

## MM 52: Materials for Energy Storage and Conversion - Ion Diffusion

Time: Thursday 10:15–11:30

Location: IFW D

MM 52.1 Thu 10:15 IFW D

**measurement of Li mobility in lithium iron phosphate by APT at different field strength** — ●AHMED ABDELKARIM<sup>1,2</sup>, PATRICK STENDER<sup>1</sup>, and GUIDO SCHMITZ<sup>1</sup> — <sup>1</sup>Institute for Materials Science, Department for Material Physics, Stuttgart University, Stuttgart, Germany — <sup>2</sup>Spectroscopy Department, Physics Division, National Research Center (NRC), Cairo, Egypt

Lithium is considered to be the cornerstone of the energy storage in batteries. However, even for well-studied lithium insertion compounds such as Lithium Iron Phosphate (LFP) it is profoundly unclear how the ionic transport appears on a microscopic, even on atomic level scale. Ionic transport is 3 dimensionally studied by Atom Probe Tomography (APT). New unique insights into the mechanisms of Li movements have been provided. Through self-created fine columnar pathways, Li is pulled and Li enrichment/depletion regions are observed. It is demonstrated that this in-situ Li motion is dependent on the field strength of the measurements. In response to the applied fields, Li ions are undoubtedly redistributed. By mathematically modelling, the Li diffusion process is evaluated. Li diffusion in amorphous LFP shows a faster diffusion than crystalline over the whole laser range and is calculated to be a factor of about 100 faster at laser power 30 mW.

MM 52.2 Thu 10:30 IFW D

**Atomistic analysis of migration properties of Li in  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) solid electrolytes** — DANIEL PFALZGRAF<sup>1,2</sup>, ●DANIEL MUTTER<sup>1</sup>, DANIEL F. URBAN<sup>1</sup>, and CHRISTIAN ELSÄSSER<sup>1,2</sup> — <sup>1</sup>Fraunhofer IWM, Freiburg, Germany — <sup>2</sup>University of Freiburg, Germany

LATP [ $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ] is considered as one of the most promising ceramic materials to replace hazardous liquid electrolytes in all-solid state Li-ion batteries. This is mainly because of a three-dimensional structural diffusion network enabling fast transport of Li ions through well-defined channels. It has been observed that an Al ratio of  $x = 0.3$  leads to the best performing compounds in terms of ionic conductivity. But a comprehensive understanding of this phenomenon is still missing. In this study, atomistic simulations based on density functional theory were performed to analyze the influence of Al substitution on Ti lattice sites on the migration behavior of Li. In LATP, the migration is dominated by a correlated mechanism involving three Li ions. In a systematic manner it is explored how different combinations of Al and Ti around the migration path change the energies of initial and final configurations as well as the energy barrier. "Al-like" and "Ti-like" behaviors can be identified, and the influence of the change of the LATP unit-cell volume with Al concentration is analyzed. We discuss the advancements and limitations of our approach in finding building blocks to describe quantitatively the Li migration in various arrangements of Al and Ti in LATP.

MM 52.3 Thu 10:45 IFW D

**Investigating diffusion of lithium intercalated in graphite by a combination of multiscale modeling and NMR** — ●CRISTINA GROSU<sup>1,2</sup>, SANDRA DÖPKING<sup>3</sup>, CHIARA PANOSSETTI<sup>2</sup>, SIMON ANNIES<sup>2</sup>, STEFFEN MERZ<sup>1</sup>, PETER JAKES<sup>1</sup>, SEBASTIAN MATERA<sup>3</sup>, JOSEF GRANWEHR<sup>1,4</sup>, and CHRISTOPH SCHEURER<sup>2</sup> — <sup>1</sup>IEK-9, FZJ Jülich — <sup>2</sup>Chair for Theoretical Chemistry, TU Munich — <sup>3</sup>Institute for Mathematics, FU Berlin — <sup>4</sup>ITMC, RWTH Aachen

Lithium ion batteries play a key role in the implementation of fully sustainable electrical mobility. Long lifetime, fast recharging and

safety are required for the acceptance of any battery powered vehicle. Graphite is still state of the art as negative electrode. Despite decades of investigation into the mechanism of lithium intercalation, the ion mobility and the underlying microscopic processes are still not fully understood, limiting progress in performance and lifetime prediction of a battery. In particular, improvements in fast charging of batteries mandates a deeper understanding of the lower states of charge (SoC), below or around 20%. We propose a combination of advanced NMR experiments, i.e spin alignment echo (SAE), with a theoretical multi scale modelling approach to investigate relevant phenomena such as lithium ion diffusion in graphite. Here, we present a novel multi-level accelerated first-principles kinetic Monte Carlo (1p-kMC) model to assess in detail the mobility at a low SoC, i.e  $\text{LiC}_{108}$ . In particular, an external potential is applied in order to mimic the driving force causing (dis)charge of the battery.

MM 52.4 Thu 11:00 IFW D

**Measurements of lithium-ion conductivity at the grain level** — ●PEIHUA HUANG, PATRICK UREDAT, JULIAN ZAHNOW, and MATTHIAS T. ELM — Center for Materials Research, Justus-Liebig-University Gießen, Germany, Heinrich-Buff-Ring 16, 35392 Gießen

Although lithium ion batteries (LIBs) have been commercialized since last century, there is still potential to improve the overall cell performance. One possibility for improvement is the optimization of the cathode of a LIB, where secondary particles of the active material are embedded in a conducting agent and binder material. The secondary particles themselves have a complex architecture consisting of primary particles in the nanoscale. As the microstructure has a strong influence on the transport properties, the characterization of the grain boundaries themselves is desirable. To study the transport across a grain boundary, thin layers of lithium cobalt oxide were deposited under various conditions by pulsed laser deposition. The films were subsequently annealed at various temperatures to facilitate grain growth to the micrometer range. Efforts on contacting single grain with micro-fabrication techniques have been made in order to study the lithium ion transport behavior at the grain level. For comparison, also the lithium ionic conductivity of the thin films has been measured.

MM 52.5 Thu 11:15 IFW D

**First-principles study of magnesium transport in spinel chalcogenides** — ●MOHSEN SOTOUDEH<sup>1</sup>, MANUEL DILLENZ<sup>1</sup>, and AXEL GROSS<sup>1,2</sup> — <sup>1</sup>Institute of Theoretical Chemistry, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm — <sup>2</sup>Helmholtz Institute Ulm (HIU) for Electrochemical Energy Storage, Helmholtzstraße 11, 89081 Ulm

The ionic conductivity of spinel host materials has been studied using first-principles electronic structure calculations. The band-gap underestimation in density-functional theory has been corrected using the Hubbard U correction to the GGA Hamiltonian. In particular, we studied the influence of the metal distribution in the spinel materials and the ion concentration on the diffusion process. We carefully analyze the electronic and geometrical factors that determine the ion mobility and find an interesting correlation between ion concentration, lattice constant and the energetic ordering of magnesium insertion into tetrahedral and octahedral sites. Furthermore, we provide a mechanistic picture of the processes underlying Mg insertion and diffusion.

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