FM 5: Focus Session: Holistic structural and safety assessment of battery materials and cells

chairs: Carlos Ziebert (Karlsruhe Institute of Technology, DE), Philipp Finster (KIT, DE)

The focus session is dedicated to the characterization of microstructure, electrochemical, thermal and safety properties of Lithium-ion and Post-Lithium cells and their individual active and passive materials. This is required to obtain quantitative and reliable data, which are necessary to improve the current understanding in order to design and develop better and safer materials and cells. Potential topics include, but are not limited to electrochemical characterization techniques , thermal characterization techniques, safety testing, development of safer materials and cell designs, thermodynamic modelling of materials, modelling of thermal runaway and propagation.

Time: Monday 15:00–18:00 Location: BEY/0E40

FM 5.1 Mon 15:00 BEY/0E40

Hot-pressing enhances mechanical strength of PEO solid polymer electrolyte for all-solid-state sodium metal batteries

— •Lanqing Zhao[1,2], Huaping Zhao[1], Feng Liang[2], and Yong Lei[1] — [1]Institut für Physik & IMN MacroNano* (ZIK), Technische Universität Ilmenau, 98693, Ilmenau, Germany — [2]Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, 650093, Kunming, China

A PEO-based composite polymer electrolyte (CPE) was successfully prepared using an emerging solvent-free hot-pressing method, with Na3Zr2Si2PO12 (NZSP) and NaClO4 incorporated to improve ionic conductivity. Benefiting from its good mechanical strength and interfacial contact with the electrodes, the Na||Na3V2(PO4)3@C all-solid-state sodium metal battery (ASSSMB) delivers a high-capacity retention of 97.1% after 100 cycles at 0.5 C and 60 °C. Furthermore, the ASSSMB with an electrolyte thickness of approximately 20 μm also demonstrates excellent cycling stability. This study provides a promising strategy for designing stable polymer-ceramic composite electrolytes through hot-pressing to realize high-energy-density sodium metal batteries.

FM 5.2 Mon 15:15 BEY/0E40

Suppressing Li movement in solid-state electrolyte via Cryo EM Workflows: LLZO case study

— •yuqi liu[1], yuwei zhang[1], Jazmin Durate[1], Yug Joshi[1], and Baptiste Gault[2] — [1]Max Planck Institute for Sustainable Materials, 40237 Düsseldorf, Germany — [2]Univ Rouen Normandie, CNRS, INSA Rouen Normandie, Groupe de Physique des Matériaux, UMR 6634, F-76000 Rouen, France

Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) is widely used to examine solid-state battery materials and prepare site-specific samples for advanced techniques such as Electron Backscatter Diffraction (EBSD), Transmission Electron Microscopy (TEM), and Atom Probe Tomography (APT). However, the electron beam can induce irreversible damage particularly in lithium-containing systems by driving lithium displacement and expulsion, thereby compromising data reliability.

In this work, we investigate how cryogenic conditions mitigate beam-induced damage in LLZO, with an emphasis on lithium expulsion under varying beam parameters. We demonstrate that lithium mobility is significantly suppressed at cryogenic temperatures, leading to a marked reduction in beam-driven lithium redistribution. Based on a comprehensive set of cryogenically prepared EBSD and APT datasets, we show that cryo-enabled workflows are essential for obtaining structurally and chemically artefact-free characterization of LLZO and, more broadly, for reliable analysis of solid-state battery materials.

FM 5.3 Mon 15:30 BEY/0E40

Synthesizing the Solid-State Electrolyte LLZO via the Mixed-Oxide Route: The Li loss - Reality or Fiction?

— •Daniel Wagner, Torsten E.M. Staab, and Dominik Boras — LCTM/IFB, Julius-Maximilians Universität Würzburg, D-97070 Würzburg, Röntgenring 11

The solid-state electrolyte LLZO is discussed for applications in all solid-state batteries. Undoped and Fe-doped LLZO ($Li_7La_3Zr_2O_{12}$) samples have been synthesized via the mixed-oxide route, i.e. grinding of the educt's powders followed by calcination at 950°C for 6h and a second grinding before pressing into pellets and finally sintering them at 1200°C. The excess Li content and the restrictiveness for atmospheric gas exchange during the synthesis has been varied through usage of lidded crucibles. The samples were characterized by thermogravimetric analysis (TG), mass spectroscopy of its decomposition gas (TG/MS), X-Ray-diffraction (XRD) in reflection geometry and scanning electron microscopy (SEM).The formed phases (cubic and tetragonal) were identified by XRD. The phase fraction showed a clear influence of a varying lithium-excess and/or usage of a restricted gas exchange capability. Lattice defects were investigated by the method of positron annihilation lifetime spectroscopy (PALS). PALS showed clear differences after calcination and at different stages of sintering for both un-doped and Fe-doped samples. One option may be increasingly filled Li-lattice sites after the calcination step or a formation of amorphous Li containing phases. No traces of Li were found in the decomposition gases.

FM 5.4 Mon 15:45 BEY/0E40

Microstructure of Metal Anodes used in Solid-State Batteries and Strategies for Its Control

— •Till Fuchs — Center for Materials Research & Institute of Experimental Physics I, Justus-Liebig-University Giessen

The microstructure of materials fundamentally dictates their mechanical, electrochemical, and transport properties. Electron backscatter diffraction (EBSD) enables direct microscopic visualization of these microstructural features, providing quantitative insight into crystallographic orientation, grain morphology, and defect structures. This technique has become essential for understanding how processing pathways and operational conditions shape functional materials.

In a series of recent studies on lithium metal, we demonstrated how its microstructure can be visualized and conceptualized in detail, how it evolves depending on electrochemical cycling and charging conditions, and how it can be deliberately modified or controlled through the use of engineered interlayers. These findings highlight the interplay between microstructure and performance, and show how EBSD-guided analysis can inform strategies for guiding the growth morphology of alkali metal anodes during operation.

The principles established in lithium metal research are then extended to a broader class of energy materials, including nickel-rich layered oxides (NCM) and solid electrolytes. These systems exhibit their own characteristic microstructural challenges, from anisotropic degradation to cracking and dendrite formation in solid electrolytes.

FM 5.5 Mon 16:00 BEY/0E40

Decoding Complex Solid Electrolyte Architectures by an NMR Simulation Approach

— •Javier Valenzuela Reina[1], Vera Barysch[2,3], Simone Köcher[2,1], Josef Granwehr[2,3], and Christoph Scheurer[1,2] — [1]Fritz-Haber-Institute der MPG, Berlin — [2]IET-1, Forschungszentrum Jülich — [3]RWTH Aachen

Advancing next-generation lithium batteries requires a detailed understanding of hybrid electrolytes and the complex organic-ceramic interfaces they contain. Nuclear magnetic resonance (NMR) spectroscopy provides a non-destructive, highly sensitive probe of interfacial structure and ion transport, which however is challenging to interpret unambiguously.

In this work, we combine different NMR experiments with theoretical modeling and high-throughput density-functional theory (DFT) simulations to investigate the structural chemistry of Al-doped lithium lanthanum zirconium oxide (LLZO), a leading hybrid electrolyte candidate. By integrating ^{27}Al, ^{7}Li, and ^{1}H NMR measurements with first-principles calculations and simulated NMR parameters, we resolve key features of the Al-doping mechanism and elucidate both bulk and surface environments within the material.

Our results illustrate how a tightly coupled experimental-computational strategy can reveal interfacial behavior that is otherwise difficult to access, and highlight its promise for guiding the design and optimization of hybrid electrolytes with complex interfaces.

Coffee break

FM 5.6 Mon 16:30 BEY/0E40

The Inclusive Investigation of Defect Thermodynamics for Cl-Ion Battery Materials using Grand Canonical Diagrams — •Johannes Döhn[1] and Axel Gross[1,2] — [1]Institute of Theoretical Chemistry, Ulm University, Germany — [2]Helmholtz Institute Ulm, Germany

In our contribution we use the example of chloride perovskites to discuss the crucial role of defect thermodynamics for electrode and solid electrolyte materials in Cl-ion batteries. In this regard, the energetic relation between the pristine compound, the formation of defects and the conversion into other materials under varying electrochemical conditions is of great importance, though still underexplored.

Here, we suggest an analysis based on grand canonical approaches which is frequently applied using the concepts of ab initio thermodynamics or the computational hydrogen electrode. Grand canonical diagrams contain in a compact form information on the relative stability of the pristine and defective materials as well as potential decomposition products at varying potentials and loadings. Thus they can help to predict whether topotactic or conversion reactions are to be expected during chlorination/dechlorination. Furthermore, relevant properties as the open circuit voltage or the electrochemical stability window can be read off directly from the diagrams.

We demonstrate that this inclusive investigation of all relevant thermodynamic properties presented here enables a comprehensive and intuitive access to the eludication of materials properties which can hardly be gained otherwise.

FM 5.7 Mon 16:45 BEY/0E40

Polaron Calculations at Scale via a DFT-Based Landau-Pekar Model — •Daria Ustimchuk, Karsten Reuter, and Christian Carbogno — Fritz-Haber-Institut der MPG, Berlin

Polarons are of ubiquitous importance in material science, be it for charge retention in energy materials or as charge reservoirs in heterogeneous catalysis. While perturbation theory allows for an accurate and efficient assessment of isolated polarons in perfect crystals [1], addressing higher concentrations in complex, disordered compounds typically requires costly hybrid density-functional theory calculations in many, extended supercells. To facilitate such investigations, we here present several strategies to accelerate the required calculations. In line with Landau-Pekar schemes, we model the mechanisms underlying polaron formation at different levels of theory, e.g., using the harmonic approximation or machine-learning potentials for describing lattice distortions and Madelung or Born effective charges for electrostatic screening effects. We discuss the pros & cons of these techniques by carefully benchmarking their accuracy and reliability for polaron formation in MgO and BiVO$_4$. Furthermore, we apply them to lithium titanium oxide (LTO), a prototypical anode material hosting elevated polaron concentrations. We demonstrate how the proposed approaches allow to semi-quantitatively predict the relevant energetics and geometric distortions, and thereby substantially accelerate the exploration of the humongous phase space associated with polaron formation in disordered energy materials.

[1] W.H. Sio *et al.*, Phys. Rev. Lett. **122**, 246403 (2019).

FM 5.8 Mon 17:00 BEY/0E40

Grain-Boundary-Driven Activity Enabled by Grain Size Engineering in Iron-Air Batteries — •Adam Cohen Miles[1], Yujun Zhao[1], Yan Ma[1,2], Dierk Raabe[1], and Yug Joshi[1] — [1]Max Planck Institute for Sustainable Materials, Max Planck Str. 1, 40237 Düsseldorf — [2]Department of Materials Science & Engineering, Delft University of Technology, Mekelweg 2, Delft 2628 CD, the Netherlands

Iron-air batteries are gaining renewed attention as cost-effective candidates for long-duration energy storage. While research to date has focused on improving anode performance through surface area enhancement or chemical additives, the role of iron microstructure in dictating electrochemical behavior remains unexplored. Here, we systematically isolate and examine the effect of grain size on the electrochemical activity of high-purity iron anodes by eliminating confounding factors such as porosity, dopants, and additives. The results reveal a strong inverse correlation between grain size and electrochemical performance, with ultrafine-grained anodes exhibiting substantially higher current densities and diffusive contributions than coarser grained counterparts. This enhancement is attributed to the increased grain boundary density, which promotes charge transfer and mitigates surface passivation. These findings represent the first direct demonstration of grain-size-controlled electrochemical activity in iron-air systems and establish microstructural engineering as a powerful design lever for performance optimization.

FM 5.9 Mon 17:15 BEY/0E40

Bismuth telluride (Bi2Te3) incorporated on 3D-printed carbon electrode for rechargeable aqueous ammonium-ion battery — •Sunny Nandi[1] and Martin Pumera[2] — [1]NTC, University of West Bohemia in Pilsen, Pilsen, Czech Republic — [2]NTC, University of West Bohemia in Pilsen, Pilsen, Czech Republic

Lithium-ion batteries are leading the battery market but there are ever growing concerns over the sustainability of Li-based batteries due to paucity and escalating cost of Li-resources. Therefore, it become increasingly important to develop a low cost and easily processable novel energy storage technologies in the future. Hence, ammonium-ion battery based on aqueous electrolyte hold great potential owing to their low cost, high safety and excellent electrochemical characteristics. In an effort to develop such NH4+ ion based rechargeable electrochemical cells. Herein, for the first time, we report here the working of a rechargeable aqueous ammonium (NH4+) ion battery by integrating a topological insulator, bismuth telluride (Bi2Te3), onto a 3D printed nanocarbon electrode as anode and copper hexacyanoferrate (CuHCF) as the cathode. Taking advantage of the 3D porous framework and the non-metallic nature of NH4+ ions, the ammonium-ion cell delivers a high energy density of 134.8 Wh kg*1 and a power density of 1800 W kg-1 in 1 M (NH4)2SO4, outperforming previously reported studies. Furthermore, ex-situ characetrization clearly explain the plausible storage mechanism of NH4+ insertion. We show immense promise of the system by recycling and reusing the used 3D printed nanocarbon electrode for next-generation energy storage systems.

FM 5.10 Mon 17:30 BEY/0E40

Investigation of Degradation Mechanisms in High-Nickel NMC Cathodes for Lithium-Ion Batteries — •Yosra Dammak — Max Planck Institute for Sustainable Materials, Düsseldorf, Germany

High-nickel layered oxides like NMC955 are attractive cathode materials for lithium-ion batteries. However, their long-term use is often hindered by structural and mechanical degradation during cycling.

This study examined the influence of electrode microstructure and cycling parameters on the performance and degradation of NMC955 cathodes, comparing two average grain sizes: NMC-1.0 (1 micrometer) and NMC-0.5 (0.5 micrometer). The finer-grained NMC-0.5 consistently outperformed NMC-1.0, showing higher specific capacity, better capacity retention, and superior rate capability. Post-mortem analysis indicated that NMC-1.0 suffered from extensive intergranular cracking, while NMC-0.5 particles mostly remained intact. Microstructural analysis (SEM and EBSD) revealed that the coarser NMC-1.0 accumulated higher, heterogeneously distributed strain, especially at the grain boundaries, which promoted fracture. Conversely, the finer NMC-0.5 accommodated strain through more distributed deformation, facilitated by faster grain boundary diffusion. Both grain sizes maintained their layered structure as confirmed by XRD.

In summary, the enhanced electrochemical and microstructural stability of the finer-grained NMC-0.5 is attributed to its ability to manage strain more effectively, contrasting with the strain-induced cracking observed in the coarser NMC-1.0.

FM 5.11 Mon 17:45 BEY/0E40

Sodium Contamination Impact on Performance of Lithium-Ion Battery Cells — •Slaheddine Jabri[1], Krum Banov[2], Anita Röstek[3], Wibke Dempwolf[4], Olaf Rienitz[3], Petr Novák[2], Markus Etzkorn[1], and Uta Schlickum[1] — [1]Institute of Applied Physics Mendelsohnstraße 2, 38106 Braunschweig, Germany — [2]Institute of Energy and Process Systems Engineering, Langer Kamp 19b, 38106 Braunschweig, Germany — [3]Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany. — [4]Institut für Technische Chemie, Hagenring 30, 38106 Braunschweig, Germany

Sodium impurities can enter battery materials through several contamination sources, particularly when NaCl or NaOH are used in the recycling processes. Residual sodium is difficult to eliminate completely, and due to its high solubility, it easily dissolves into the electrolyte, where it may influence the cell performance. In this work, the electrochemical testing of high power NMC881-Graphite cells was studied using LP572 electrolyte containing sodium Na+ impurities with various concentrations. It was found that the discharge capacity decreased drastically and increase of impedance compared to Na+ free electrolyte. The Na+ ion sodium could intercalate between the Graphen layers like Li+ and due to its big ionic radius and higher charge density modify the C-C bonding and lattice parameters. The degradation effects could be found with 3 ppm Na level as impurity in electrolyte.