

## SYLI 3: Sulphate- and phosphate-based electrolytes

Time: Monday 17:15–18:00

Location: IFW A

SYLI 3.1 Mon 17:15 IFW A

**Aliovalent substitution in garnet type solid-state electrolytes for solid-state lithium-ion batteries** — ●ANJA PAULUS<sup>1</sup>, MAIKE WIRTZ<sup>1</sup>, SABRINA HEUER<sup>1</sup>, PETER JAKES<sup>1</sup>, HANS KUNGL<sup>1</sup>, and RÜDIGER ALBERT EICHEL<sup>1,2</sup> — <sup>1</sup>Fundamental Electrochemistry (IEK-9), Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany — <sup>2</sup>Institut für Physikalische Chemie (IPC), RWTH Aachen University, D-52074 Aachen, Germany

Conventional lithium-ion batteries consist of an electrolyte containing toxic, flammable organic liquids which lead to several safety issues such as leakage and burning of the battery. In order to overcome these safety issues solid-state electrolytes could be an alternative to obtain powerful lithium-ion batteries. The garnet type electrolyte Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> shows promising properties in terms of high lithium-ion conductivity and a good stability against lithium. There are two modifications known for this material, on the one hand a tetragonal one which is thermodynamically stable at room temperature and on the other hand a cubic high temperature modification. The cubic structure shows a lithium conductivity of two orders of magnitude higher than the conductivity of the tetragonal one. One possibility to stabilize the cubic structure at room temperature or lower temperatures is by aliovalent substitution. Aluminum substitution on the lithium site shows a lithium conductivity of  $3.41 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  for Li<sub>6.4</sub>Al<sub>0.2</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> at room temperature [1]. Our focus is to study the influence of aliovalent substitution on the properties of garnet type solid-state electrolytes by various techniques. I.C.Tsai et al., J. Electroceram., 2015, 35, 25-32.

SYLI 3.2 Mon 17:30 IFW A

**Defect chemistry of solid electrolyte Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> by first-principles calculations** — ●MARCEL SADOWSKI, SABRINA SICOLO, and KARSTEN ALBE — Institute of Materials Science, Technische Universität Darmstadt, Jovanka-Bontschits-Str. 2, 64287 Darmstadt, Germany

Glassy, glass-ceramic and crystalline lithium thiophosphates have attracted interest as solid electrolytes for all-solid-state batteries. Despite similar structural motifs, these materials exhibit a wide range of compositions, structures and ionic conductivities. For the glass-ceramic consisting of crystalline Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> and glassy Li<sub>4</sub>P<sub>2</sub>S<sub>7</sub>, for example, contradictory ionic conductivities were reported. In this contribution we present density functional theory (DFT) calculations on the

defect thermodynamics and kinetics of crystalline Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub>. [1] Despite the existence of low energy diffusion paths, the overall conductivity is inhibited by high defect formation energies. This supports the hypothesis that the conductivity of the Li<sub>4</sub>P<sub>2</sub>S<sub>7</sub>/Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> composite material is determined by the relative amount of glassy and crystalline phases.

Furthermore, thermodynamics predict the instability of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> against metallic lithium. Corresponding interface models for different surface terminations of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> show the barrierless formation of an interphase reminiscent of Li<sub>2</sub>S, which might act as a passivating layer and protect the electrolyte from further decomposition.

[1] C. Dietrich, M. Sadowski, S. Sicolo, D. A. Weber, S. J. Sedlmaier, K. S. Weldert, S. Indris, K. Albe, J. Janek, W. G. Zeier, Chem. Mater. DOI:10.1021/acs.chemmater.6b04175 (2016).

SYLI 3.3 Mon 17:45 IFW A

**Systematic Search for Lithium Ion Conducting Compounds by Screening of Compositions Combined with Atomistic Simulation** — ●DANIEL MUTTER<sup>1,2</sup>, DANIEL URBAN<sup>2</sup>, and CHRISTIAN ELSÄSSER<sup>1,2</sup> — <sup>1</sup>Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg — <sup>2</sup>Fraunhofer Institut für Werkstoffmechanik (IWM), Wöhlerstraße 11, 79108 Freiburg

Solid state electrolytes (SSEs) with high Li conductivity can significantly improve Li ion accumulators in terms of electrochemical efficiency, thermal and mechanical stability, and environmental compatibility, leading to an enhanced range of applications for these high energy density batteries. Compounds crystallizing in the structure of NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NZP) are regarded as promising SSEs, mainly because of their three-dimensional diffusion network enabling fast transport of Li ions through well defined channels. Starting from LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, we analyzed a large variety of NZP compounds by systematically screening the relevant parts of the periodic table, replacing atoms on the Ti and P sublattices by isovalent elements. The influence of these elemental substitutions on structural stability, preferred Li sites, ionic mobility, migration paths and diffusion mechanisms were analyzed by means of a combined approach of multiple computational methods with different levels of accuracy, ranging from static energy landscape and molecular dynamics simulations with ionic bond valence potentials to density functional theory calculations combined with the nudged elastic band method.