Machine Learning Aided Atomistic Modeling of Solid State Electrolyte Interphase Formation for $Li/Li_7P_3S_{11}$

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1. Introduction

All-solid-state batteries (SSBs) with lithium (Li) metal anodes are promising candidates for high-capacity, rechargeable energy storage systems due to their improved volumetric and gravimetric energy densities [1, 2, 3, 4, 5] and reduced safety risks compared to conventional Li-ion batteries [6, 7]. However, the performance and capacity of SSBs are limited by the solid electrolyte (SSE)-anode interface, which generates products that hinder ionic transport [8, 9, 10]. This limitation emphasizes the need for modeling the initial stages of solid-state reactivity at this interface to enhance our understanding and improve performance. While first-principles methods, such as density functional theory (DFT) [11, 12], provide accurate predictions of thermodynamic properties, reactivity, and electronic structure, they are constrained by high computational costs that scale unfavorably with system size [13]. In this work, we present a computational framework that uses machine learning interatomic potentials (ML-IAPs) and active learning to systematically generate an interfacial reactivity dataset, enabling extended spatial and temporal atomistic descriptions beyond traditional DFT methods.

2. Machine Learning for Chemistry

Current state-of-the-art ML-IAPs encounter challenges in molecular dynamics (MD), including instabilities such as void formation and phase separation. Although increasing dataset size has been a common strategy to enhance sampling along the potential energy landscape (PES), it often results in longer training times and decreased efficiency [14]. This work addresses the challenges of using machine learning interatomic potentials (ML-IAPs) for reactive chemical systems by generating datasets specifically for binary reactions and incorporating active learning techniques inherent to the model architecture [15, 16, 17]. By identifying undersampled regions of the PES and employing active learning sampling strategies, we curate a refined dataset that is recalculated using DFT for quantum-mechanical accuracy [11, 12]. This iterative active learning process captures configurations relevant to chemical reactions while minimizing the time and data required for accurate predictions of thermodynamic and kinetic properties. We also introduce validation metrics to assess the model's ability to access states beyond equilibrium, comparing them to DFT benchmarks. Once finalized, the ML-IAP can be applied to ML-MD simulations, maintaining DFT-level chemical accuracy while effectively mapping transport properties, transition states, phase transformations, and interphase morphology.

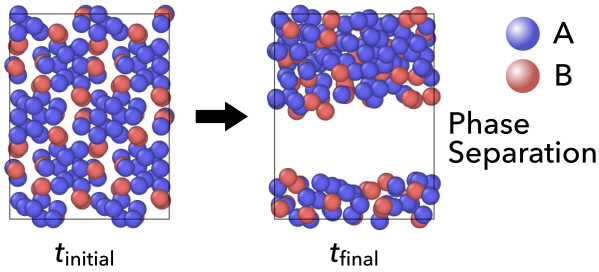

Fig. 1: ML-MD simulation demonstrating unphysical phase separation in a crystalline structure over time. The instability of ML-IAPs can manifest as improper phase separation, void formation, and ballistic atomic mobility, highlighting the need for improved ML-IAPs through enhanced training on high-quality data. Such improvements are essential for achieving more accurate atomic interactions and reliable predictions of material behavior.

3. Our Approach

We develop a machine learning framework designed to understand the atomic-level mechanisms driving surface reactivity and influencing material performance in Li metal batteries, specifically focusing on the $Li/Li_7P_3S_{11}$ system. Recognizing the significant impact of training data on the performance of ML-IAPs [14], we implement high-throughput dataset generation using active learning sampling strategies tailored for Li-P-S reactivity, supported by the computational infrastructure of the Materials Project [18]. This approach incorporates both crystalline and noncrystalline structures, ensuring comprehensive dataset coverage and avoiding configurations that fall outside the training dataset. The resulting dataset, comprising static and dynamic DFT data, characterizes the initial states of the solid-state interface, including both equilibrium and non-

equilibrium conditions. The ML-IAP-based atomic cluster expansion (ACE) method extends solid-state reaction simulations and scales linearly with system size. We employ active learning within the ACE framework to identify essential structures and train ACE potentials on local site-specific multibody interactions, facilitating efficient learning of the relevant chemical space. Additionally, fine-tuned universal interatomic potentials are tested and found to be viable substitutes, underscoring their potential for generalization across various ML-based chemical reactivity applications.

4. Our Findings

Our results indicate that the reaction between Li and $Li_7P_3S_{11}$ leads to the formation of a heterogeneous, amorphous interphase with a layered morphology, characterized by alternating regions of higher concentrations of phases such as Li_2S and Li_xP. These experimentally identified phases reduce ionic transport efficiency across the battery system. The ML-aided simulations facilitate spatially resolved modeling to identify the layering, crystallinity, and morphology of these phases, which can now be validated with available *in-situ* X-ray photoelectron spectroscopy (XPS) observations [19, 20]. Our model aligns well with other ML-IAP models for similar systems while also predicting stable amorphous and non-equilibrium structures, diverging from the crystallization behavior observed in other models [21, 22]. The implementation of the ML-IAP model enables us to predict ionic transport properties, which typically require extended timescale MD simulations, particularly for correlated ionic mobility. Through ML-MD, we can obtain correlated ionic fluxes in both crystalline and amorphous phases and derive transport properties such as the Onsager transport coefficients. Our findings suggest that the correlated mobility of P ions between Li and S ions creates effective 'kinetic traps' for P ions, leading to the kinetic passivation of the solid-state interface (SSI). This insight enhances our understanding of the atomistic mechanisms underlying the formation of passivating interphases in the $Li/Li_7P_3S_{11}$ system. Finally, ML-aided MD extends the spatio-temporal regimes that can be simulated. We find that the interplay of thermodynamics and kinetics influences the morphology of the interface, driven by correlated ionic motion through the amorphous and crystalline interphase domains. Our results indicate that interphase formation occurs in two stages: a fast diffusion regime followed by a slow diffusion regime, during which nanocrystallization and bulk distortion take place. Our ML-driven framework for simulating and modeling SSI formation provides a foundation for extending first-principles-informed chemical reactivity simulations to more complex phenomena and experimental conditions, facilitating a detailed atomic description of elusive underlying mechanistic behavior.

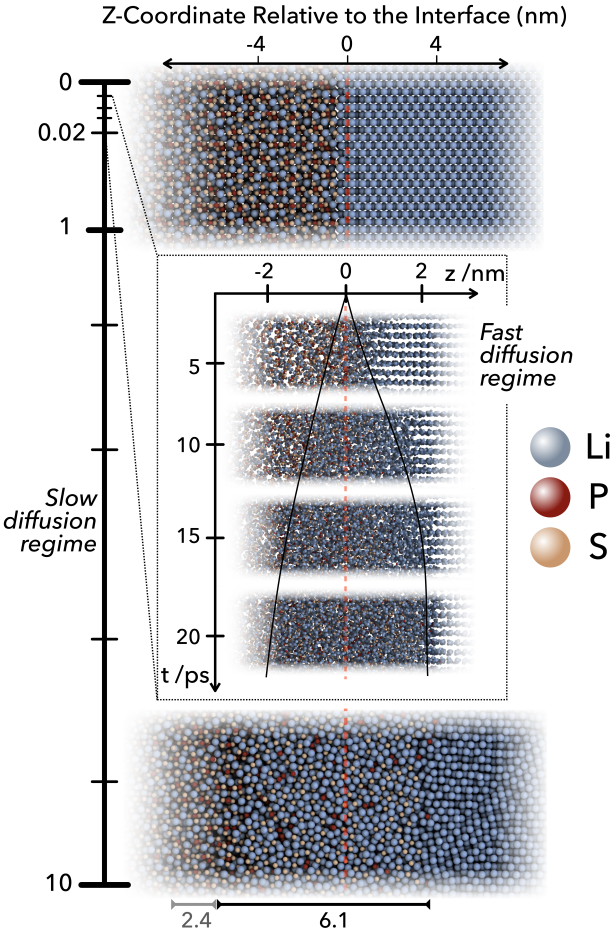

Fig. 2: NpT simulation of the (100)/(100) $Li/Li_7P_3S_{11}$ interface over 10 ns using ML molecular dynamics with the final generation of fitted ML-IAPs. The snapshots showcase the evolution of the simulation at specific timestamps. The fast diffusion regime, observed within the first 20 ps, indicates the initial formation of the interphase and its growth across the original interface boundary. In contrast, the slow diffusion regime reflects the stabilization of the interphase region, characterized by periodic atomic movement, extending up to 10 ns.

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Appendix A. Generalized Workflow for Interfacial Reactivity Datasets

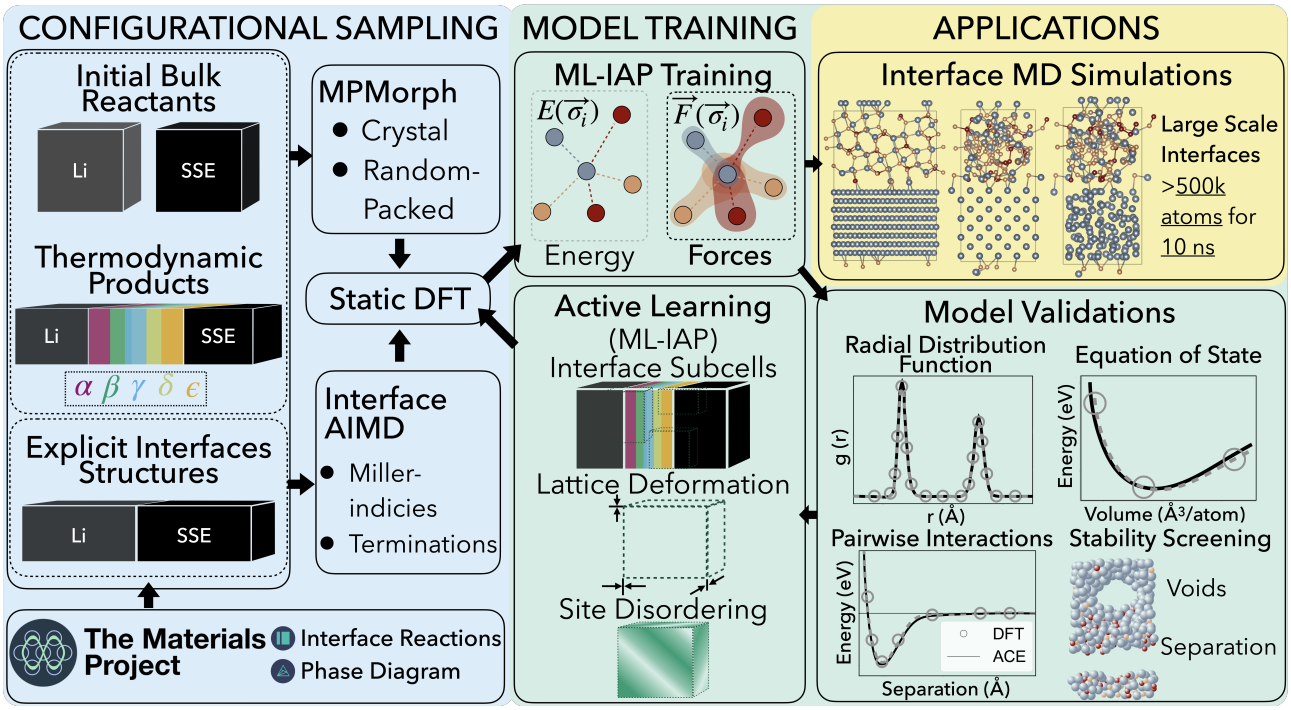

Fig. A1: Illustration of the modeling framework which includes 1) initial configurational sampling: user-specified samples of equilibrium and non-equilibrium structural configurations based off of the reactant compositional space and thermodynamically predict phase presence, 2) model training: iterative ML-IAP training with an active learning schema and validation from RDFs, EOS, pairwise interactions and stability screening, 3) applications: direct simulations of interfacial structures in ML-molecular dynamics at extended length and timescales.