Predicting Crystal Structures and Ionic Conductivities in $Li_3YCl_{6-x}Br_x$ Halide Solid Electrolytes Using a Fine-Tuned Machine Learning Interatomic Potential

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Understanding lithium-ion transport in solid electrolytes is crucial for the rational design of all-solid-state batteries. Among emerging candidates, the $Li_3YCl_{6-x}Br_x$ family of ternary halides offers a unique combination of electrochemical stability, mechanical robustness, and compositionally tunable ionic conductivity [1–4]. However, establishing microscopic composition-structure-transport relationships remains challenging due to the vast compositional space, structural complexity, and the high computational cost of *ab initio* molecular dynamics (AIMD).

Here [5], we investigate lithium-ion transport across the $Li_3YCl_{6-x}Br_x$ compositional range ($0 < x < 6$) using a fine-tuned machine learning interatomic potential (MLIP) based on the Crystal Hamiltonian Graph Neural Network (CHGNet) [6] (**Figure 1**). Starting from experimentally refined disordered structures of Li_3YCl_6 and Li_3YBr_6 [2], we generate symmetry-inequivalent ordered configurations via substitution and enumeration, followed by MLIP-based structure optimization and energy ranking. An iterative workflow, combining molecular dynamics (MD) simulations and targeted density functional theory (DFT) calculations, systematically improves the model, particularly for strained and out-of-equilibrium configurations relevant to ion migration.

Benchmarking demonstrates significant improvements in energy, force, and stress predictions compared to the pretrained CHGNet. The fine-tuned model enables stable *NpT* MD simulations up to 800 K, producing equilibrated volumes consistent with SEvEnNet [7] and AIMD. Two-nanosecond *NVT* MD simulations in the *NpT*-equilibrated cells yield statistically converged diffusion coefficients across the $Li_3YCl_{6-x}Br_x$ compositions.

The simulations reproduce key experimental trends [1–4]: anisotropic lithium diffusion in Li_3YCl_6, due to face-sharing octahedral sites; isotropic diffusion in Li_3YBr_6; and composition-dependent phase stability, including the trigonal-to-monoclinic structural transition [3]. Additionally, we show that for bromide-rich monoclinic $Li_3YCl_{6-x}Br_x$ ($x \geq 3$), Br → Cl substitution systematically increases ionic conductivity, providing insights into structure-transport relationships.

Our results establish a computationally efficient framework for modeling lithium transport in halide solid electrolytes through targeted MLIP fine-tuning, achieving near-*ab initio* accuracy at four orders of magnitude lower cost - accelerating the discovery of next-generation solid electrolytes.

References

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Figures

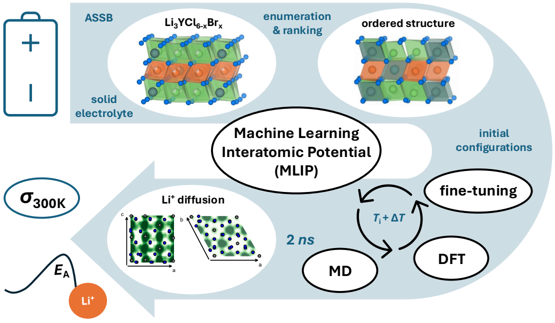

Figure 1. Overview of the general idea and workflow using Li_3YCl_6 structural models as an example.