

KFM 25: Materials for Storage and Conversion of Energy (joint session MM/KFM)

Time: Thursday 11:45–13:00

Location: C 264

KFM 25.1 Thu 11:45 C 264

Unraveling, with *ab initio* modeling, the connection between electronic structure and dynamical properties of the sodium bismuth titanate. — ●MARCIN KRYŃSKI — Warsaw University of Technology, Warsaw, Poland

Oxide ion solid electrolytes have drawn significant attention as they find applications in many electrochemical devices like oxygen sensors, oxygen pumps and solid oxide fuel cells [1]. Recently, ceramic compounds based on the perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) attracted major attention due to its high Curie temperature ($\sim 325^\circ\text{C}$), large remnant polarization ($38 \mu\text{C}\cdot\text{cm}^{-2}$) and exceptional fast oxygen-ion conduction. Interestingly, NBT shows high ionic conductivity only if the molar ratio between Na and Bi atoms is above unity. Below this value, a sudden drop of conductivity is observed. In this project we employ state of the art Density Functional Theory, using Strongly Constrained and Appropriately Normed functional (SCAN) together with Dudarev approach of on-site Coulombic interaction to model oxide ion dynamics of NBT electrolyte. For the first time, we correlate dynamical properties of mobile ions with the composition-dependent presence of small polarons. Furthermore, we look at the charge transfer during dynamical processes, change of the dipole moment as well as the bond strength. All this allows us to form a coherent picture of the diffusion processes being strongly correlated to the electronic structure of the NBT and how those two aspects of this compound are modulated by the composition. This work was supported by the National Science Centre, Poland under grant number UMO-2018/30/M/ST3/00743.

KFM 25.2 Thu 12:00 C 264

Exploration of Cathode-Stable Layered Solid-State Electrolytes — ●SINA ZIEGLER, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin

Promising higher safety and capacity, all-solid-state lithium batteries are envisioned to replace standard lithium-ion batteries in the near future. Lithium thiophosphates achieve the highest lithium-ion conductivities of all solid-state electrolytes (SSE) known to date, but their instability towards high-performance electrodes remains a critical challenge. To address this issue, we investigate the concept of rare-earth lithium halides as a material-efficient, nanometer thick cathode coating in contact with thiophosphate electrolytes. Halides provide wide electrochemical stability windows as well as good chemical and thermodynamic stability.

To determine a suitable halide/thiophosphate combination, we aim to identify an energetically feasible reaction pathway in the multidimensional phase diagram between the two materials. The corresponding stabilities of the emerging SSE/halide interfaces are examined by *ab initio* thermodynamics to screen reaction free enthalpies of possible interface reactions. Next, an end member analysis is performed to analyze possible compositions of interface products and possible secondary phases. Machine-learning interatomic potentials are trained on promising material combinations to validate the approach.

KFM 25.3 Thu 12:15 C 264

Understanding Anion-trapping in composite solid-state electrolytes with active ceramic fillers — ●MAURICIO BONILLA¹, HENRY CORTES¹, ERNESTO MARINERO², JAVIER CARRASCO^{3,4}, and ELENA AKHMATSKAYA^{1,4} — ¹BCAM - Basque Center for Applied Mathematics, Bilbao, Spain — ²School of Materials Engineering, Neil Armstrong Hall of Engineering, Purdue University, West Lafayette, IN, USA — ³Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Vitoria-Gasteiz, Spain — ⁴IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Developing high-performance solid-state electrolytes (SSEs) is a key step in the development of safe and efficient solid-state batteries. Composite SSEs (cSSEs) comprising active particles dispersed in an ion-

conducting polymer matrix constitute a promising strategy to obtain higher ionic conductivity (IC), and interfacial and mechanical stability than single-phase SSEs. Recent experiments showed that garnet particles enhance the IC of cSSEs and that this effect can be tuned through aliovalent doping. However, the underlying mechanism is not well understood. Here, we use an enhanced hybrid Monte Carlo technique and MD simulations to bridge this gap. By focusing on the cSSEs comprising Ga-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ particles in a polyethylene oxide (PEO) + $\text{LiC}_2\text{F}_6\text{NO}_4\text{S}_2$ (LiTFSI) matrix, we show how the dynamic electrostatic trapping of TFSI⁻ anions leads to IC enhancement by increasing the Li⁺ transference number. Moreover, we show that such enhancement can be modulated through the Ga dopant content.

KFM 25.4 Thu 12:30 C 264

Can Migrating Ions Block and Deactivate the Active Sites in Solid Oxide Cells? — ●PATRICIA KÖNIG, HANNA TÜRK, THOMAS GÖTSCH, FRANZ-PHILIPP SCHMIDT, AXEL KNOP-GERICKE, ROBERT SCHLÖGL, THOMAS LUNKENBEIN, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin

Degradation of the air electrode in electrolysis mode during the oxygen evolution reaction severely limits the commercial adoption of solid oxide cells. Up to now, the atomistic structure of this active catalyst region is essentially unknown, which prevents a detailed analysis of the actual degradation mechanisms.

In prior research, we identified a complex ion at the solid/solid interface of the sintered anode [1], featuring partial amorphization and varying elemental distributions deviating from the confining bulk phases. Located around the complex ion area, we propose deactivation mechanisms driven by strong cation inter-diffusion. To assess if these cation migrations impede active sites and cell functionality, we conduct a large-scale study on possible active site structural motifs. We sample structures with polarons near oxygen defects, altering ion dopant concentrations to simulate ion migration effects. By employing density-functional theory to compute EELS spectra, we link oxygen defects and their proximity to polarons to distinctive peaks in experimentally recorded EELS spectra. Ultimately, this approach aids in identifying active site structures and deactivation mechanisms, enhancing future cell design with improved efficiency and durability.

[1] H. Tuerk *et al.*, Adv. Mater. Interfaces **8**, 2100967 (2021).

KFM 25.5 Thu 12:45 C 264

Anharmonic Lattice Dynamics of Solid-State Ion Conductors from Machine-Learning Molecular Dynamics — ●TAKERU MIYAGAWA, MANUEL GRUMET, NAMITA KRISHNAN, WALDEMAR KAISER, and DAVID A. EGGER — Physics Department, TUM School of Natural Sciences, Technical University of Munich, Germany

Solid-state ionic conductors (SSICs) are playing an important role in electrification of transport and energy industries. Recent studies suggested that the host lattice dynamics play a critical role in the ionic conduction mechanisms [1]. Several SSICs exhibit anharmonic lattice vibrations taking mobile ions into anharmonic regions of their potential energy surface [2, 3]. Here, we investigate the role of anharmonic host lattice vibrations and their impact on the conduction of mobile cations in SSICs by using machine-learning molecular dynamics (MLMD). Particularly, we focus on different classes of superionic conductors that all exhibit anharmonicities: AgI, a strongly disordered Ag-conductor [2]; Na_3PS_4 , a Na vacancy conductor [3]; and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, showing concerted Li migration [4]. Our results demonstrate the potential of MLMDs in understanding coupled host lattice-mobile ion dynamics and show guidelines for the design of novel SSICs with higher ionic conductivities.

[1] Zhang; Nazar Nat. Rev. Mater. **7**, 389-405 (2022). [2] Brenner *et al.* Phys. Rev. Mater. **4**, 115402 (2020). [3] Brenner *et al.* J. Phys. Chem. Lett. **13**, 25, 5938-5945 (2022). [4] Fang; Jena, Nat. Comm. **13**, 2078 (2022)