Modeling Lattice-Driven Li-Ion Migration in Garnet Electrolytes

Jose María Castillo Robles[1]*, Manuel Dillenz[1], Juan Maria García Lastra[1], Ivano E. Castelli[1]
1 Department of Energy Conversion and Storage, Technical University of Denmark
**Email:jmcro@dtu.dk*

Ion transport in solids is commonly described as an activated hopping process, $k = \nu_0 \exp(-\Delta G^{\ddagger}/k_B T)$, where the attempt frequency ν_0 derives from the vibrational partition functions of the equilibrium and transition states. Lattice vibrations are therefore already embedded in the standard picture of ionic conduction, yet which modes actually govern migration remains unresolved. Only in a small class of conductors do the mobile ions possess distinct "ion-only" low-frequency modes; in most technologically relevant electrolytes they instead participate in vibrations of larger structural sub-units, and ion migration is supported by the projection of the vibrational displacement onto the hopping coordinate. Whether barrier crossing is dominated by a few local hopping modes or by the collective contribution of many, and what makes a mode transport-relevant in the first place, remains an open question.

To address this, we develop a fine-tuned MACE-OMAT machine learning interatomic potential for Ta-doped and Al-doped $Li_7La_3Zr_2O_{12}$ (LLZO) which enables both nanosecond-scale molecular dynamics and dense phonon sampling of a 188-atom supercell tractable for a garnet of this size. With this potential we first map Li migration barriers and minimum-energy pathways by nudged elastic band (NEB), and then project the LLZO phonon eigenvectors onto the mass-weighted atomic displacements between each successive pair of NEB images along multiple distinct hopping pathways. This image-by-image decomposition resolves which vibrational coordinates actually carry the hop: the dominant contributions concentrate in a well-defined low-frequency window, and the hop proceeds through the concerted displacement of several Li ions, pointing to a collective rather than single-ion mechanism. Since migration is intrinsically large-amplitude motion, we then quantify how far these transport-relevant modes depart from harmonic behaviour, combining mode-resolved Grüneisen parameters with the anharmonicity measure $\sigma_A(T)$ extracted from MACE-driven molecular dynamics.

To validate these computational insights, we compared our predictions against IR-pump experiments, which confirmed that selectively driving the IR-active modes identified through our NEB projections measurably influences Li-ion transport — establishing their direct involvement in the migration process. Ultimately, this combined simulation and spectroscopy approach provides a microscopic, mode-resolved picture of ion migration in LLZO and opens a path toward the spectroscopic control and rational design of next-generation solid electrolytes.