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Distinguishing the mixed conduction interphase: a machine learning molecular dynamics study on the $\text{Na}_3\text{PS}_4/\text{Na}$ battery interface

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E-mail: kapersson@lbl.gov**Keywords:** solid electrolyte, machine learning interatomic potential, molecular dynamics, sodium-ion battery, interfaceSupplementary material for this article is available [online](#)

Abstract

The interphase formed between solid electrolytes and alkali metal anodes determines whether decomposition is self-passivating, solid electrolyte interphase (SEI) or continuously propagating, mixed conducting interphase (MCI). We employ machine learning interatomic potential molecular dynamics to simulate the $\text{Na}_3\text{PS}_4/\text{Na}$ interface at scales of 500 000 atoms and 10 ns. Three features distinguish this system from the passivating $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ interface: (1) P–P transport correlations enabling cooperative phosphorus migration toward the anode, (2) amorphous Na_2S domains lacking nanocrystalline order, and (3) persistent Na–P connectivity pathways spanning the interphase from the onset of decomposition. These characteristics are consistent with mixed ionic-electronic conducting behavior and inconsistent with self-limiting SEI character. While definitive classification requires direct electronic conductivity measurements of the amorphous interphase, this work establishes atomistic mechanistic criteria for interphase classification and demonstrates that MLIP simulations can access the length and time scales necessary to resolve transport mechanisms at solid electrolyte interfaces.

1. Introduction

All-solid-state batteries employing inorganic solid electrolytes have received considerable attention due to their potential advantages in safety and energy density over conventional liquid-electrolyte systems [1]. However, the interface between the solid electrolyte and the alkali metal anode remains a challenge to predict its practical electrochemical performance. When thermodynamically unstable solid electrolytes are placed in contact with metallic lithium or sodium, spontaneous reduction reactions decompose the thiophosphate framework into multi-component interphases. The transport properties and stability of these interphases affect long-term battery performance [2].

Two distinct interphase classifications have been established in the literature: the solid electrolyte interphase (SEI) and the mixed conducting interphase (MCI) [3]. A passivating SEI is ionically conductive but electronically insulating; it permits ion transport while blocking electron transfer to the reaction front, thereby rendering the interphase self-limiting. In contrast, an MCI conducts both ions and electrons, enabling continuous electron supply to the electrolyte interface and sustaining propagating decomposition reactions.

Cubic Na_3PS_4 is a solid electrolyte exhibiting room-temperature ionic conductivity of approximately 0.2 mS cm^{-1} [4, 5]. While the bulk transport properties of this material have been characterized, the atomistic mechanisms governing interphase formation at the $\text{Na}_3\text{PS}_4/\text{Na}$ interface remain incompletely understood. Experimental techniques such as electrochemical impedance spectroscopy (EIS) provide macroscopic measurements of interfacial resistance [6], but cannot resolve the atomic-scale structure

and transport processes within the interphase. It remains debated whether the decomposition products of Na_3PS_4 (such as NaP , Na_3P , and Na_2S) impart partial electronic conductivity that drives continuous MCI growth, or whether they successfully passivate the interface as an SEI [6].

Ab initio molecular dynamics (AIMD) can access atomic resolution but is limited to timescales of approximately 10–100 ps for systems containing a few hundred atoms, precluding observation of interphase growth and evolution [7, 8]. To address this gap, we employ machine learning interatomic potential (MLIP) molecular dynamics simulations. The potential is trained through an active-learning workflow in which the atomic cluster expansion is coupled with an extrapolation-grade uncertainty metric, so that the reactive, far-from-equilibrium configurations arising as the interface decomposes are sampled iteratively. Such configurations are captured poorly by static, bulk-derived training sets. However, these are necessary to capture in an evolving interface. The MLIP approach thereby enables simulations of systems exceeding 500 000 atoms for durations of 10 ns, approaching experimentally relevant length and time scales while retaining near-DFT accuracy. We apply this methodology to characterize the $\text{Na}_3\text{PS}_4/\text{Na}$ interface and compare the results systematically with the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system, which has been shown to form a passivating SEI [9].

We investigate the atomistic mechanisms of the $\text{Na}_3\text{PS}_4/\text{Na}$ interphase formation via three complementary approaches. First, we characterize the structural evolution and morphology of decomposition products during interphase growth. Second, we employ Onsager transport analysis to quantify correlated motion between atomic species. Third, we identify the connectivity pathways to assess electronically conductive phases percolation throughout the interphase. We also compare these findings with the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system, which exhibits passivating SEI behavior, to establish the mechanistic criteria distinguishing SEI from MCI character.

2. Methods

2.1. MLIP development

We developed a MLIP for the Na–P–S system using density functional theory (DFT) data computed with the $r^2\text{SCAN}$ functional [10]. To generate representative configurations spanning the relevant chemical and structural space, we constructed the training dataset as follows:

- **Phase identification:** Identify initial reaction phases and their corresponding thermodynamic products via Interface Reactions and Phase Diagram applications from Materials Project [11, 12]. The full list of crystalline phases includes: Na , Na_3PS_4 , Na_2S , NaP , Na_3P , Na_3P_{11} , NaP_7 , Na_2PS_3 , and their respective polymorphs.
- **Amorphous and disordered structures:** Representative disordered and amorphous configuration were generated using the MPMorph workflow [13] from *atomate2* [14] for all the aforementioned phases in the Na–P–S compositions. Structures were sampled from AIMD trajectories at elevated temperatures (900 K, 1200 K, 1500 K) to capture initial set of non-equilibrium configurations.
- **Crystalline phases:** Known crystalline polymorphs were also sampled at elevated temperatures using the same MPMorph workflow to capture thermally activated bonding environments in strained unit cells.
- **Interfacial configurations:** Interfacial configurations of $\text{Na}/\text{Na}_3\text{PS}_4$ with unique Miller indices ($|h|, |k|, |l| \leq 2$) and termination sites were constructed using the *CoherentInterfaceBuilder* in *pymatgen* [15], employing the Zur and McGill methodology to minimize epitaxial strain [16, 17]. A total of 21 distinct interfaces were generated and simulated under NVT conditions with periodic boundary conditions; further details are provided in section 2.2.

Single-point $r^2\text{SCAN}$ calculations were subsequently performed on all sampled AIMD frames to ensure compatibility with the MatPES $r^2\text{SCAN}$ settings [18] and to obtain higher-accuracy energies and forces. Figure 1 illustrates the MLIP development workflow, including the active learning loop employed for iterative dataset refinement. Validation metrics, including equation of state reproduction, dimer dissociation curves, and bulk transport properties, are summarized in section 3.1; complete benchmarking data are provided in the Supporting Information. The workflow follows the methodology described by Li *et al* [19].

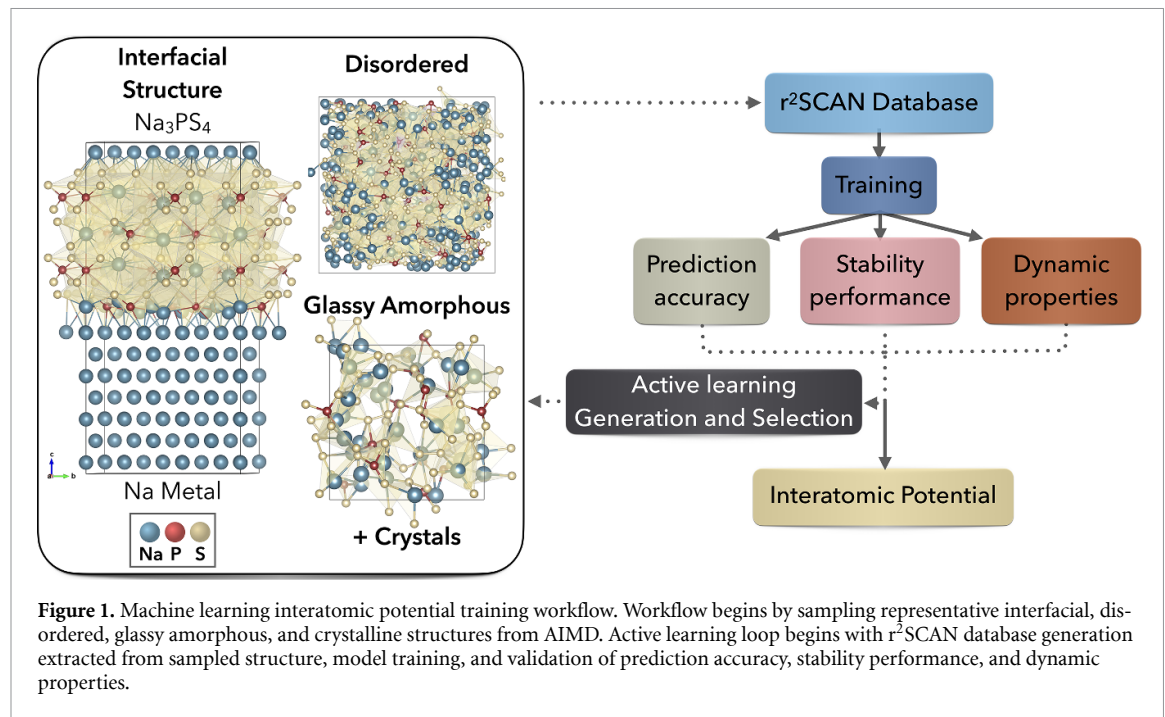


Figure 1. Machine learning interatomic potential training workflow. Workflow begins by sampling representative interfacial, disordered, glassy amorphous, and crystalline structures from AIMD. Active learning loop begins with r²SCAN database generation extracted from sampled structure, model training, and validation of prediction accuracy, stability performance, and dynamic properties.

2.2. DFT calculations

All AIMD and static DFT simulations were performed using the Vienna *Ab Initio* Simulation Package [20–25]. To balance computational cost and accuracy, AIMD simulations employed the PBEsol functional [26, 27], whereas static DFT calculations used the r²SCAN meta-GGA functional [10]. Static calculations used a plane-wave energy cutoff of 680 eV and an electronic self-consistency convergence criterion of 1×10^{-5} eV with spin-polarization enabled.

AIMD simulations were performed non-spin-polarized in the *NVT* ensemble using a Nosé–Hoover thermostat with a 2 fs time step; Brillouin zone sampling was restricted to the Γ -point. Crystalline supercells of approximately 100–200 atoms were simulated for 20 ps at 300, 900, and 1500 K, chosen to access thermally activated configurations while remaining below the melting points of the relevant phases. Amorphous and disordered structures were generated using the MPMorph workflow [14]. High-throughput calculation management, structure modifications, and data parsing were facilitated by the pymatgen [15], atomate2 [14], Jobflow [28] and Fireworks [29] open-source Python packages.

2.3. Molecular dynamics

All molecular dynamics simulations reported in this work were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [30] with Kokkos [31] in conjunction with the machine-learned atomic cluster expansion interatomic potential [32–34]. The ACE extrapolation grade formalism was employed for on-the-fly monitoring, evaluated every 10 timesteps. Configurations exceeding $\gamma = 1.5$ were flagged and added to the active learning dataset, while simulations were terminated if $\gamma > 5$ [35]. For the 500 000-atom Na₃PS₄/Na interface simulation, energy minimization was performed using the conjugate gradient algorithm, followed directly by NpT production without additional equilibration. This protocol was necessitated by the electrochemically reactive nature of the interface: extended equilibration would initiate decomposition reactions before reaching a converged configuration. The simulation employed a 1 fs timestep at 300 K using a Nosé–Hoover thermostat ($\tau_T = 1.0$ ps) and isotropic pressure coupling at 1 bar via a Nosé–Hoover barostat ($\tau_P = 1.0$ ps). The production trajectory spanned 10.5 ns.

Molecular dynamics simulations for Onsager transport analysis employed a melt-quench protocol [13, 36] to generate amorphous structures. Unit cell sizes ranged from 200 to 1000 atoms depending on composition. Starting from crystalline structures, temperature was ramped from 300 K to 5000 K over 100 ps (*NpT*, 1 bar), then cooled to the target temperature over 100 ps. After 10 ps of density equilibration, the volume was fixed and the ensemble switched to *NVT* for production. Production simulations were performed at 500, 900, 1200, and 1500 K for 1 ns each using a 1 fs timestep and Nosé–Hoover thermostat ($\tau_T = 1.0$ ps). The 1 ns duration ensured adequate sampling of the linear diffusive regime for mean-squared displacement fitting for Onsager coefficients fitting, detailed in section 2.4.

2.4. Onsager transport coefficient calculation

The Onsager transport coefficients quantify correlated motion between ionic species. We compute these coefficients from molecular dynamics trajectories using the Green–Kubo formalism [37–39], whereby

$$L_{ij} = \frac{1}{6k_BTV} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Sigma_\alpha [\mathbf{r}_\alpha^i(t) - \mathbf{r}_\alpha^i(0)] \cdot \Sigma_\beta [\mathbf{r}_\beta^j(t) - \mathbf{r}_\beta^j(0)] \rangle \quad (1)$$

with V and T denoting the volume and temperature of the system, k_B the Boltzmann constant, and $\mathbf{r}_\alpha^i(t)$ the position of the α th particle of species i at time t . It follows from equation (1) that the diagonal terms L_{ii} describe self-diffusion of species i , while the off-diagonal terms L_{ij} capture correlated motion between species i and j . Coefficients were extracted from the linear diffusive regime of mean-squared displacement data for amorphous Na–P–S structures, following the methodology of Karan *et al* [37] and Li *et al* [19]. The physical basis for this choice, the mapping of each proxy composition onto the corresponding region of the interphase, and the associated uncertainty are detailed in the Supporting Information.

2.5. Connectivity pathway analysis

Connectivity analysis for Na–P percolation pathways employed a bond-graph approach with species-specific cutoff distances of 3.2 Å (Na–P) and 2.5 Å (P–P), corresponding to first coordination shell minima validated against RDF analysis of crystalline reference phases. The algorithm identifies Na–P and P–P bonds originating from the bulk Na_3PS_4 and classifies clusters as either continuously connected across the interphase (from solid electrolyte to Na anode) or non-percolating. Analysis was performed at regular intervals throughout the 10 ns trajectory to track temporal evolution; highlighted Na–P sites in subsequent figures represent percolating clusters. We note that this analysis identifies topological connectivity rather than electronic conductivity directly.

3. Results and discussion

3.1. MLIP performance and benchmarks

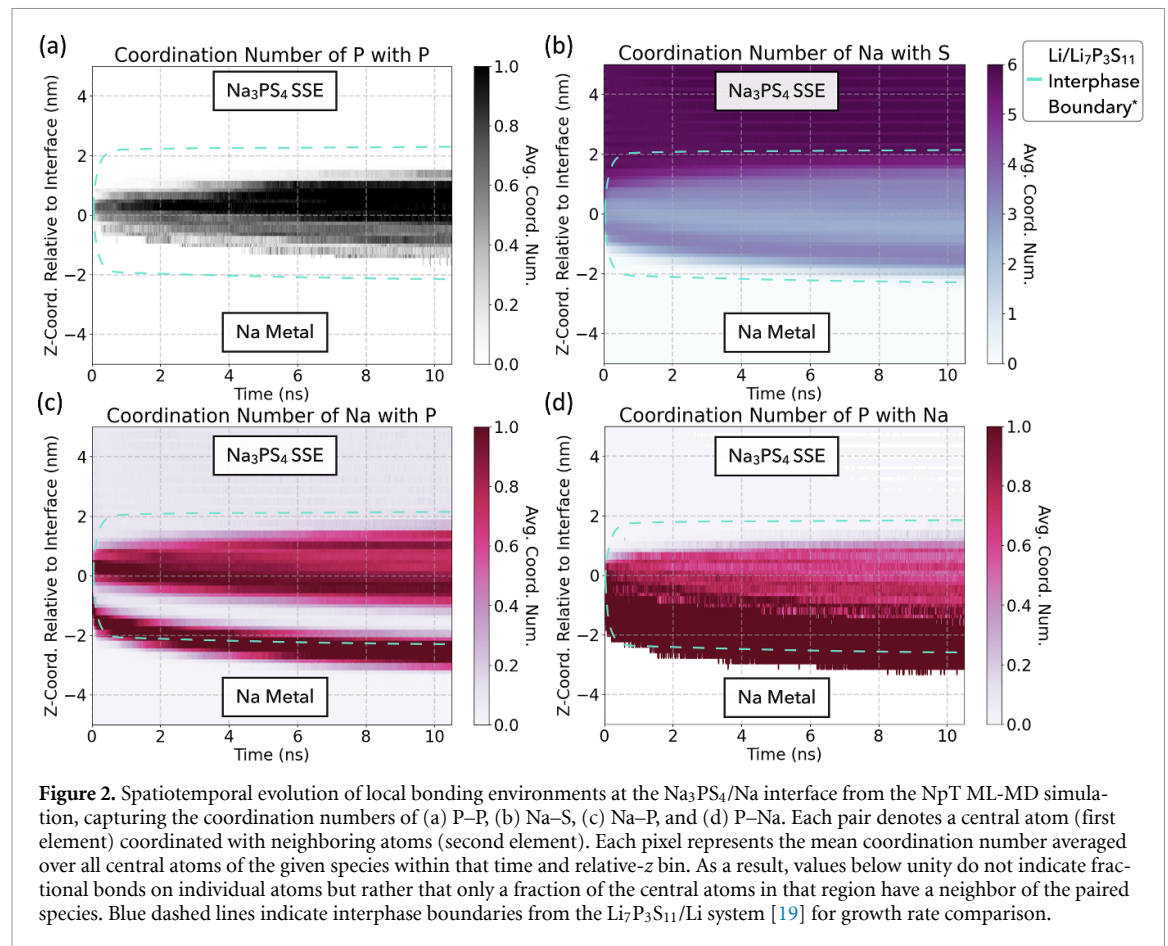
The initial dataset comprised over 24 000 structures. Configurations with maximum site-wise force magnitudes exceeding 80 meV Å^{−1} were filtered out, leaving 20 114 structures for training. The training procedure followed the two-step process outlined in our previous study [19]: a 99:1 forces-to-energy loss weighting in step 1, followed by 95:5 weighting in step 2. The final model achieved RMSE values of 39.64 meV/atom (training) and 36.46 meV/atom (test) for energies, and 171.58 meV Å^{−1} (training) and 188.79 meV Å^{−1} (test) for forces. Training and test set distributions are provided in the supporting information.

The MLIP was validated against DFT dimer binding curves, equation of state fits, and radial distribution functions from AIMD (see supporting information). The model accurately reproduces equilibrium bond distances, volumes, and bulk moduli for relevant Na–P–S phases. Notable limitations include deviations in long-range Na–S interactions and ground-state energies for Na, Na_2PS_4 , and Na_3PS_4 ; however, these do not affect the dynamic and structural properties central to this study. Additional discussions and figures are documented in the supplemental information.

Because low energy and force errors do not by themselves guarantee physically realistic dynamics [40], we assessed the potential using simulation-level observables rather than pointwise errors alone. In addition to the structural (radial distribution function) and transport benchmarks against AIMD noted above, the ACE extrapolation grade (γ) was monitored on-the-fly throughout production (evaluated every 10 timesteps; section 2.3) to detect sampling outside the training distribution, with simulations terminated if $\gamma > 5$. The production NpT trajectories remained thermodynamically stable over the full 10.5 ns, exhibiting no energy drift or density collapse. The amorphous cells used for transport analysis displayed stable diffusive dynamics. Together these checks provide evidence that the simulated trajectories are physically reliable

3.2. Structural evolution of the $\text{Na}_3\text{PS}_4/\text{Na}$ interface

Figure 2 presents the spatiotemporal evolution of the $\text{Na}_3\text{PS}_4/\text{Na}$ interface over the 10 ns simulation, with the dashed line indicating the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system from our previous study [19] for comparison. The coordination numbers reported in each heatmap pixel are averaged over all atoms of the central species within the corresponding time and z -position bin. Consequently, values below unity do not indicate fractional bonding on individual atoms but rather reflect that only a small fraction of central atoms in that region possess a neighbor of the given species. The heatmaps reveal progressive growth of the



interphase region as Na diffuses into the solid electrolyte while P and S species migrate toward the metal anode. Figure 2(a) shows increasing P–P coordination in the center of the interphase, skewed toward the Na_3PS_4 side, with a gradient of decreasing P–P bonding toward the Na anode. Figure 2(b) reveals pronounced Na–S coordination close to the anode, indicating a S-rich layer within the heterogeneous interphase morphology. This is corroborated by figure 2(c), where the absence of Na–P bonds marks the Na–S layer location, while an additional Na–P-rich region appears between the Na–S layer and the Na metal. Figure 2(d) confirms that P atoms exist within the Na–S layer but are predominantly coordinated to Na rather than other species. Figures 2(c) and (d) highlight the continuous growth of the interphase into the Na metal layer.

The interphase in the $\text{Na}_3\text{PS}_4/\text{Na}$ system exhibits logarithmic growth into the Na metal, with rapid initial expansion that slows but does not cease as the simulation approaches 10 ns. This contrasts with the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system, which plateaus after initial growth, consistent with self-passivating SEI behavior [19]. A key structural difference emerges between the Na and Li systems: whereas Li_2S domains in the lithium system exhibit nanocrystalline signatures with sharp compositional boundaries, the Na_2S domains remain amorphous throughout the 10 ns trajectory. Figure 3 compares the sulfide-rich regions in both systems. The Li_2S layer (figure 3(b)) contains distinct crystalline domains with ordered atomic arrangements (circled regions), whereas the Na_2S layer (figure 3(a)) exhibits a homogeneous, disordered structure with minimal crystalline order. This observation was reproducible across repeated simulations with identical MD parameters. Beyond visual inspection, the structural order of the interphase Na_2S region demonstrates amorphous behavior, shown via Na–S partial radial distribution function (see supporting information). While the first Na–S coordination shell is sharp and coincides with the crystalline bond length (~ 2.8 Å); the long-range translational order is suppressed roughly five-fold relative to crystalline Na_2S .

Materials Project thermodynamics [11, 12] predict that reaction at the $\text{Na}/\text{Na}_3\text{PS}_4$ interface is directed toward Na_2S formation together with a family of nearly degenerate Na–P phases (NaP , Na_3P_{11} , NaP_7 , and Na_3P), all within 20 meV/atom in reaction energy. Taking the lowest reaction energy ($\text{Na}_3\text{PS}_4 + 6\text{Na} \rightarrow \text{NaP} + 4\text{Na}_2\text{S}$) $\Delta E = -0.465$ eV/atom we can compare it to the analogous Li_2S -forming reaction in the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system ($\Delta E = -0.78$ eV/atom) [11, 12]. Neglecting entropic differences at room

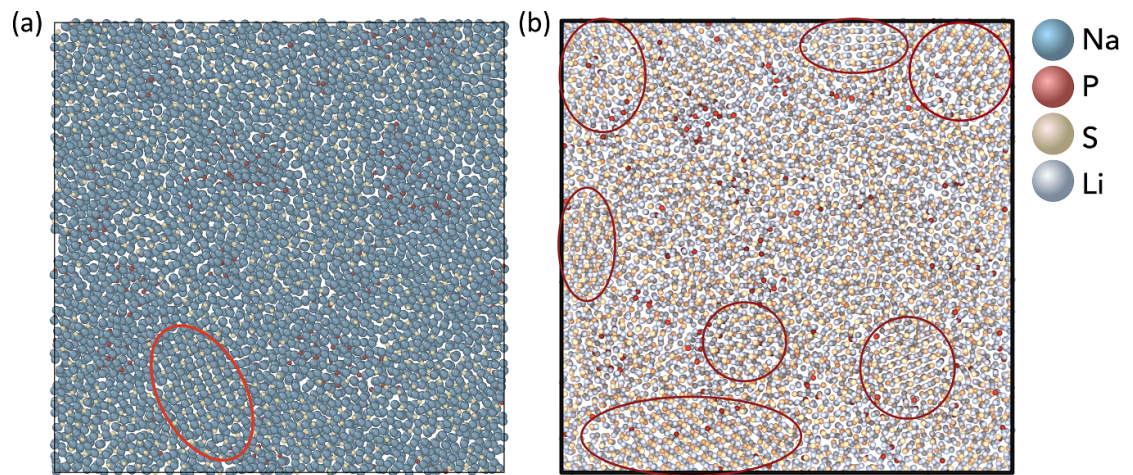


Figure 3. Structural comparison of sulfide-rich layer regions in the (a) $\text{Na}_3\text{PS}_4/\text{Na}$ and (b) $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$. The red circles show the identified nanocrystalline domains which exhibits crystal symmetry of the Na_2S or Li_2S structures. Reprinted with permission from [19]. Copyright (2025) American Chemical Society.

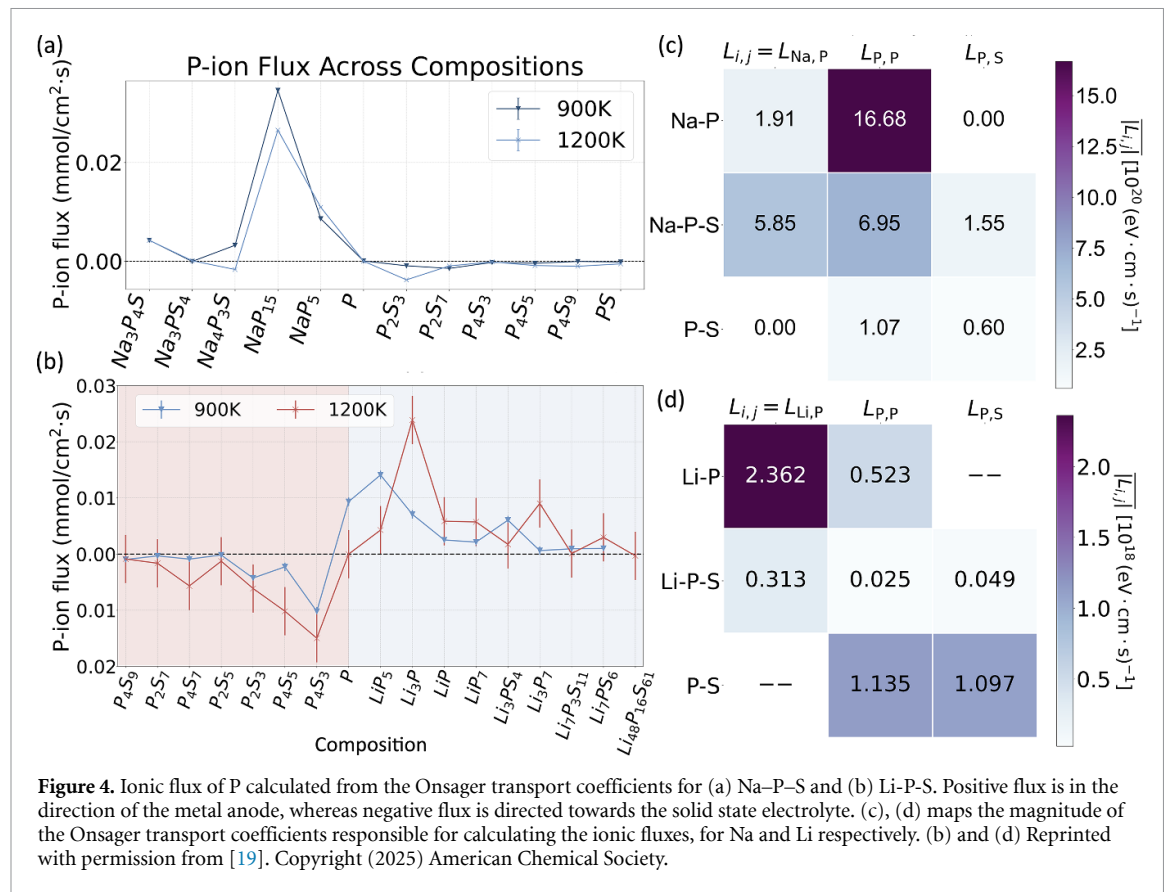
temperature, we hypothesize that this reduced thermodynamic driving force for Na_2S crystal nucleation contributes to the absence of crystallization observed in figure 3. However, alternative explanations cannot be excluded, including differences in interfacial nucleation energies between the Li and Na systems, limitations of the MLIP in resolving such small energy differences, or insufficient simulation timescales to capture crystallization. Resolving the mechanistic origin of amorphous Na_2S formation will require dedicated nucleation studies beyond current MLIP capabilities.

3.3. Onsager transport analysis

Having characterized the structural evolution, we now examine the transport properties of the interphase. The Onsager transport coefficients quantify correlated transport motion between species and provide insight into collective transport mechanisms. To approximate ionic fluxes, we computed Onsager coefficients from MD simulations of homogeneous amorphous structures under applied chemical potential gradients, representing conditions within the interphase. Full ionic flux and chemical potential gradients data are presented in the Supporting Information; here, we focus on P-ion fluxes to highlight differences between the $\text{Na}_3\text{PS}_4/\text{Na}$ and $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ interphases.

Figure 4(a) presents P-ion fluxes for relevant local amorphous compositions that are likely to occur within the interphase. The dominant driving force acts on Na–P phases, where P ions exhibit positive flux toward the Na metal anode. In contrast, figure 4(b) shows that in the Li system, consistently, the P flux depends on the local coordination environment: P coordinated with S tends toward negative flux (toward the SSE), while P in the presence of Li exhibits flux toward the anode. This disparity is highlighted by comparing the Onsager transport coefficient matrices for the Na (figure 4(c)) and Li (figure 4(d)) systems. The dominant coefficient in the Na–P–S system arises from P–P interactions in Na–P phases, exceeding the Li system by approximately an order of magnitude. In the $\text{Na}_3\text{PS}_4/\text{Na}$ system, the P–P correlation coefficient ($L_{\text{PP}} = 16.68 \times 10^{20} \text{ (eV}\cdot\text{cm}\cdot\text{s)}^{-1}$) is the dominant term in the transport matrix. This positive correlation indicates collective P motion, a signature of P clustering and coordinated transport toward the Na metal interface.

By contrast, the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ system exhibits qualitatively different transport behavior [19]. The dominant features are Li–P interactions in Li–P phases and P–S correlations in P–S phases, with similar magnitudes that produce competing driving forces and composition-dependent flux directions. The P–S coupling stems from anticorrelated motion: when S moves in one direction, P tends to move in the opposite direction. Combined with crystalline Li_2S domains that physically block diffusion pathways, this anticorrelation traps P within the interphase. In the Na–P–S system, P–S anticorrelation is less pronounced, allowing P–P correlations in Na–P compositions to dominate. We attribute these positive P–P correlations in part to electrostatic screening by the larger Na^+ cation (ionic radius $0.95 \text{ \AA}$ vs $0.60 \text{ \AA}$ for Li^+) [41], which reduces repulsion between negatively charged P-containing species.



3.4. Na–P connectivity pathways

The increased P transport observed in the Na₃PS₄/Na system suggests that P may diffuse continuously through the interphase. We now examine whether this transport gives rise to pathways with likely electronically conductive character. Electronic conductivity in such interphases likely proceeds via polaron hopping; however, capturing polaron transport in amorphous structures via *ab initio* methods is computationally prohibitive. Instead, we use topological connectivity of Na–P networks as a proxy for potential electronic percolation, given the semiconducting nature of Na–P phases. This analysis assesses only the structural topology of the Na–P network and does not explicitly model electronic transport. Moreover, the interatomic potential is not charge-aware, and neither an external electric field nor an explicit electrochemical potential is imposed. Figure 5 presents a direct visualization of the Na–P connectivity network within the interphase.

The connectivity analysis employs cutoff distances of 3.2 Å (Na–P) and 2.5 Å (P–P), as described in section 2.5. We identify only clusters that form continuous connections across the full interphase thickness, from the Na₃PS₄ layer to the Na metal anode. Indeed, a percolating Na–P cluster forms immediately upon interface contact and persists throughout the entire 10 ns simulation. This immediate, persistent connectivity indicates that topological connectivity pathways that may support electronic percolation occur during the decomposition reaction at the SSE/anode interface, contingent on the semiconducting character of amorphous Na–P phases. The percolating Na–P network first appears at 0.23 ns and persists in 99.8% of subsequent frames. These network formation regularly occur even given a cutoff distance sweep of Na–P and P–P bond distances (see Supporting Information).

The stoichiometric basis for percolation can be understood through the thermodynamic and metastable reaction products. Reduction of Na₃PS₄ by Na metal yields the product Na₂S as well as a possible range of Na–P phases such as NaP, Na₃P₁₁, Na₃P, NaP₇, and Na₂PS₃ which are all highly energetically competitive; the reaction energy being within ~20 meV/atom from *r*²SCAN data in the Materials Project data [11, 12, 42] (see supporting information). The dominant interphase products are amorphous phases with compositions near Na₂S and various Na–P stoichiometries. Table 1 summarizes the available theoretical and experimental literature evidence for the electronic properties of these phases, highlighting the strong contrast between Na–P and Na–S compositions.

The electronic conductivity of crystalline Na₃P (12 S cm⁻¹) exceeds that of Na₂S (10⁻¹⁶–10⁻¹² S cm⁻¹) by 13–16 orders of magnitude [46]. Furthermore, table 1 shows that all crystalline Na–P phases

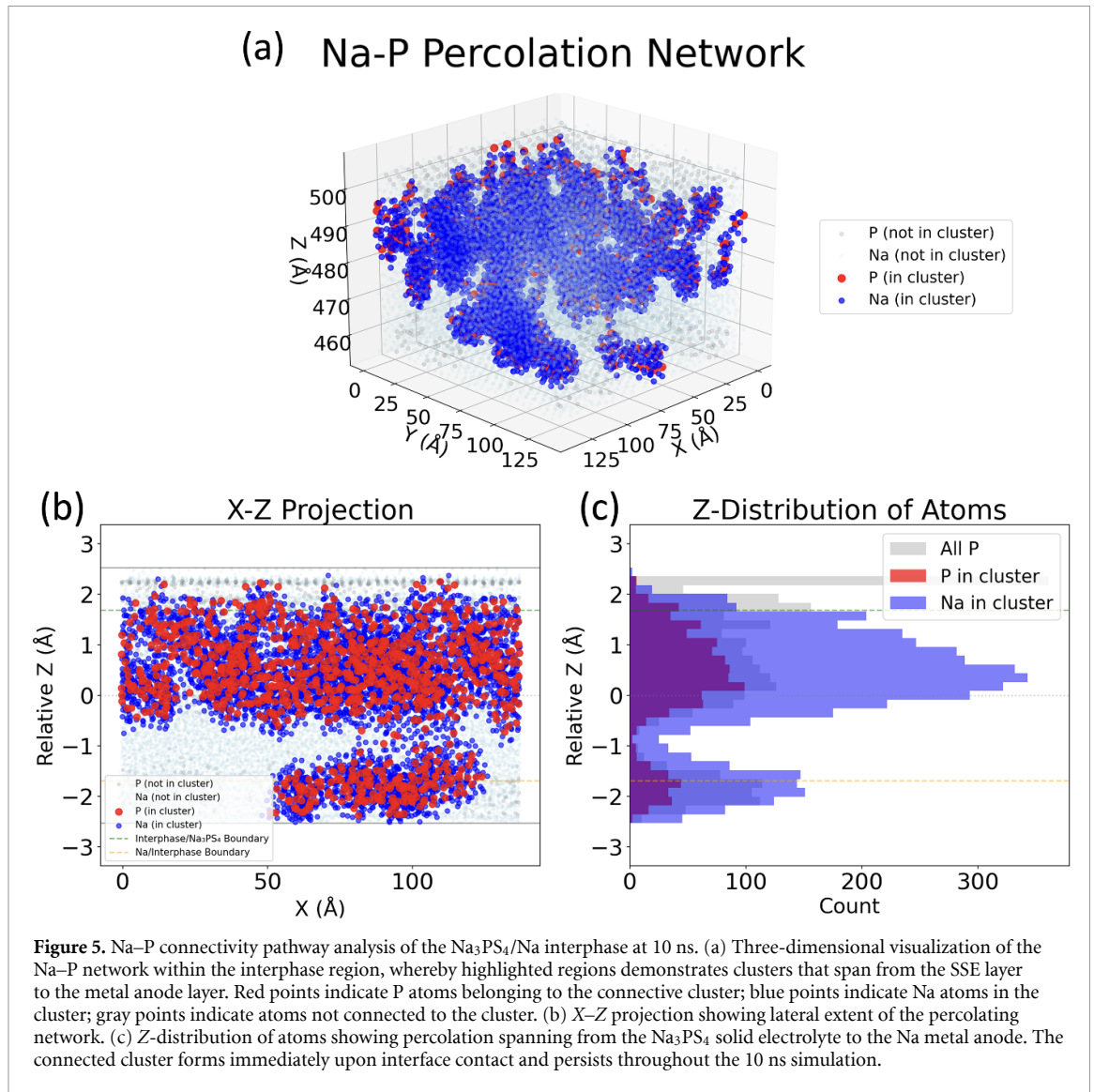


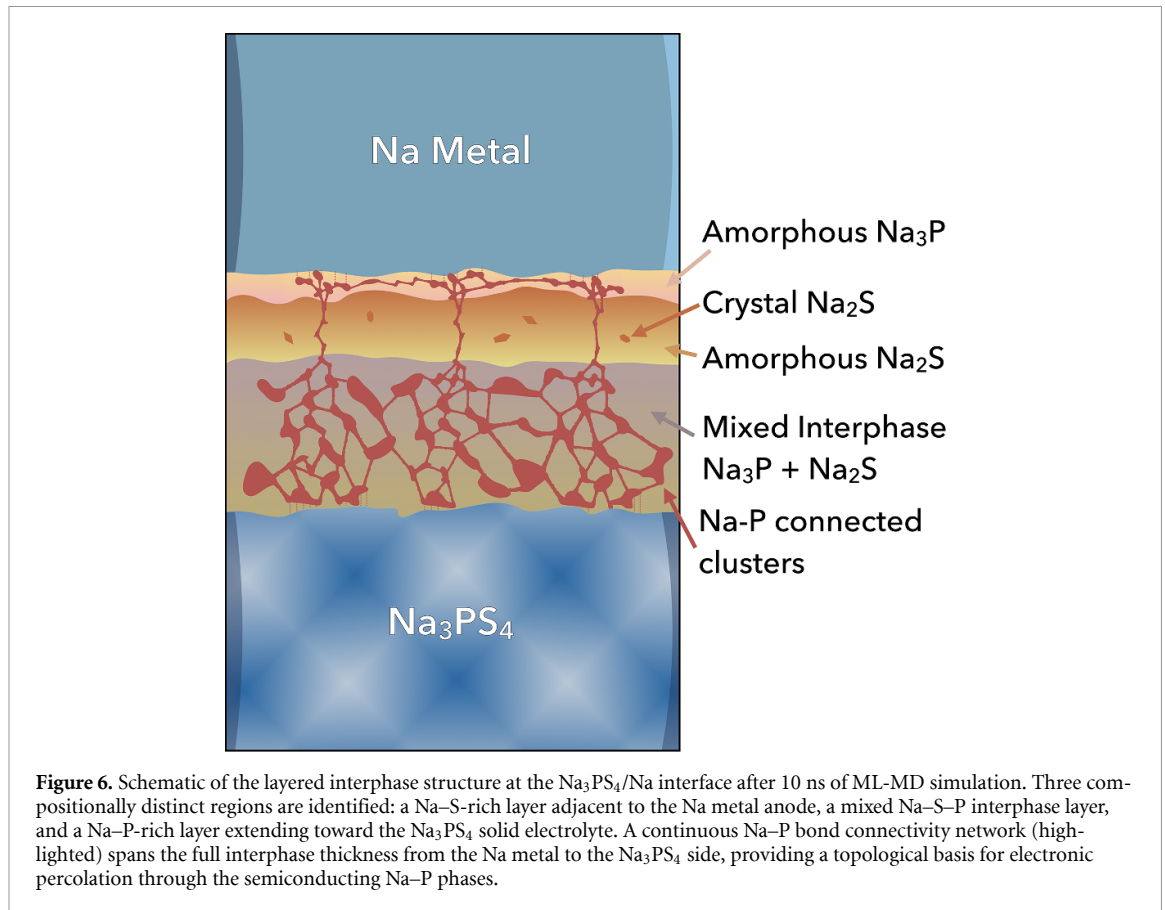
Figure 5. Na–P connectivity pathway analysis of the $\text{Na}_3\text{PS}_4/\text{Na}$ interphase at 10 ns. (a) Three-dimensional visualization of the Na–P network within the interphase region, whereby highlighted regions demonstrates clusters that span from the SSE layer to the metal anode layer. Red points indicate P atoms belonging to the connective cluster; blue points indicate Na atoms in the cluster; gray points indicate atoms not connected to the cluster. (b) X–Z projection showing lateral extent of the percolating network. (c) Z-distribution of atoms showing percolation spanning from the Na_3PS_4 solid electrolyte to the Na metal anode. The connected cluster forms immediately upon interface contact and persists throughout the 10 ns simulation.

Table 1. Electronic properties of interphase products based on literature.

Phase	Bandgap (eV)	Characteristic
Na_2S	3.22 [43], 2.99 [44]	Wide-gap insulator [45]
NaP	~ 0.74 [46] ^a	Semiconducting
Na_3P	~ 0.4 [43], 0.8^a [46]	Semiconducting
Na_3P_{11}	1.66 [46]	Wide-gap semiconductor
NaP_7	2.0 [47]	Semiconductor
Li_2S	3.24–5.08 [48, 49] ^a	Wide-gap insulator
Li_3P	3.6 (direct), 2.03 (indirect) [50] ^a	Wide-gap semiconductor

^a Computational predictions

exhibit lower optical bandgaps than Na_2S . We note that amorphous bandgaps can differ significantly from their crystalline counterparts. While definitive conclusions would require modeling polaron hopping within the heterogeneous interphase, these results suggest a possible mechanism for MCI behavior in which electrons are transported from the Na metal anode through the Na–P network to the reaction front. Direct verification, however, will require explicit electronic-structure calculations of the heterogeneous interphase, a highly challenging task that depends critically on accurately capturing the assembly and evolution of diverse interfacial non-crystalline morphologies. The P-ion flux analysis (figure 4(a)) provides further support for this picture. Maximum P flux occurs through P-rich compositions (NaP_{15} , NaP_5), indicating that high P mobility enables formation of Na-rich phases (NaP , Na_3P), precisely the phases that constitute the percolation pathways.



3.5. Implications for interphase classification

The structural and transport characteristics established in this work provide a basis for classifying the $\text{Na}_3\text{PS}_4/\text{Na}$ interphase, summarized schematically in figure 6. Three features distinguish this system from the passivating SEI behavior observed at the $\text{Li}_7\text{P}_3\text{S}_{11}/\text{Li}$ interface: (1) P–P transport correlations enable cooperative P transport throughout interphase formation and growth, (2) amorphous Na_2S domains lack nanocrystallinity, and (3) persistent Na–P connectivity pathways provide a likely electronic percolation mechanism from the onset of decomposition. Collectively, these characteristics indicate that the $\text{Na}_3\text{PS}_4/\text{Na}$ interphase exhibits characteristics consistent with MCI-like behavior, permitting both ionic and electronic transport.

Prior experimental work by Wenzel *et al* reported linearly increasing interfacial resistance over 35 hours at the $\text{Na}_3\text{PS}_4/\text{Na}$ interface using EIS [6]. The atomistic mechanisms identified here suggest an interpretation of this observation: the interphase continues to grow via electronic transport along the connected Na–P network, with each additional increment in thickness increasing ionic resistance and impedance to Na^+ transport. Since EIS measures ionic impedance, electronic percolation constitutes a parallel conduction pathway that is not detected by the measurement. Thus, linear resistance increase is consistent with MCI behavior.

The specific rate-limiting mechanism controlling growth kinetics remains an open question. Three candidate mechanisms are consistent with our observations: (1) Na^+ diffusion through the amorphous $\text{Na}_2\text{S}/\text{Na–P}$ matrix, (2) reaction kinetics at the interphase/electrolyte boundary, or (3) electronic transport limitations at grain boundaries and compositional interfaces. The heterogeneous morphology of the interphase precludes definitive discrimination via *ab initio* electronic structure calculations. Future experimental studies employing transference number measurements or composition-resolved conductivity mapping may distinguish among these candidates.

Finally, we comment on the limitations of the present work. First, the reaction kinetics observed here are undeniably faster than expected from room-temperature experiments. One possible explanation is the well-known tendency of MLIPs to overestimate diffusion and ionic mobility, as previously noted by Zheng *et al* in reproducing diffusivities from amorphous AIMD calculations [51]. The atomically perfect interface matching employed in the simulations may also accelerate reactivity. For this reason we

emphasize that the conclusions of this work concern the qualitative mechanism of interphase formation, namely the positive P–P transport correlations, the formation of an amorphous Na₂S layer, and the persistent Na–P connectivity, and not the absolute growth rate, which we do not claim to predict quantitatively. These three mechanistic features were reproduced across independent simulations initialized with different random seeds and spanning a range of system sizes (from 5000 to 500 000 atoms) and interface orientations, indicating that they occur systematically regardless of the interface construction. In addition, the present study neglects the role of electric fields in the interfacial oxidation and reduction reactions; future work employing charge-aware MLIPs [52] may enable more detailed investigation of charge transfer processes within the interphase. Finally, while our analysis establishes topological connectivity and transport correlations as necessary but not sufficient conditions for MCI behavior, definitive classification will require direct measurement or calculation of electronic conductivity in the amorphous heterogeneous interphase, which remains beyond current computational capabilities.

4. Conclusion

We developed a machine learning interatomic potential for the Na₃PS₄/Na system and performed molecular dynamics simulations at scales exceeding 500 000 atoms and 10 ns. Three characteristic features of interphase formation emerge. (1) Onsager transport analysis reveals strong P–P correlations enabling cooperative P transport toward the Na anode, in contrast to the composition-dependent, partially anti-correlated P fluxes in the Li₇P₃S₁₁/Li system. (2) The Na₂S domains remain amorphous throughout the simulation, lacking the nanocrystalline order observed for Li₂S, consistent with the lower thermodynamic driving force for Na₂S formation (−0.465 eV/atom vs −0.78 eV/atom). Finally, (3) Na–P connectivity pathways form immediately upon interface contact and persist throughout the trajectory, providing a topological basis for electronic percolation through the semiconducting Na–P network.

Collectively, these findings suggest that the Na₃PS₄/Na interphase exhibits behaviors consistent with mixed ionic-electronic conducting (MCI) character, in contrast to the passivating SEI behavior observed in the Li₇P₃S₁₁/Li system. We propose that the continuous P transport, amorphous sulfide matrix, and persistent topological connectivity pathways are chemical and morphological markers inconsistent with the self-limiting behavior characteristic of a passivating SEI. We anticipate that future experimental studies employing transference number measurements or charge-aware MLIP simulations will provide further refinement on the specific rate-limiting mechanism controlling interphase growth.

In summary, this work demonstrates that MLIP simulations can access the length and time scales necessary to resolve atomistic transport mechanisms at reactive solid electrolyte interfaces and illustrate the morphological differences between passivating and non-passivating SEI formation. Our results offer preliminary guidance for rational design of solid electrolytes with controlled interfacial properties.

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Data availability statement

The datasets generated and analyzed during this study, including the training dataset and the interphase trajectories, are available on MPContribs and the Materials Project. The analysis code used in this work, including the connectivity/percolation, Onsager transport, and plotting scripts, will be made openly

available upon publication at <https://github.com/BryantLi-BLI/naps-mic> [53]. Additional data can be provided from the corresponding author upon reasonable request.

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