

PROCEEDINGS

Lithiation-Dependent Solid Electrolyte Interphase Nucleation Pathways in Si/Li₆PS₅Cl Interfaces Uncovered by Machine Learning-Accelerated Simulations

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ABSTRACT

Solid electrolyte interphase (SEI) formation mechanisms in silicon-anode all-solid-state batteries (ASSBs) remain the critical unresolved bottleneck for commercialization, hindered by experimental inaccessibility and fundamental limitations in simulating complex reactive interfaces across electrochemical conditions. We bridge this gap using a machine learning force field (MLFF) with sub-100 meV Å⁻¹ accuracy, enabling large-scale, quantum-fidelity simulation of the full reactive interface. This comprehensive model (3072 atoms, 5 elements, 2000 ps) simultaneously captures the coupled dynamics of silicon lithiation, electrolyte decomposition, and SEI formation. The results reveal that SEI nucleation initiates predominantly at the highly lithiated stage, driven by chemo-mechanical strain-induced dissociation of thiophosphate units (<50 ps). The self-assembled SEI evolves into a compositionally graded bilayer: a Li⁺-deficient Li₂S/LiCl-rich electrolyte-adjacent matrix and a Li⁺-abundant Li₂S/Li₃P-dominated anode-proximal zone, delivering exceptional ionic conductivity (27.2 mS cm⁻¹) via Li₂S percolation highways. However, this structure exhibits mechanical vulnerability (8.11 GPa modulus) and defect-mediated electronic leakage. Finally, we establish lithiation-state control and interface engineering as dual design principles to overcome SEI-driven failure. This work provides an atomic-resolution framework for rationally designing degradation-resistant ASSBs, fundamentally accelerating the transition from empirical optimization to knowledge-driven battery engineering.

KEYWORDS

Machine learning force field (MLFF); solid electrolyte interface (SEI); silicon anode; Li₆PS₅Cl; all-solid-state battery (ASSB)

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