understand the non-equilibrium processes occurring in functioning materials under realistic conditions, in real time, and on the nano- to meso-scale. Currently, operando imaging of lithium-ion dynamics is typically achieved by sophisticated synchrotron X-ray or electron microscopy techniques. However, these techniques are usually expensive and challenging to access, and often cannot operate at realistic fast-cycling rates.

Via a selection of case studies, this presentation will showcase the development and application of an alternative approach using 'charge photometry', a laboratory-based optical microscopy methodology, to examine lithium-ion dynamics and degradation processes in individual active particles, under operating conditions. This technique probes state-of-charge and morphology changes in the active particles, based on changes in the scattering intensity of visible light from the sample surface.[1]

Firstly, we image non-equilibrium lithium-ion gradients within particles of nickel manganese cobalt oxide (NMC) at near-full lithium-content, and we relate this kinetic limitation to first-cycle capacity losses.[2] We then compare fresh particles to those that have been aged over 200 cycles. We identify an increased asymmetry in the ion gradients in the aged particles, pointing towards heterogenous local ion-flux around the surface, which we attribute to the build-up of an uneven surface rocksalt layer.[3] Secondly, we examine high-rate niobium tungsten oxide (NWO) anode materials, and reveal the mechanism by which lithium-ion gradients lead to particle fracture during delithiation at rates of > 5C.[4] Finally, we employ a focus-stacking technique to capture the large volume changes in micron-sized silicon anodes, enabling quantification of single-particle expansion factors and analysis of particle fragmentation in realistic operating electrodes.

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Atomistic modelling for battery materials development

Jacob Gavartin

Schrödinger Technologies Ltd, U.K.

Despite rapid recent progress in the battery industry the challenges remain: affordable and safe batteries with higher power density, capacity, rate capability, faster charging and improved degradation resilience and recyclability are still in short supply. Given the complexity of the problems, an atomic level understanding of battery materials becomes essential for development of novel components; often inspiring and guiding experimental programs. To understand microscopic properties of novel cathode, anode, electrolyte and their interfaces the atomistic modelling tools must be accurate, effective, robust and easily operable. Atomistic modelling must also incorporate the multivariate nature of energy storage problems. Combining *in silico* materials screening with materials informatics and machine learning approaches leading to accurate descriptors reflecting properties of individual battery components as well as different aspects of their integration. In this presentation, we discuss the range of powerful computational approaches integrated in the Schrödinger Materials Science Suite. Capabilities include complex structure generation and analysis tools for calculation of ionic diffusivity, viscosity, loading, mechanical properties and electrochemical properties of Solid-Electrolyte Interfaces (SEI).

Bringing fast charging batteries to the market: the road to commercialisation for new anode materials

Rowena Brugge

Nyobolt

Founded in 2019, Nyobolt is a vertically integrated battery company bringing to market ultra-fast charging and high-power battery technologies. Nyobolt's long-life, high-power technologies provide a solution to critical unmet needs in applications ranging from industrial to automotive and off-highway. As well as providing customers with improved performance and operational benefits, Nyobolt's technology enables smaller, longer-lasting batteries. Nyobolt's proprietary niobium tungsten oxide (NWO) anode powder was developed and patented by the University of Cambridge in the UK (at Prof. Clare Grey's lab).

Session 5:

Measuring impedance under rheological shear conditions in slurries as a predictor for conductive networks in finished electrodes

Mark Phipps

TA Instrument / Waters

"Lithium-ion batteries (LIB) are manufactured through a multistep process combining various active and inactive materials. Material selection and processing conditions can greatly affect the final battery performance. In particular, electrodes are one of the most important components that influence battery performance. Electrode quality directly contributes to the overall battery's energy density and electrochemical performance. Electrodes typically include conductive additives such as carbon black particles to compensate for the poor conductivity of the active materials. The carbon black particles agglomerate around the active particles to form a percolation network to conduct electrons to the current collector. The conductive network structure is highly important to the final electrode performance, but shear-induced changes during coating can disrupt the electrically conductive network. Simultaneous rheology and electrochemical impedance spectroscopy directly measure shear-induced changes in the microstructure, replicating slurry coating conditions and enabling measurements of time-dependent recovery after shear. This measurement confirms that the electrically conductive network is maintained in the finished electrode, predicting successful electrode performance prior to full battery assembly.”

Towards new battery electrode materials through synthesis and structure control

Peter Slater
University of Birmingham

Research into Lithium ion battery materials has grown substantially over the last decade following their introduction into hybrid and all electric vehicles. This growth is forecast to increase as governments worldwide look to transition towards zero emission transport, as well as to introduce large scale stationary energy storage to complement renewable energy expansion. In this talk I will highlight educational resources describing how Li ion batteries work, and describe our recent research on the development of new materials, illustrating how both doping strategies and control of synthesis routes are important. In addition, I will outline some of the fundamental features, benefits and challenges with mechanochemical synthesis.

Solid State Ionic Modelling of Niobium Based Oxides for Battery Applications

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Mixed niobium based oxides are increasingly gaining research and commercial momentum as next generation battery materials. They generally present in the Wadsley-Roth (W-R) crystal structures consisting of a central block, with Nb in corner sharing sites and edge sites that adjoin neighbouring blocks. In particular, the transition of Nb (3+ ◊ 5+) oxidation states allow for high lithium intercalation. The niobium oxides can be partnered with other transition metals (TM) such as Vanadium (V), Phosphorous (P), Tungsten (W) and Titanium (Ti) among others, to avail a plethora of materials for exploration. Ranging in the size of block (3x3 ◊ 3x5 and mixed block systems) and varying oxidation states which result in increasing the ion storage capacity of these materials. Which makes them very attractive for battery applications.

In this talk, several W-R materials will be discussed. Where materials modelling techniques have been used to better understand the influence of the transition metal reducibility on structural, electronic as well as transport properties. The talk will include a review of the literature as well as our most recent work, on several mixed niobium oxides.

Our recent work suggests the expansion and contraction of the blocks influences the volume expansion as Li intercalates. The electronic structure calculations give insights on the reducibility of the transition metal cations while the dynamical simulations suggest favourable pathways and the influence of the TM on the transport properties.

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Modelling battery electrode manufacturing: coating, drying, and calendaring

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Calendering of porous battery electrodes has significant influences on the structural, electrical, and electrochemical properties, ultimately impacting the battery’s energy density, power density, cycle life, and safety. Fine-tuning calendering parameters is essential for optimising battery performance while maintaining cost-effectiveness in manufacturing. The discrete element method (DEM) is employed to study calendering of porous electrodes with different sizes and morphologies together with different compression rates. Using computational fluid dynamics (CFD), the key influential factors of the calendered electrodes, i.e. porosity, and permeability, tortuosity are calculated. These parameters are then used in electrochemical-thermal modelling of a lithium-ion battery under charge/discharge conditions. The preliminary results show that for a given active material particle size, increasing the calendering rate will reduce the porosity and permeability. However, the tortuosity will increase about. Based on electrochemical-thermal modelling of a 53 Ah lithium-ion pouch cell under 5C discharge rate, increasing tortuosity will lead into deterioration of electrochemical performance.

New Frontiers for Molecular Modelling: the Li-ion Battery from First Principles

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The performance of electrochemical devices such as batteries and fuel cells hinges on atomic-level processes that govern ion transport and the chemistry of electrode-electrolyte interfaces. Understanding these mechanisms from first principles could help establish the structure-function relationships underpinning battery operation and guide the design of improved materials and devices. However, the time and length scales on which these processes unfold are prohibitively expensive for ab initio methods. The emergence of Machine Learning interatomic potentials (MLIPs) in the past decade, has made it possible to significantly extend the scales of molecular dynamics (MD) simulations to thousands of atoms and hundreds of nanoseconds while maintaining the ab initio accuracy. In practice, however, training MLIPs can be a tedious task [1] plagued by many challenges: how to choose representative training data? what is the right model architecture? which hypermeters need tunning? etc. Recent advances in our MLIP understanding [2] have led to the development of Foundational ML (FML) models [3,4] which are trained on large datasets and show a great deal of out-of-the-box transferability across chemical systems and simulation conditions. Here we demonstrate the performance of MACE-MP-0 [3] (a foundational model trained on the Materials Project database [5]) in simulating a full Li-ion battery system: Cu | H-capped graphite+Li | EC/EMC+LiPF6 | NMC+Li. Previous work [1] has shown that modelling even the neat solvent can be a challenge to MLIPs owing to the weak, but crucially important, inter-molecular interactions. The out-of-the-box MACE-MP-0 (without any retraining) generates stable MD trajectories for the neat electrolyte, with both density and diffusivity reproducing the expected results. The full battery environment was simulated in the NVT ensemble to suppress issues arising from unphysical strains at the interfaces. All trajectories were stable at 500 K for the entire length of the simulation (100-200 ps). The Li-ions were found to spontaneously de-intercalate from both the graphite anode and NMC cathode and the entire electrolyte remained fluid. The H-capped graphite was found to be inert, whereas the cathode-electrolyte interface exhibited pronounced reactivity. Evident from the start of the simulation was the extensive proton transfer from the carbonate solvent (EMC in particular) to the oxygen atoms in NMC. This in turn led to continuous breakdown of solvent molecule (which became radicals), and chemisorption onto the cathode surface. Notably, substantial amounts of CO2 and H2O were generated in the process, and oxygen atoms were easily extracted from the cathode leaving behind binding sites for the oxygen-rich carbonate molecules. These early simulations demonstrate MACE-MP-0 robustness in modelling a complex battery environment comprising four different materials, four interfaces and nine distinct chemical species in a single simulation. These tests also showcase the initial steps in modelling the SEI formation with ab initio accuracy – which has been a long-held dream of the scientific community.

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Session 6:

The role of Na substitution on structural transformations in layered Na-ion battery cathode materials

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Layered transition-metal oxides, LiMO2 (M = Ni, Mn, Co and/or Al) have played a central role as cathodes in Li-ion batteries. The Na analogues of these materials, NaxMO2, are some of the leading candidates for high-capacity cathodes in Na-ion batteries. However, structural transitions involving shearing of the MO2 layers during electrochemical cycling critically impacts their electrochemical performance. The inclusion of substitutional elements such as Li and Cu into the MO2 layers has been shown to partially suppress structural transformations.1,2 The impact of Na substitution into the MO2 layers of Na-ion cathodes has, however, not been studied in detail. In this work, we demonstrate the transformative role that MO2 layer Na substitution plays on the electrochemical performance of novel layered Nax(M1-yNay)O2 materials.

In this work, we demonstrate how Te6+ substitution into the NaxNiO2 family of materials leads to changes in the local structure on electrochemical cycling. Using a combination of X-ray diffraction and solid-state nuclear magnetic resonance (NMR), it can be shown that Te6+ substitution facilitates the inclusion of Na-ions into the MO2 layer.3 The presence of MO2 layer Na ions results in favourable electrochemical properties due to the suppression of long-range Na-ordering. Paramagnetic NMR measurements show that while the long-range Na ordering is suppressed in the Na-Ni-Te-O system, there is significant local ordering of the Na sites in the MO2 layer, with a strong preference for the formation of nearest neighbour Na-Na motifs that are distinct from analogous Li compounds.

Complimentary density functional theory (DFT) calculations are used to understand energetics of local structural orderings and to assign the complex paramagnetic NMR spectra. An advanced DFT basin-hopping methodology is developed to probe the intricate relationship between structural transitions and Na-vacancy in different Na-Ni-Te-O polymorphs. The combined experimental and computational approach developed in this work is further extended to understand the changes the local structure during desodiation of the isostructural Na-Ni-Fe-Sb-O family of materials.4

The conclusions from this work provide novel guidelines for the design of high-performance layered Na-ion cathode materials and a deeper understanding of the crystal chemistry of Na substitution in layered transition metal oxides.

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Elucidating Dehydration of Prussian White cathodes: A Journey from Lab to Upscaled Sodium-ion Cell Prototypes

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Sodium-ion batteries (SIBs) are considered the next generation sustainable, low cost and efficient energy storage technology. Owing to their lower cost and higher sustainability compared to the current lithium-based technology, SIBs have the potential to dominate the future stationary energy storage market and the electrified transport sector with niche high power application. Great achievements in terms of materials development have been reported in the recent years as demonstrated by the interest of several companies in this battery technology. This presentation gives an overview on the journey toward the development of Prussian white containing 1Ah sodium-ion cell highlighting the importance of a comprehensive understanding of the material properties and their processability for a successful transition from lab scale to upscaled cell prototypes.

Identifying and preventing degradation in metal anodes

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An ideal battery anode concept is one where the active metal ions can be reduced and oxidised directly from the current collector. This metal anode offers the potential for excellent capacities, as it does away with the need for an intercalating host, however brings with it a host of problems, such as continued interphase formation and dendritic growth, which lead to capacity fade and cell failure. We have been working on identifying these failure modes, and characterising how we might mitigate against them, by apply operando electrochemical transmission electron microscopy (TEM) along with a host of supporting techniques. This allows us to directly identify how degradation occurs with Li, Na, Ca, and Zn metal anodes.