Active Learning Interatomic Potentials-Enhanced Molecular Dynamics for Grain Boundary Engineering in Antiperovskite Solid Electrolytes

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1. Introduction

Lithium-rich antiperovskite solid electrolytes, particularly mixed-halide systems such as $Li_3OCl_xBr_{1-x}$, are promising candidates for all-solid-state lithium batteries due to their high intrinsic ionic conductivity and favourable electrochemical stability. [1] However, in practical polycrystalline electrolytes, grain boundary resistance often dominates overall lithium transport, severely limiting device performance.

Experimental and computational studies have suggested that grain boundaries in $Li_3OCl_xBr_{1-x}$ exhibit strong structural and compositional sensitivity, yet a mechanistic understanding of how grain boundary morphology and chemistry jointly regulate lithium transport remains elusive. In particular, bromine-rich compositions tend to form structurally disordered or amorphous grain boundaries, while chlorine-rich systems display improved transport and mechanical properties. Capturing these effects at the atomic scale is challenging due to the large configurational complexity, including mixed halide compositions, amorphous regions, and point defects, which are difficult to treat using conventional density functional theory (DFT) alone.

Here, we address this challenge by developing an AI-driven atomistic modelling framework that enables large-scale, dynamic simulations of grain boundaries in $Li_3OCl_xBr_{1-x}$ electrolytes. By combining active-learning-based machine learning interatomic potentials with diverse structural sampling, we systematically investigate how grain boundary morphology and composition control lithium transport and mechanical stability. This approach establishes a general strategy for grain boundary engineering in complex solid electrolytes.

2. Substantial section

2.1 Machine-Learning Interatomic Potential with Comprehensive Structural Diversity

To accurately capture the complex atomic environments, present in $Li_3OCl_xBr_{1-x}$ electrolytes, we developed a machine learning interatomic potential based on the MACE framework, trained via an active learning strategy. As shown in Figure 1, the training dataset encompasses a wide range of representative structures, including:

(1) Bulk crystalline phases with varied Cl/Br ratios
(2) Amorphous structures generated via melt–quench protocols
(3) Grain boundary models with distinct morphologies
(4) Point defects, including Schottky defects, Frenkel pairs, and anion swaps

This diverse dataset ensures robust coverage of the relevant configurational space encountered during grain boundary formation and lithium transport.

The resulting MLIP achieves high quantitative accuracy, with root-mean-square errors of 1.43 meV atom^{-1} in energy and 20.37 meV Å^{-1} in forces, closely reproducing DFT reference calculations. Importantly, active learning progressively improves sampling coverage, enabling reliable extrapolation to previously unseen defected and amorphous environments.

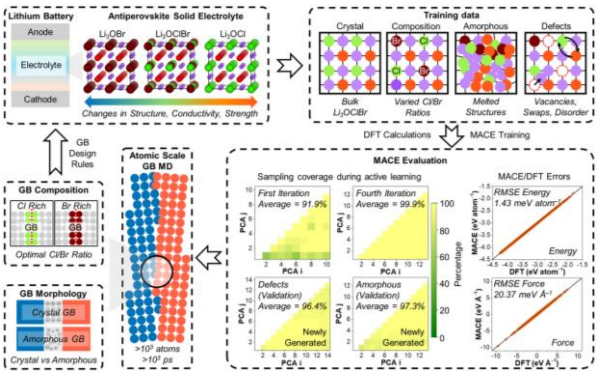

Fig. 1: Workflow for active learning interatomic potentials-enhanced molecular dynamics for grain boundary engineering in antiperovskite solid electrolytes.

2.2 Large-Scale Molecular Dynamics of Grain Boundary Transport

Using the trained MLIP, we performed large-scale molecular dynamics simulations on grain boundary models containing more than 10^3 atoms over nanosecond timescales. These

simulations allow direct observation of lithium diffusion pathways, grain boundary structural evolution, and compositional segregation effects under realistic conditions.

Our simulations reveal a striking contrast between bromine-rich and chlorine-rich grain boundaries. In Li_3OBr, grain boundaries undergo pronounced amorphization, accompanied by severe disruption of lithium diffusion networks. This structural collapse results in dramatically reduced lithium mobility and weakened mechanical stability at the interface.

In contrast, increasing chlorine content at grain boundaries progressively restores crystallinity, even in interfacial regions. Li_3OCl-rich grain boundaries maintain ordered atomic arrangements, suppress amorphous phase formation, and exhibit significantly enhanced lithium-ion conductivity. These improvements are accompanied by increased mechanical robustness, highlighting the dual functional role of chlorine enrichment.

2.3 Compositional Control as a Grain Boundary Design Strategy

To isolate the role of grain boundary chemistry, we systematically substituted chlorine for bromine at Li_3OBr grain boundaries while keeping the bulk composition fixed. Remarkably, this targeted substitution reproduces the favorable structural and transport characteristics observed in chlorine-rich systems, confirming that grain boundary composition alone can dictate interfacial behavior.

These results establish a clear and generalizable design principle: promoting chlorine enrichment at grain boundaries in mixed-halide lithium-rich antiperovskite electrolytes simultaneously enhances lithium transport and mechanical integrity, without requiring bulk compositional changes.

2.4 Implications for Solid-State Battery Design

By integrating AI-driven interatomic potentials, large-scale molecular dynamics, and systematic compositional control, this work provides an atomistic foundation for grain boundary engineering in solid electrolytes. Beyond $Li_3OCl_xBr_{1-x}$ systems, the presented framework is broadly applicable to other complex solid-state ionic conductors where interfacial phenomena dominate performance.

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