

## KFM 7: Materials for the Storage and Conversion of Energy (joint session MM/KFM)

## Lithium-based Materials

Time: Monday 17:15–18:30

Location: H22

KFM 7.1 Mon 17:15 H22

**Lithium diffusion pathways in modern solid state Li conductors** — ●MYKHAYLO MONCHAK<sup>1</sup>, VOLODYMYR BARAN<sup>2</sup>, STEFAN STRANGMÜLLER<sup>3</sup>, and ANATOLIY SENYSHYN<sup>3</sup> — <sup>1</sup>Institut für Angewandte Materialien, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany — <sup>2</sup>Deutsches Elektronen Synchrotron, 22607 Hamburg, Germany — <sup>3</sup>Heinz Maier-Leibnitz Zentrum, Technical University of Munich, 85748 Garching, Germany

The rapid development of energy storage demands cheaper, more robust electrode and electrolyte materials with improved electrochemical performance. Energy storage and conversion primarily rely on diffusion-based processes, making understanding diffusion pathways crucial. However, determining diffusion pathways in polycrystalline (non-cubic) materials is challenging using bulk or local measurements. Theoretical approaches like molecular dynamics simulations face numerous computational limitations. Alternatively, diffusion processes can be predicted from crystal structures using scattering density maps (electron for X-ray or neutron for neutrons). These maps analyzed via probability density functions or reconstructed through the maximum entropy method (MEM) are highly reliable. MEM is particularly effective for powder-averaged diffraction data, detecting weak structural disorders. This study applies high-resolution neutron powder diffraction and MEM analysis to explore state-of-the-art lithium conductors considered for application in all-solid-state Li-ion batteries, providing insights into their diffusion pathways and systematics.

KFM 7.2 Mon 17:30 H22

**"Effortless Embedding": Non-Parametric Solid-State Embedding for NMR Computations using All-Electron DFT** — ●FEDERICO CIVAIA<sup>1</sup>, SIMONE S. KÖCHER<sup>2,1</sup>, KARSTEN REUTER<sup>1</sup>, and CHRISTOPH SCHEURER<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin — <sup>2</sup>Institute of Energy Technologies (IET-1), Forschungszentrum Jülich GmbH, Jülich

Solid-state electrolytes are crucial in lithium-ion battery research, because of the pressing need for safe and durable high-energy storage solutions. Understanding Li-ion dynamics in these materials is essential for developing improved battery technologies. Owing to its non-destructive nature and sensitivity to atomic environments, solid-state nuclear magnetic resonance (SS-NMR) spectroscopy has become an invaluable tool for probing diverse Li-ion environments and investigating Li-ion mobility.

To facilitate the interpretation of experimental Li SS-NMR spectra, we are developing a method for computing NMR parameters of diamagnetic Li compounds using the linear-scaling, all-electron, density functional theory code FermiONS++ [1]. To allow the description of both crystalline and disordered materials, we employ a SS embedding method. In this regard, we present a consistent, non-parametric hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) methodology for systematic and reproducible structure generation and SS embedding calculations.

[1] J. Kussman *et al.*, J. Chem. Phys. **138**, 134114 (2013); J. Chem. Theory Comput. **11**, 918 (2015).

KFM 7.3 Mon 17:45 H22

**Insights into Li-ion battery cathode redox chemistry via charge transfer multiplet simulations of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$**  — ●RUIWEN XIE<sup>1</sup>, MAXIMILIAN MELLIN<sup>2</sup>, WOLFRAM JAEGERMANN<sup>2</sup>, JAN. P. HOFMANN<sup>2</sup>, and HONGBIN ZHANG<sup>1</sup> — <sup>1</sup>Theory of Magnetic Materials Group, Department of Materials and Geosciences, Technical University of Darmstadt — <sup>2</sup>Surface Science Laboratory, Department of Materials and Geosciences, Technical University of Darmstadt

The evolution of electronic structure during discharging and charging processes with Li intercalation and deintercalation in transition metal oxide cathode materials involves changes in oxidation states, non-rigid

band behavior, and oxygen's role in charge compensation, which significantly impact cathode performance. To gain deeper insights, we combine experimental x-ray photoelectron spectroscopy (XPS) at various voltages with many-body electronic structure simulations. The electronic structures of  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x\text{NiO}_2$  were calculated using Density Functional Theory and Dynamical Mean-Field Theory (DFT+DMFT). We found that Li intercalation and deintercalation shift the hybridization between Co/Ni *d* and O *p* orbitals relative to the Fermi energy, altering Co/Ni *d* occupancy. Based on this, we performed XPS calculations using the multiplet ligand-field model in Quanta to revisit the transition metal 2p satellite structure evolution. This study provides crucial insights into the interplay between electronic structure and Li intercalation dynamics for enhancing cathode performance.

KFM 7.4 Mon 18:00 H22

**Modelling LLZO Grain Boundaries with Amorphous Domains by Adaptively Trained Machine-Learning Interatomic Potentials** — ●YUANDONG WANG, YUTE CHAN, HAO WAN, KYEONGHYEON NAM, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin

Garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) is a highly promising solid state electrolyte (SSE) for lithium batteries. However, its practical application faces challenges, primarily arising from Li dendrite formation and the impact of grain boundaries (GBs) on Li transport and stability. Amorphous LLZO combines several desirable properties like blocking Li dendrite growth, high Li mobility and high electronic impedance. Controlling amorphous domains between crystalline grains could therefore offer an intriguing approach to tune electrolyte performance. For this, an atomistic understanding of the interplay between composition, structure and the properties of LLZO glass-ceramics is crucial.

This study introduces a Machine Learning Interatomic Potential (MLIP) tailored to accurately represent amorphous and GB structures in LLZO. Developed through an iterative training protocol using simulated annealing, this MLIP includes diverse structures in its training set, ensuring comprehensive modeling of complex LLZO phases. The MLIP enables large-scale molecular dynamics simulations, allowing the construction of realistic amorphous and GB models, and providing a foundation for in-depth analysis of LLZO structural and electrochemical behavior.

KFM 7.5 Mon 18:15 H22

**Early Stage of Li Cluster Nucleation at the Li Anode-Solid Electrolyte Interface in Solid-State Batteries** — ●YUN AN<sup>1,2</sup>, TAIPING HU<sup>2</sup>, QUANQUAN PANG<sup>2</sup>, and SHENZHEN XU<sup>2</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>School of Materials Science and Engineering, Peking University, Beijing, China

Li dendrite formation inside all-solid-state lithium batteries (ASSBs) strongly impedes their practical applications. Despite this recognized challenge, a comprehensive understanding of the Li dendrite nucleation mechanism remains elusive. In particular, the initial sites of Li dendrite formation are still ambiguous: do Li clusters form directly at the Li anode surface, or do they nucleate at a distance from the Li metal surface?

Here, based on deep-potential molecular dynamics simulations combined with enhanced sampling techniques, we investigate the atomic-level mechanism of Li cluster nucleation sites in ASSBs. We observe isolated Li clusters initially forming inside the solid electrolyte interphase (SEI), located approximately 1 nm away from the Li anode/SEI boundary, rather than directly connected to the Li anode. The local electronic structure of the spontaneously formed SEI is a key factor enabling the Li cluster formation within SEI. Our work provides atomic-level insights into initial Li-dendrite nucleation sites in ASSBs and could guide future design for developing Li-dendrite-inhibiting strategies.