

Reconstructions and Dynamics of β -Lithium Thiophosphate Surfaces

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Lithium thiophosphate (LPS) is a promising solid electrolyte for next-generation lithium-ion batteries due to its superior energy storage, high ionic conductivity, and low-flammability properties. Despite its potential, the high reactivity of LPS with common contaminants such as atmospheric water, preparation solvents, and electrode materials poses significant challenges for commercialization. The lack of understanding regarding the structure, morphology, and chemical behavior of the surface of LPS slows down the search for solutions to these issues. Here, we utilize a machine-learning interatomic potential to achieve a fundamental atomistic understanding of the mechanical and chemical properties of the β -Li₃PS₄ surfaces. Employing molecular-dynamics simulations, we identify relevant complexions formed by surface reconstructions, determine their surface energies, and compute the Wulff shape of β -LPS. The most stable complexions exhibit properties distinctly different from the bulk, including amorphization, increased density, decreased conductivity, and large deformation of the structural building blocks. We demonstrate that these surfaces are not static but undergo significant dynamical activity at room temperature, which is clearly identified by an analysis featuring a time-averaged structural descriptor. Finally, we examine the changes of the electronic structure induced by the surface complexions as well as their effect on the reaction enthalpy with water, which provides us with details on changes in surface reactivity and active sites, underlining the importance of investigating surface complexions under realistic conditions.

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I. INTRODUCTION

Solid-state batteries (SSBs) are emerging as a promising advancement in sustainable energy storage, offering significant improvements in safety and performance compared to conventional lithium-ion batteries (LIBs), while still being suitable for the same applications [1–3]. Unlike conventional LIBs, which use flammable liquid electrolytes, SSBs utilize solid-state electrolytes (SSEs), thus minimizing safety hazards by eliminating the possibility of leakage of dangerous substances. Potential performance enhancements include increased temperature ranges [1,4], faster charging without electrolyte polarization [5] due to the higher conductivity of lithium ions in many SSEs, as well as potentially higher energy and power densities by potential usage of Li metal anodes and bipolar stacking [6].

Among many available SSEs, lithium thiophosphate (LPS) is notable for its high ionic conductivity [7,8], mechanical and electrochemical stability [9,10], long life-cycle [11], and the resource-efficient composition of the Earth-abundant elements sulfur and phosphorous, enabling cheap sustainable applications at large scales [12].

Despite the many advantages of LPS as SSEs, LIBs containing it are still under development, due to the high reactivity of LPS toward many electrode materials as well as water. This necessitates handling the material in inert atmospheres with water-free solvents, which significantly increases production costs and hinders commercialization [13,14].

Currently, passivation strategies, such as material doping with, e.g., halides [15–17] or softer bases according to the hard and soft acids and bases (HSAB) concept [18–21], as well as solvent inclusion [22] or coatings with Li⁺-conducting materials such as Al₂O₃ or polymeric binders [23–27], are being explored. However, these approaches are also restricted by the high reactivity of the material [13,26,28]. The lack of understanding of the surface structure, morphology, and chemical behavior of LPS slows down the development of this technology, emphasizing the need for fundamental insights into surface reaction

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mechanisms and interfacial properties. Obtaining atomistic insights on LPS is rather challenging, given that LPS is a complex material with multiple possible compositions and crystal structures. Here, we concentrate on Li_3PS_4 , which has three crystal polymorphs (α , space group $Cmcm$; β , $Pnma$; and γ , $Pmn2_1$ [29–31]) as well as amorphous glassy structures. Sufficiently high ionic conductivity for battery applications has been observed for the α , β , and amorphous structures. Among these, the β phase has received a lot of attention by researchers since it has been successfully stabilized at room temperature by Liu *et al.* in 2013 [7].

In recent years, computational studies have addressed the bulk and surface [12,32–37] properties of LPS. The majority of these studies have been limited by the use of empirical potentials [38,39] and *ab initio* molecular dynamics (AIMD) [40], based on density-functional theory (DFT) with the generalized gradient approximation (GGA) [41–43]. The former can provide useful mechanistic insights, but have not yet been able to correctly predict the activation energies of the conductive phases [39] and are not suitable for a detailed study of the surface properties. Quantum mechanical approaches, on the other hand, are more accurate and can give insightful evidence of relevant effects [32,44,45] but their high computational cost hinders their applicability to the large systems required to study surface effects, e.g., surface reconstruction and dynamics under realistic conditions. To address this cost-accuracy trade-off, one can use machine learning to construct interatomic potentials, which, once properly trained over accurate quantum mechanical data, have the accuracy of DFT at a cost only marginally higher than classical force fields [46–58]. Such machine-learning interatomic potentials (MLIPs) have already provided many insights into the properties of bulk LPS [12,17,36,37]. Furthermore, their reduced computational demand enables simulations of larger systems beyond the practical limits of DFT, making it possible to adequately investigate the structure of grain boundaries [59], and has helped to uncover the nature of relevant surface complexions of other materials [60,61].

In the following, we first elucidate the surface morphology of β -LPS (Li_3PS_4) using MLIP-driven molecular dynamics (MD) to achieve thorough energetic relaxation. We then characterize these surfaces and find properties that are distinctly different from those of the bulk. MD simulations of a reconstructed (100) surface provide insights into the surface stability and dynamics under realistic conditions. Then, we take a look at the electronic structure of the low-energy complexions, which provides information on the reactivity of the surface. Finally, we discuss the impact of the surface complexion for the stability of the SSE by investigating the thermodynamic stability of LPS when interacting with water—one of the issues that directly hamper the progress of this class of materials toward widespread technological applications.

II. RESULTS AND DISCUSSION

A. Surface reconstructions and surface energies

β -LPS has a $Pnma$ crystal structure, in which the lithium ions can occupy three different possible lattice sites. These sites are termed d , b , and c Wyckoff sites [32]. Their position in a DFT relaxed unit cell of β -LPS is shown in Fig. 1. The lattice parameters of the DFT calculation as well as of the fitted MLIP agree reasonably with experimental values (cf. Table S1 in the Supplemental Material [62]).

We use this relaxed unit cell to cut several β -LPS surfaces with low Miller indices. We then perform MD simulations to determine the surface stabilities under realistic conditions (300 K, ambient pressure). During the simulation, the surfaces undergo reconstructions, resulting in surface structures possessing a lower potential energy. This is illustrated in Fig. 2(a), where we compare the different LPS surface energies γ (for definition, see Sec. S-B in the Supplemental Material [62]), after a static relaxation (black circles), as often performed when surfaces are investigated, with the surfaces that we have obtained after the MD simulations (blue diamonds). Considering the statically relaxed structures, one can see that the surfaces vary greatly in their stability. They follow roughly the correlation of the surface energy to the coordination number of the sulfur atoms, which has been described by Kim *et al.* [33] (for the definition of surface energy and sulfur coordination number, see Sec. S-B in the Supplemental Material [62]). In comparison, all surfaces that have been obtained from an MD simulation and then relaxed have a lower surface energy compared to the statically relaxed structures (except for the (210), which has the same surface energy). MD relaxation also changes the order of the most stable

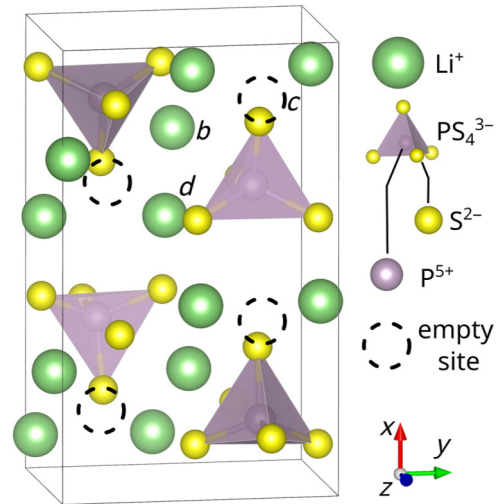


FIG. 1. A density-functional theory (DFT) relaxed unit cell of β -LPS with fully occupied d and b Wyckoff sites and empty c sites (dashed black circles). d , b , and c Wyckoff sites labeled according to Ref. [32].

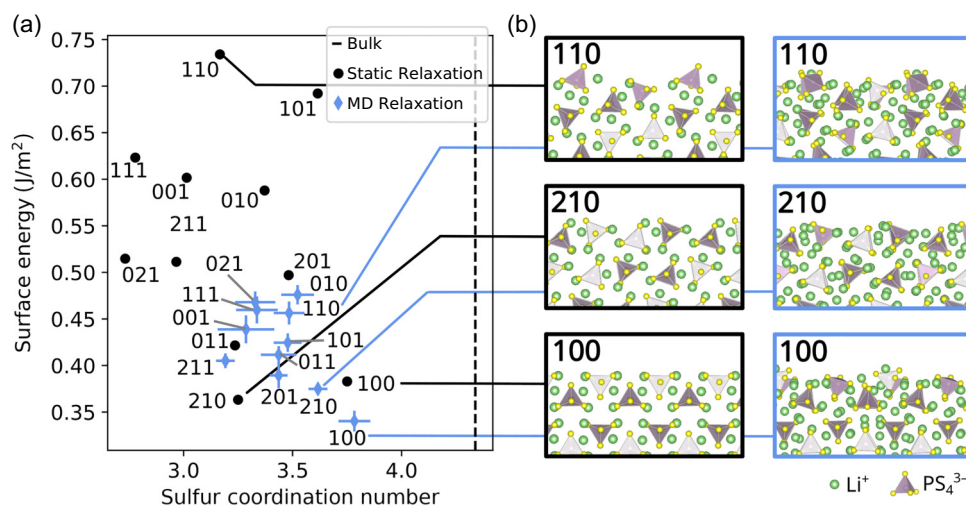


FIG. 2. (a) The surface energy of selected low-Miller-index surfaces of a static relaxation with the MLIP and the relaxation after a short MD simulation plotted against the sulfur coordination number. For the structures obtained from MD simulations, the energy is averaged over ten randomly selected and relaxed snapshots along the (minimum 220-ps-long) MD and the error bars are their standard deviation. (b) The structures of selected LPS surfaces in the y - z plane after static relaxation (left) and after an MD simulation followed by a relaxation (right). The surface Miller indices are given in the top left of each panel.

surfaces, with the (100) surface being a bit more stable than the (210) surface after reconstruction. Other surfaces, such as the (110), show a drastic increase in stability. In general, it can be observed that the reconstructed surfaces are closer to each other in surface energies, clustering at values between 0.35 and 0.48 J/m² (for the values, see Table S3 in the Supplemental Material [62]). This clustering in energy is accompanied by a reduced spread of the sulfur-ion coordination number, which increases for all surfaces. Similarly, the lithium-ion coordination increases (cf. Fig. S5 in the Supplemental Material [62]). For many catalytic and electrochemical systems, the coordination of surface ions has been correlated with their reactivity, with higher-coordinated atoms being less reactive [63,64]. Thus, this provides indications that the reconstructed relaxed surfaces might be less reactive than the statically relaxed one. As we shall see later, this is not the case: the dynamical reconstruction yields a distribution of surface sites with differing total structures, some being *more* reactive than those on the statically relaxed surface.

An explanation for the drastic change in surface energies during the MD simulation can be found when observing the structure of the surfaces. During the MD simulation, the lithium ions are given the chance to hop between sites and thus can redistribute to the most energetically favorable configuration. Note that this is not only happening at the surface but also in the bulk. At elevated temperatures (637 K), it has been experimentally found that the d sites in β -LPS are fully occupied, whereas the b (70%) and c (30%) sites are partially occupied [31]. We also find in our simulations that all start from a purely d- and b-site occupation of lithium ions (as shown in Fig. 1) after a short

simulation time the c sites are also partly occupied. Visualizing the surface, however, the lithium ions become more randomly distributed and many of them cannot be clearly assigned to Wyckoff sites anymore. Such drastic redistribution, which requires not only an escape of the local energy well but also the breaking of the symmetry of the structures, cannot be found by static relaxation but is readily obtained with finite-temperature MD equilibration.

For the PS₄³⁻ tetrahedra, rotations are possible during MD simulation, which does not only lead to lower surface energies but also to changes in the surface morphology. When comparing to the sulfur coordination number, it also becomes obvious that the sulfur ions become more buried in the surface during the reconstruction, as the coordination number increases for the surfaces. These changes can clearly be observed in Fig. 2(b), which compares surface cuts after a static relaxation (left) with the corresponding surface complexions after an MD simulation followed by relaxations (right). When comparing the structure before and after the MD simulation, one clearly observes a strong restructuring of the surfaces and a loss of the crystal order of the underlying bulk. As previously discussed, this is especially pronounced for the Li⁺ ions, which are now occupying poorly defined positions in the crystallographic lattice. Note that the depictions of the reconstructed surfaces are only one possible realization of the structure at this specific Miller index and that dynamic movements of lithium ions as well as (as we will see later) tetrahedra rotations drive a dynamic evolution of the surface structure over time.

At this point, it is noteworthy that the surfaces of LPSs are not uniquely defined by their Miller indices, meaning

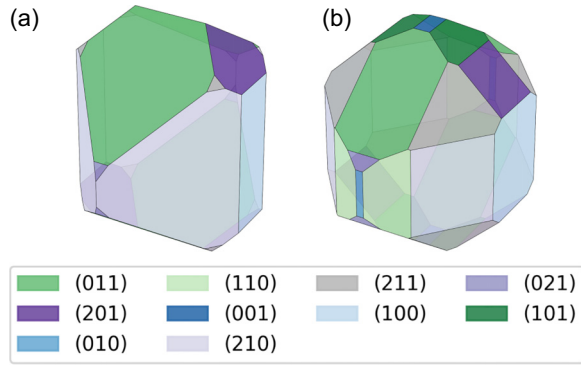


FIG. 3. Wulff constructions of LPS (a) after static relaxation and (b) after an MD simulation that have allowed for surface reconstructions.

that adding or omitting some PS_4^{3-} or lithium ions of a specific surface does not alter the Miller index. Thus, for one Miller index, multiple possible surface terminations exist, which differ in, e.g., lithium or sulfur richness [65]. However, as we have observed in this study, the naturally occurring surface reconstructions are governed by ion diffusion and redistribution. Hence, different surfaces with the same Miller index are energetically very similar after an MD simulation. As a result, the surfaces have comparable properties almost regardless of their initial surface termination (cf. Fig. S6 in the Supplemental Material [62]).

1. Wulff construction

We have computed the Wulff shapes for both the statically relaxed and reconstructed surfaces. In Fig. 3, we present the resulting Wulff constructions (for comparison with previously reported Wulff shapes, see Fig. S9 in the Supplemental Material [62]). In the case of the statically relaxed structure [Fig. 4(a)], the (210) and (011) surfaces dominate. In contrast, the Wulff shape of the reconstructed surfaces differs significantly, incorporating a greater variety of surface orientations and appearing more spherical overall. This is expected, as all the surface complexions exhibit comparable surface energies, preventing any single surface from dominating.

B. Structural characterization of the surface complexion

As we have seen in the previous section, the reconstructed surfaces are energetically more favorable than the statically relaxed structures. In this section, we analyze in more detail the nature of the surface reconstruction.

In Figs. 4(a) and 4(b), we show the spatially resolved one-dimensional fast Fourier Transform (FFT) of a (100) surface without [Fig. 4(a)] and with [Fig. 4(b)] an MD simulation before the relaxation. In these semireciprocal plots, the vertical axis aligns with the (100) surface cell depicted

in Fig. 4(c) and the density shown in Fig. 4(d), which corresponds to the z direction in the coordinate system, and with the Gibbs dividing surface corresponding to the zero of the scale. The horizontal axis shows the Fourier transform of the atom density of the cell in [Fig. 4(c)] at the corresponding distance from the surface.

In Fig. 4(a), which has been computed from the statically relaxed structure, the index reflections do not change significantly toward the surface, indicating that the order of ions is preserved. This, however, changes in [Fig. 4(b)], which shows the partial Fourier transform of the reconstructed (100) surface. Although the persistence of low-index reflections confirms that long-range order is still present, the short-range order of the crystal changes toward the surface. First, there is a shift of the reflection at $k = 6.8\text{--}7.6\text{ nm}^{-1}$ (marked with an arrow). This, together with the loss of signals at high k (encircled area), indicates the loss of high-index reflections due to the reduction of short-range order. Hence, the crystal amorphizes toward the surface, with the PS_4^{3-} tetrahedra remaining in place, though partly rotated. Furthermore, the lithium ions are no longer at clearly defined lattice sites. This also explains the higher similarity of surface energies for the different reconstructed surfaces, as the partly amorphized surface complexions are able to reorient high-energy surface features and are thus less dependent on the Miller index of the surface and the underlying bulk crystal orientation. Based on the distance-resolved profiles in Fig. 4(b), one can observe that the loss of short-range order associated with the surface reconstruction extends about 1 nm into the surface (indicated by a dashed white line). In Fig. 4(d), we show that the atom density of the cell increases toward the surface. The amorphization thus also leads to a partial intrusion into the empty sites in the LPS crystal, leading to a denser packing. In Fig. 4(d), we also show the diffusion coefficient (blue line) of the lithium ions computed in 5-Å-thick slices of the z axis of the surface slab. The middle of each slice is used as the z -axis value, e.g., the data point at 2.5 Å covers the distance 0–5 Å from the surface in the z direction. The diffusion decreases toward the surface, which is most likely related to the increased density, as the surface collapse during reconstruction populates the empty sites and thus reduces the number of jump destinations for the ions, which diffuse by hopping between nearest-neighbor vacancy sites in bulk LPS [32]. We have found this decrease of ionic conductivity for most investigated surfaces and it seems to be independent of the diffusion direction (see Fig. S7 in the Supplemental Material [62]). Notably, surfaces such as (210), which exhibit lower structural collapse and small energy change after MD relaxation (see Fig. 4), tend to show a smaller reduction in surface diffusion coefficients (for more detail, see Fig. S8 in the Supplemental Material [62]).

The observed surface reconstruction meets perfectly the criteria to be classified as a surface complexion [60,66],

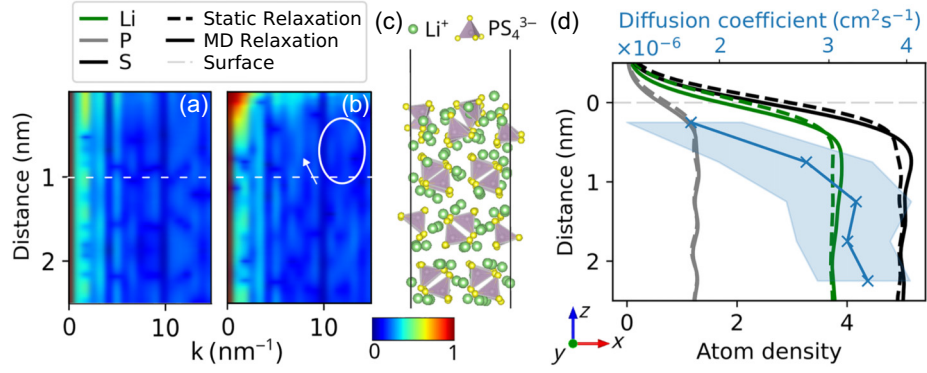


FIG. 4. The properties of the (100) surfaces after the formation of the complexion. A partial Fourier transform of the density of a cell with a (100) surface at $z = 0$ of the relaxed cell of (a) the static relaxation and (b) after an MD simulation and relaxation. The density is mimicked by overlaying each atom with a normalized Gaussian (for details, see Sec. IV). Areas remarkably different in the surface area in comparison to (a) are marked with a white arrow or are encircled. (c) An image of the surface aligned with the vertical axis in (a), (b), and (d). (d) The ionic diffusion coefficient (blue) from MD simulations for the reconstructed surface on a logarithmic scale with the standard deviation of the three MD simulations per surface displayed as an envelope. Also, (d) depicts the element-resolved densities (green, gray, and black) after an MD simulation followed by a relaxation (solid) compared to a static relaxation (dashed).

which feature typically (partial) amorphization, a thickness of around 1 nm, and distinctly different properties relative to the bulk. Complexions have been shown to be the most stable surface termination for other materials [61,66] as well as some material interfaces [3,67–70]. Experimentally, highly surface-sensitive methods are needed to resolve the surface structure and its properties, because the surface complexion is very thin.

C. Dynamical behavior of the surface complexion

As we have already discussed, room-temperature simulations of the complexion show a dynamical evolution of the structure. In order to characterize this further, we analyze the behavior of the phosphorous-centered atomic environments, using smooth overlap of atomic position (SOAP) features to capture the spatial distribution of S, P, and Li neighbors. In order to deemphasize short-time local fluctuations, and inspired by approaches that identify long-time behavior of structural descriptors [71–77], we perform a moving average of the descriptors over the trajectory

$$\bar{\zeta}(A_i, t) = \int ds \zeta(A_i, s) g(s - t). \quad (1)$$

The resulting time-averaged descriptor $\bar{\zeta}$ for the atom i in structure A at time t is thus obtained by integrating the descriptor in a time interval discretized in s and broadened by a Gaussian g .

We then perform a principal-component analysis (PCA) of the time-averaged descriptors. The results of this analysis are shown in Fig. 5 (top). In the figure, separate colors are used for each of the four surface tetrahedra and their individual positions in the simulation cell are displayed,

with the color coding used shown in the left inset of the depicted PCA.

The PCA shows that there are two distinct states for PS_4 tetrahedra in the complexion, with one larger state

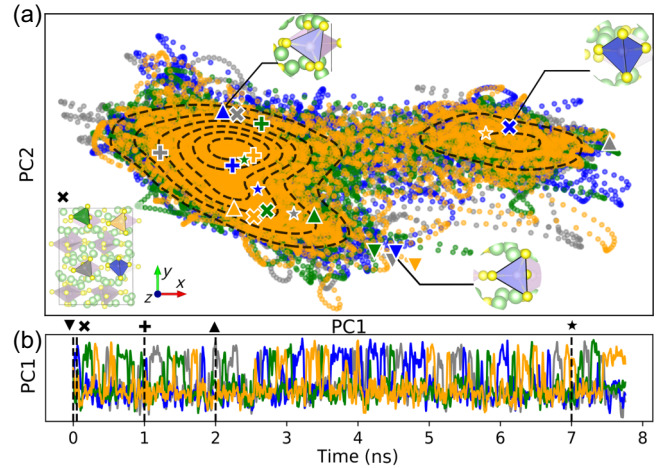


FIG. 5. (a) Principal-component analysis (PCA) of the atomic environments of the phosphorous atoms with time-averaged smooth overlap of atomic position (SOAP) vectors, during one 7.75-ns-long MD simulation at 500 K of a (100) surface. The trajectories of the different tetrahedra are visualized in gray, blue, green, and orange (compare their respective locations in the top view of the surface at the bottom left). The black dashed lines represent the level curves, showing the position of the two minima. Certain points in time are indicated with special markers ($\blacktriangledown$, $\times$, $+$, $\blacktriangle$, and $\star$) corresponding to the initial surface structure obtained from a DFT relaxation ($\blacktriangledown$), as well as tetrahedra environments at 0.05 ns, 1 ns, 2 ns, and 7 ns of the molecular-dynamics simulation [cf. the corresponding markers in (b)]. (b) The temporal evolution of PC1.

on the left corresponding to tetrahedra exposing one plane to the surface and a more localized state on the top right of the PCA that consists of tetrahedra with an exposed edge on the surface. These states are clearly separated by the first principal component (PC1), which correlates with the overall coordination number of the phosphorous within a cutoff of 5.5 Å (cf. Fig. S11 in the Supplemental Material [62]). However, the coordination number offers a less clear-cut separation of the two states (cf. Fig. S10 in the Supplemental Material [62]). The correlation of PC1 with the ionic coordination of the phosphorous roots from the redistribution of the surrounding atoms, and especially lithium ions, according to surface tetrahedra alignment, resulting in a higher coordination and slight “burying” of the edge-exposing tetrahedra. This correlation also explains the wider spread of the left cluster in the PCA, which includes surface tetrahedra with their exposed plane completely parallel to the surface (left top of PCA in Fig. 5; cf. the round inset in the top middle), as well as tetrahedra with exposed planes that are more tilted relative to the surface (bottom middle area of Fig. 5 and the corresponding round inset) and thus more “buried” into the surface.

The temporal evolution of PC1, as depicted at the bottom of Fig. 5, shows rapid switches of the tetrahedra between the two states with lifetimes in the order of around 100 ps. Notably, at any point in time just one tetrahedron is switching to this state, showing that there is a coupling between neighboring tetrahedra. This correlated flipping aligns very well with the mechanism of transitions between

different polymorphs [36]. Nevertheless, to rule out finite-size effects from this observation, we have performed similar simulations for larger atomistic cells, which have shown still active switching between the surface states (cf. Sec. S6 in the Supplemental Material [62]). Note that these simulations have been carried out at 500 K; however, a conservative estimation of the reaction rate at 300 K shows that this is still a process that takes place on a timescale of less than 200 ms (cf. Sec. S-E 3 in the Supplemental Material [62]). Thus, the surface is highly dynamic in operating conditions and a correct description of its reactivity must include these surface reconstruction phenomena. To obtain an indication of the effect of these dynamic structural changes on the reactivity of the surface, we have performed electronic structure calculations.

D. Electronic structure of the surfaces

In Fig. 6(a), we show the density of states (DOS) of the relaxed bulk structure, the statically relaxed and MD-relaxed surfaces, as well as the averaged DOS of four surface structures taken directly from the MD simulation at 500 K without relaxation, which is closer to the realistic operation conditions of LIBs. The DOS of the bulk structure has the largest band gap (4.61 eV), which is slightly narrowed to 4.45 eV at the statically relaxed surface and reduced further to 3.98 eV for the MD-relaxed structure. For the structures taken directly from the MD simulation without relaxation, the band gap is renormalized to 3.31 eV, as a consequence of thermal disorder.

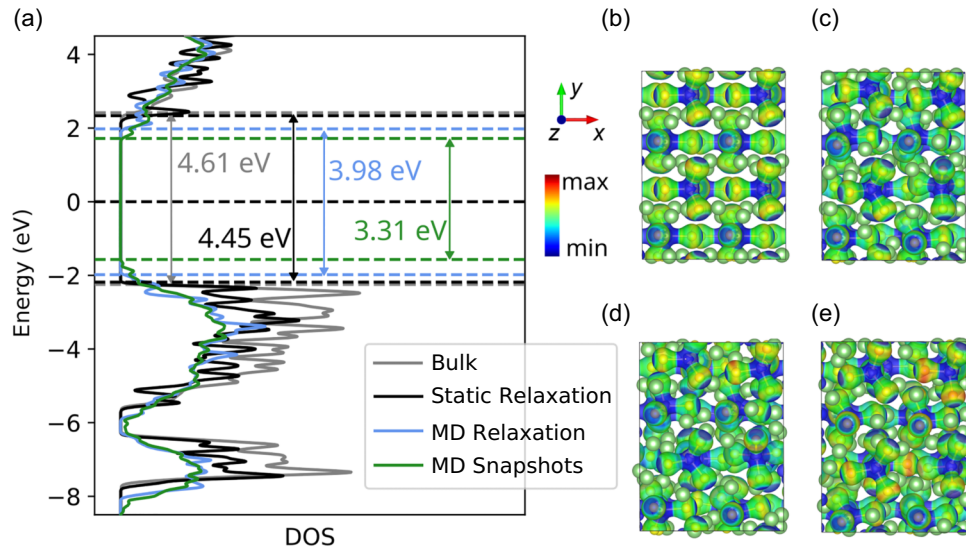


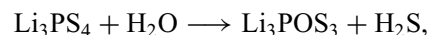
FIG. 6. The electronic structure of the (100) surface complex. (a) The density of state (DOS) of the LPS bulk, a statically relaxed structure, an MD-relaxed structure with a rotated tetrahedron, and snapshots from an MD simulation. (b)–(e) The top view of the electrostatic potential computed with DFT of a (100) surface for (b) the statically relaxed structure, (c) a relaxed MD structure with a rotated tetrahedron, taken after 50 ps, as well as (d), (e) unrelaxed MD snapshots at 50 ps and 1000 ps, respectively. The isosurface level used was 0.074 a_0^{-3} and the electrostatic potentials were aligned so that the electrostatic potential of the fixed atom layer aligned (cf. Fig. S24 in the Supplemental Material [62]).

The partial density of states (pDOS) reveals that for all structures, the highest occupied states are the sulfur p -states, whereas the lowest unoccupied states consist of sulfur p - and d -states (cf. Fig. S18 in the Supplemental Material [62]).

In Figs. 6(b)–6(e), we illustrate the electrostatic potential of the statically relaxed [Fig. 6(b)] and the MD-relaxed [Fig. 6(c)] surfaces and unrelaxed MD snapshots [Figs. 6(d) and 6(e)] in the same potential range for the top view of a (100) surface (for other views, see Figs. S20, S21, S22, and S23 in the Supplemental Material [62]). The statically relaxed structure has a homogeneous distribution of the electrostatic potential at the surface, in which all PS_4^{3-} tetrahedra have the same maximum, which is similar to the potential of the underlying bulk. In contrast, the electrostatic potential of the MD-relaxed structure varies more between the different tetrahedra and individual sulfur atoms. This effect is even more pronounced for the MD snapshots, where the electrostatic potential shows local fluctuations that also change between the snapshots. Overall, the structure appears to be very dynamical, with constant alteration of the surface moieties and thus reactive sites. The broader range of local potentials of such a dynamic surface will obviously have implications for the study of the surface reactivity. However, to quantify the impact of the surface dynamics and the concomitant fluctuations of the electrostatic potential on the surface reactivity, a more detailed analysis of the relevant molecules and reaction pathways is needed.

E. Impact of the complexion on surface reactivity

In the previous sections, we have shown that the LPS surface is highly dynamic and undergoes heavy reconstruction, leading to an increase in stability and the emergence of highly heterogeneous surface sites. To provide a more direct assessment of the influence of the surface heterogeneity on its reactivity, we consider the case of LPS exposed to moisture, which is known to release toxic H_2S gas [14,20],



and is one of the problems limiting the practical application of this class of SE materials. In this section, we investigate the thermodynamic stability of the educt and product of this reaction.

In Fig. 7, we illustrate the potential energy of the statically relaxed and MD-reconstructed (100) LPS surfaces with a gas-phase water molecule (gray and blue, darker bars), as well as with the reaction product in which one sulfur of a surface PS_4 tetrahedron is exchanged with the oxygen from the water, forming H_2S . The energy of the statically relaxed surface with a gas-phase H_2O serves as reference for the potential energy. To allow for a fair comparison, we have started from the statically and MD-relaxed structures to generate the product structures and relax them statically. We verified all energies by running DFT calculations on the relaxed structures, finding an excellent agreement [the root-mean-square error (RMSE)

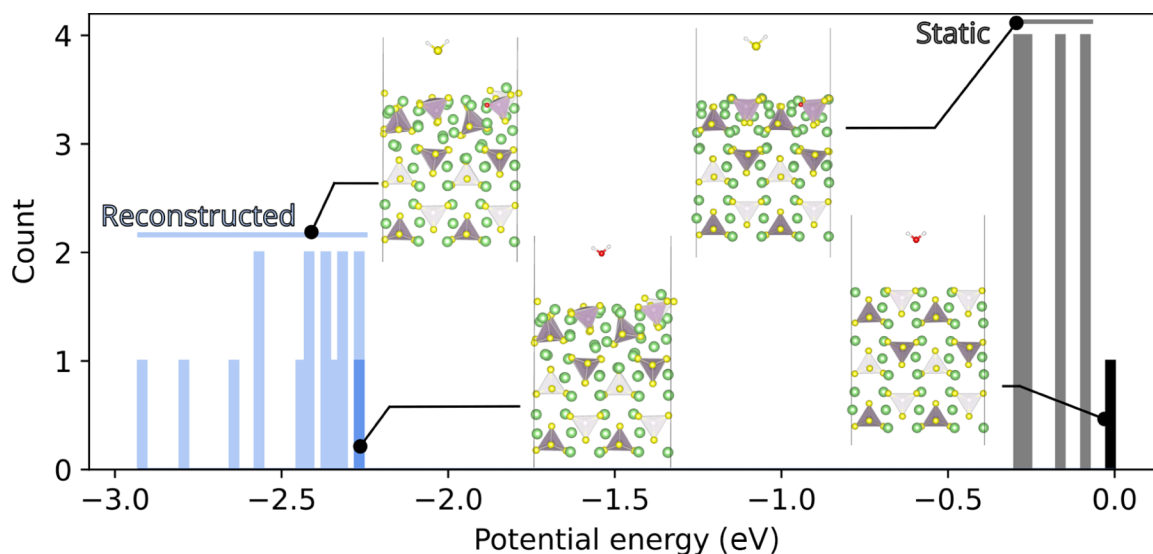


FIG. 7. The potential energy of the static and reconstructed (100) LPS surface with water (solid gray and blue bars) as well as its possible reaction products, LPS with one oxygen replacing a surface sulfur and H_2S (half-transparent gray and blue bars for initial static and reconstructed structures, respectively). We have used a 2×2 unit cell in the x - y direction, having four surface tetrahedra and containing 192 atoms in total, for which the x - z -planar view is shown as insets for the different states. The color coding is as follows: hydrogen, white; lithium, green; oxygen, red; phosphorous, gray; sulfur, yellow. For the swapped states, one of the 16 possible structures is pictured. All starting and swapped structures have been statically relaxed and energies verified with DFT (the root mean-square-error between DFT and PET-LPS is = 1.7 meV/atom).

between the point-edge transformer (PET)–LPS model prediction and DFT is 1.7 meV/atom]. In the static case, the reaction is always exothermic, with the release of H_2S leading to energy gains between -0.293 and -0.092 eV. The O substitution breaks the symmetry of the surface and we observe extended rearrangements of Li atoms in the surface layer, which contribute to the energy gain.

As discussed above, the formation of a surface complex results in extended atomic rearrangements and a large stabilization of the (100) surface, as evidenced by the dramatic drop in the potential energy (-2.277 eV for this 192-atom supercell). One could expect this better relaxed stable surface structure to be *less* reactive but this is not the case. The heterogeneity of the surface sites, which we have observed in terms of the charge density and electrostatic potential, is reflected in a much broader distribution of the reaction enthalpy, ranging between sites that only show a slight decrease in energy upon O substitution (-0.012 eV) and sites that are much more reactive, leading to exothermic reaction energies of up to -0.654 eV—more than twice as large as for the statically relaxed surface. As the most-reactive states are the ones that we can expect to be involved in the early stages of the surface reaction with water, we conclude that despite being more stable in absolute terms, the formation of a complex generates a more reactive surface, with a larger variety of possible reaction channels for the initial step of the degradation of LPS with water. It is likely that further relaxation with MD—or, more realistically, a finite-temperature study of the reactivity that takes the dynamical nature of the complex into account—would increase the thermodynamic stability of the products even further. We also expect that the surface heterogeneity will have a similar impact when investigating the reaction with surface-passivating agents, which are being considered to improve the stability of LPS, further underscoring the importance of taking complexes into account in future studies of this system.

III. CONCLUSIONS

Leveraging the recent advances in molecular-simulation methods, we have been able to uncover the surface complexes of β -LPS under realistic conditions. Our investigation shows that the surfaces reconstruct when temperature fluctuations occur leading to marked differences in structure and surface energies compared to static geometry relaxation, which retains much of the initial symmetry.

We have thus been able to identify states with a lower surface energy for each investigated Miller index [except for (210), which did not show substantial relaxation]. These new surfaces are more similar in energy, which influences the Wulff shape to be more round compared to Wulff shapes previously reported for this material, which have been based on simple DFT relaxations. Furthermore,

these newly identified surface reconstructions not only feature different properties compared to the bulk, including higher density, lower conductivity, partial amorphization, and a narrower band gap, but also structural defects associated with the rotation and reorientation of PS_4 tetrahedra.

By analyzing MD trajectories in terms of time-averaged SOAP features, we have been able to reveal the presence of clearly distinct states for the tetrahedra, as well as their dynamics. The surface complex is dynamical at room temperature and constantly moving between different surface states. A further investigation of the surface complex has revealed large fluctuations of the electrostatic potential during the dynamics, leading to a broader range of local potentials and indicating the presence of surface sites with widely different reactivities. The practical and technological implications of this heterogeneity are even clearer when considering the surface reactivity with water—one of the main issues hindering application of LPSs as SSEs. We have found that the thermodynamic stability of surface PS_4 groups against release of H_2S varies greatly on the MD-reconstructed surface and that for the most reactive sites, the reaction enthalpy can be over twice the value computed for the statically relaxed surface, despite the latter being far less stable to start with.

Overall, this study demonstrates the importance of sampling surface reconstructions in realistic thermodynamic conditions, to accurately determine the structure, energetics, and electronic properties. These observations have obvious implications for the study of surface reactivity, as well as cathode-electrolyte interfaces, although an explicit study of surface reactivity requires further extending the chemical space covered by our machine-learning potential, as well as access to longer timescales to sample dynamics and capture rare and activated events.

The concept of a heterogeneous surface with sites having widely different reactivities is also of direct relevance to guide the design of passivation strategies, as it indicates that it might not be necessary to protect every surface PS_4 group but only those that are most reactive. Beyond LPSs, our study reinforces the notion that has already become mainstream in the study of heterogeneous catalysis [78,79] that surfaces and interfaces cannot be treated as idealized static objects but often exhibit a dynamic behavior, which is commonly still ignored in simulations. Accurate yet inexpensive machine-learning potentials, such as the one we have used here, are the ideal tool to perform simulations that achieve a realistic description of these complex interfacial phenomena.

IV. METHODS

A. Dataset generation

Structures have been manipulated using the Atomic Simulation Environment (ASE) 3.22 [80]. Surfaces have been generated with PYMATGEN 2024.11.13 [81], such that

no P-S bonds have been broken and two sets of slabs, one with a minimum of 2-nm thickness and one with a 5-nm thickness, have been obtained. The thinner set has been used to generate the training data and the larger one to investigate surface reconstructions with MD (see below).

To create an initial set of training structures of the 2-nm surfaces, we have performed GEN1-xTB [82] calculations with DFTB+ [83] and i-PI [84]. These have later been complemented by MD simulations with an earlier version of our MLIP model. For all MD simulations, the most diverse have been selected, with farthest-point sampling from SCIKIT-MATTER [85], computed with DFT and added to the training set.

The resulting training set contains bulk and surface structures for all three crystal polymorphs (α , β , and γ), also including surfaces combined with relevant adsorbates (water and H_2S). To be precise, the data set consisted of a total of 6244 structures, of which 2432 were bulk, 657 were plain surfaces, 2140 were possible adsorbates such as water and H_2S as well as isolated PS_4 tetrahedra, 851 were surfaces with adsorbates, and 164 were $\text{Li}_3\text{PS}_{3-x}\text{O}_x$, with $0.75 \leq x \leq 3$. A first model, trained on this data set and called the point-edge transformer (PET) LPS, has been used for all simulations in this work.

B. Density-functional theory calculations

The DFT calculations have been performed using the Vienna *ab initio* simulation package (VASP 6.4.1) [86] with Perdew-Burke-Ernzerhof (PBE) pseudopotentials (semicore p and s states are considered valence states for Li and hard potentials for P and S). The functional used for relaxations performed at the DFT level and the creation of the dataset has been PBEsol [41], while PBE0 [87] has been used for the analysis of the electronic structure. For the surfaces, a dipole correction perpendicular to the surface slab and Grimme dispersion corrections with a zero-damping function have been used. The cells that have been used to compute the DOS and the electrostatic potential have all contained 72 Li, 24 P, and 96 S atoms [cf. Figs. 6(b) and 6(c)]. For the geometry optimization, the lowest 5 Å of the structure has been kept fixed to mimic bulk-like behavior. For the DOS of the MD snapshots, we have added and normalized the DOS of all four snapshots. Full images of the surfaces can be found in Figs. S20, S21, S22, and S23 in the Supplemental Material [62]. For the calculation of the partial DOS, we have projected on spheres centered on the individual atoms with the Shannon ionic radius of the corresponding element [88]. For the electrostatic potential, only the Hartree and ionic potential have been taken into account. The electrostatic potentials have been aligned such that the vacuum level of the fixed bulk structure has matched (cf. Fig. S24 in the Supplemental Material [62]). For the visualization of the electrostatic potential, we have

used a density isosurface level of 0.074 a_0^{-3} and electrostatic potentials on the isosurface ranging from -8.00 to -3.65 eV . The visualization has been done using VESTA 3.5.8 [89]. The corresponding pDOS has been visualized using SUMO [90].

C. MLIP fitting

We have trained a point-edge transformer (PET) [91] implemented in METATRAIN [92].

For training, we have used a training : validation : test-set split of 8:1:1. The resulting errors on the full test set were 3.9 meV/atom for the energies and 83.7 meV/Å for the forces. When only considering test structures containing Li, P, and S (= 305 structures), an even lower error of 2.9 meV/atom for energies and 54.5 meV/Å for forces has been observed (cf. Fig. S1 in the Supplemental Material [62]). We have used a Ziegler-Biersack-Littmark (ZBL) potential for short-range interactions. The obtained model has excellent agreement with PBEsol, both regarding mean errors on energies and forces and regarding more complex properties such as the bulk modulus, as is demonstrated in Tables S1 and S2 and Figs. S2, S3, and S4 in the Supplemental Material [62].

The model architecture includes two graph neural-network layers and two transformer layers of size 256 and head size 8, and uses a cutoff of 5 Å. The initial learning rate was 5×10^{-5} , the batch size was 50, and the energy to force weight for the loss was 0.05 and the loss was computed for each atom.

D. Atom density, ionic conductivity, and semireciprocal structure plots

To mimic the atomic density, the atomic positions have been overlaid with Gaussian functions in three-dimensional (3D) space. For Fig. 4(d), the density has been summed over the y direction to give a representative picture of the density of the full cell in this two-dimensional image. For the semireciprocal plots [Figs. 4(a) and 4(b)], the respective 3D atomic density obtained as described above has been computed for each z value binned in 0.1-Å bins. Each of these slices in the z direction has been further sliced in the y direction and the fast Fourier transform (FFT) has been computed (for only this one slice in the y direction to achieve higher resolution) to form a spatially resolved array of FFT signals. The atomic structures have been visualized using VESTA 3.5.8 [89]. To assess the ionic conductivity, we have performed MD simulations of 500 ps with a time step of 1 fs at NVT (500 K). Previously to this, all cells have been equilibrated under NPT conditions at 500 K and 1 bar for 20 ps. We have computed the tracer diffusion coefficients in the Einstein formalism, for which spatial resolution of the diffusion can

be achieved by calculating the lag time mean-square displacement for all lithium ions that have not left the region ± 2.5 Å around the specified point during the respective time periods [69,93]. To estimate the error of the calculations, we have performed three independent calculations for each surface.

E. Wulff constructions

The Wulff constructions have been calculated using WulffPack [94].

F. Molecular-dynamics simulations

To calculate the surface reconstructions, we have performed MD calculations of the 5-nm-thick surfaces obtained with PYMATGEN. The simulations have been performed in LAMMPS [95] with the PET MLIP via the metatensor software calculator [92]. First, we have slowly equilibrated the cells for 35 ps at 1.013 bar with a slowly increasing temperature from 0.1 to 300 K, with a time step of 0.5 fs. Then, we have run an *NVT*-ensemble calculation at 300 K for 250 ps; however, most surfaces have already been reconstructed after 50 ps. From these 250 ps long simulation, we have relaxed the structure with the lowest potential energy with the PET as a representative of the respective Miller index.

G. Temporally Gaussian-broadened SOAP and principal-component analysis

We have used a Gaussian broadening from SciPy [96] with a standard deviation for the Gaussian kernel of $\sigma = 5$ ps and “nearest” image treatment on the edges for the SOAP vectors (cutoff = 5.5 Å, $\text{Radial}_{\text{max}} = 6$, $\text{Angular}_{\text{max}} = 8$, Gaussian width = 0.3 Å, computed using FEATOMIC [98] to smoothen the noise on an MD-simulation trajectory (as described above but at 500 K) computed every 1 ps.

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The authors declare no conflict of interest.

DATA AVAILABILITY

The data that support the findings of this paper are openly available [99].

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