

Atomistic interaction at the interface between $\text{Li}_6\text{PS}_5\text{Cl}$ and Li metal in solid state batteries

Namrata Jaykhedkar¹, Janine George^{1,2}

¹Bundesanstalt für Materialforschung und -prüfung (BAM),
Unter den Eichen 87, Berlin, Germany

²Friedrich-Schiller-Universität Jena,
Max-Wien-Platz 1, Jena, Germany
namrata.jaykhedkar@bam.de

Abstract

The solid electrolyte interphase (SEI) is a heterogeneous, multilayered structure that forms at the electrode-electrolyte interface as a result of electrolyte reduction during the initial charge-discharge cycles. Owing to the intrinsic limitations of liquid-electrolyte-derived SEIs, which are chemically fragile and thermodynamically unstable, they often contribute to continuous electrolyte consumption, leakage, and thermal runaway, posing fundamental challenges to the safety and long-term reliability of conventional Li ion batteries [1]. Solid state batteries have emerged as promising next-generation energy-storage solution offering higher energy density and enhanced safety. However, poor interfacial compatibility at the solid electrolyte (SE)|electrode interface, particularly with lithium metal anodes, remains a critical bottleneck for their practical implementation [2]. To gain atomistic insight into the structural and chemical factors governing interfacial formation and stability, we select $\text{Li}_6\text{PS}_5\text{Cl}$ as a representative solid electrolyte and lithium metal as a model anode system. In the current work, we first perform machine learning (ML) accelerated molecular dynamics (MD) in VASP [3] to determine the lattice parameters and bulk moduli of $\text{Li}_6\text{PS}_5\text{Cl}$ and Li metal. This enables a quantitative assessment of lattice-mismatch-induced strain, compressibility differences, and their thermal evolution. Building on this foundation, we systematically investigate the interaction between Li and $\text{Li}_6\text{PS}_5\text{Cl}$ by progressively increasing interfacial complexity - from single Li atom adsorption on $\text{Li}_6\text{PS}_5\text{Cl}$ slab, to small clusters, and finally to layer-by-layer construction of the $\text{Li}_6\text{PS}_5\text{Cl}$ | Li interface with varying coordination environments. Extensive training of machine-learning interatomic potentials (MLPs) for the surface and interface models were first performed using reference data generated from density functional theory (DFT) calculations in VASP. The resulting datasets were used to construct and fine-tune ML models within the MACE framework [4]. MD simulations were subsequently carried out using both VASP and ASE-driven MLP-based MD, enabling a direct comparison between ab initio and ML-accelerated descriptions of the system. Adsorption energies are computed to quantify the thermodynamic driving forces governing interfacial bonding. In parallel, radial distribution functions at the interface are compared with those of the respective bulk phases to elucidate temperature-induced structural rearrangements. Dominant

bonding motifs are identified using Crystal Orbital Hamilton Population [5] analysis via *LOBSTER* [6]. This combined analysis reveals how interfacial bonding evolves with temperature and provides critical insight into chemical and mechanical stability at the interface. Our findings offer a quantitative framework for correlating bulk properties with interfacial structure, thereby informing the design of more robust SEs and engineering strategies to improve interfacial compatibility. Further, current challenges and future prospects will be briefly discussed.

References

- [1] C. Lin et al., *Process Saf. and Environ. Prot.* 189, 2024, 577-586.
- [2] A. C. Radjendirane et al., *Langmuir* 40 (32), 2024, 16690-16712.
- [3] R. Jinnouchi et al. *Phys. Rev. Lett.* 122, 2019, 225701; R. Jinnouchi et al. *J. Chem. Phys.* 152 2020, 234102.
- [4] I. Batatia et al. *NeurIPS* (2022); MACE User Guide v0.3.13; MACE foundation model
- [5] R. Nelson et al., *J. Comp. Chem.*, 41, 2020, 1931-1940.
- [6] A. Naik et al., *J. open source softw.* 9 (94), 2024, 6286.

Figures

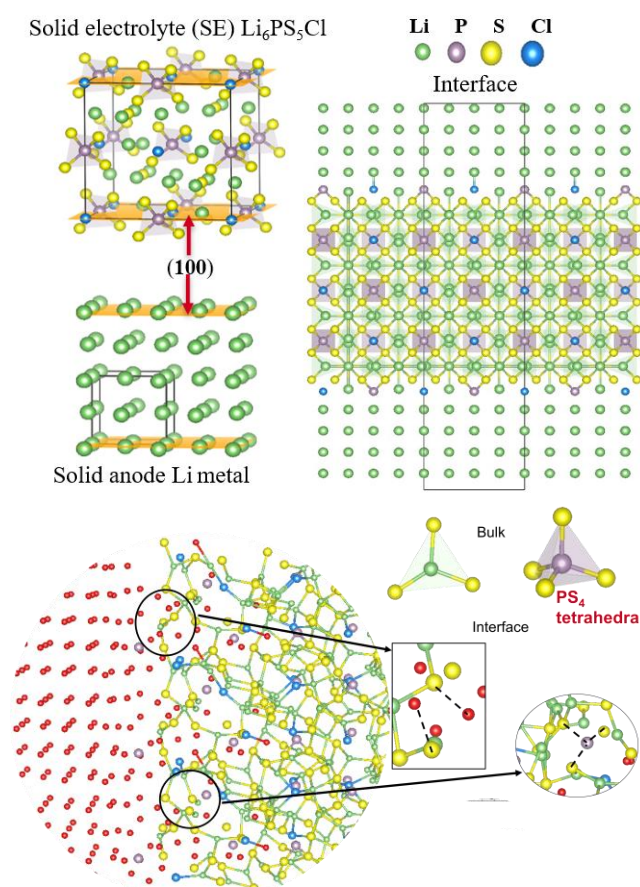


Figure 1. Top: Crystal structures of solid electrolyte (SE) $\text{Li}_6\text{PS}_5\text{Cl}$ and Li metal as anode. Atomic structure of the interface formed by cleaving [100] plane of the SE and the anode. Bottom: Atomic environment at the interface

