The development of all-solid-state lithium ion batteries has been hindered by the formation of a poorly conductive interphase at the interface between electrode and electrolyte materials. In the manuscript, we shed light on this problem by computationally evaluating potential lithium ion diffusion pathways through metastable arrangements of product phases that can form at 56 interfaces between common electrode and electrolyte materials. The evaluation of lithium-ion conductivities in the product phases is made possible by the use of machine-learned interatomic potentials trained on the fly. We identify likely reasons for the degradation of solid-state battery performance and discuss how these problems could be mitigated. These results provide enhanced understanding of how interface impedance growth limits the performance of all-solid-state lithium-ion batteries.
Ionic conduction through reaction products at the electrolyte/electrode interface in all-solid-state Li⁺ batteries

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ABSTRACT

All-solid-state lithium-ion batteries have attracted significant research interest for providing high power and energy densities with enhanced operational safety. Despite the discoveries of solid electrolyte materials with superionic conductivities, it remains a challenge to maintain high rate capability in all-solid lithium-ion batteries in long-term operation. The observed rate degradation has been attributed to reactivity and resistance at the electrode-electrolyte interfaces. We examine interfaces formed between eight electrolytes including garnet, LiPON and LGPS and seven electrode materials including NCM cathode and metallic Li anode and identify the most rapid lithium ion diffusion pathways through metastable arrangements of product phases that may precipitate out at each interface. Our analysis accounts for possible DFT error, metastability, and finite-temperature effects by statistically sampling thousands of possible phase diagrams for each interface. The lithium-ion conductivities in the product phases at the interface are evaluated using machine-learned interatomic potentials trained on the fly. In nearly all electrode-electrolyte interfaces we evaluate, we predict that lithium-ion conduction in the product phases making up the interphase region becomes the rate-limiting step for battery performance.

INTRODUCTION

Lithium ion batteries have become the dominant rechargeable energy storage devices for portable electronics and electric vehicles due to their unique properties such as high energy density, high rate capability, and long cycle life. These batteries convert Li chemical potential differences into electric current by shuttling lithium ions between two electrodes. Currently commercial lithium-ion batteries comprise carbonaceous anodes, lithiated transition metal oxides as cathodes, and conducting lithium salt (LiPF₆) dissolved in organic carbonates or esters as the electrolyte. These organic liquid electrolytes show high ionic conductivities and good electrochemical stability. There are, however, several drawbacks such as the thermal instability of LiPF₆ at high temperature, liquid electrolyte leakage and limited volumetric energy density. To resolve the intrinsic limitations of conventional lithium-ion batteries, all-solid-state batteries employing inorganic solid electrolytes are being studied widely as promising candidates for next-generation rechargeable batteries.

Considerable research efforts have focused on identifying solid-state electrolytes with high ionic conductivity. The lithium-ion conductivities of several families of solid electrolytes, such as Li₁₀GeP₂S₁₂ (LGPS) and Li₇P₃S₁₁, are approaching that of liquid electrolytes at 10⁻² S/cm. In particular, sulfide-based solid electrolytes are attracting much consideration, owing to their relatively high conductivities relative to oxide electrolytes and their moderate elastic moduli. Despite the high bulk conductivity of battery components, the actual rate capability of all-solid-state batteries is generally lower than estimated, especially at high states of charge or at high temperatures. The bottleneck for charge carrier transfer is attributed to the interface
region between the solid electrolyte and the electrode. The solid electrolytes are typically incompatible with the electrode materials and yield decomposition products during battery cycling, similar to the formation of a solid electrolyte interphase (SEI) between the liquid organic electrolyte and electrode materials in conventional Li-ion batteries. The reason for this instability can be understood by thermodynamic principles. First-principles calculations have confirmed that sulfide-based solid electrolyte materials have limited intrinsic electrochemical stability windows and that decomposition reactions of most solid electrolyte materials are thermodynamically favorable at common operating potentials of lithium-ion batteries. For example, the LGPS material is delithiated and oxidized starting at 2.14 V, and the final oxidation products of $P_2S_5$, $GeS_2$, and S are formed at the equilibrium oxidation potential of 2.31 V.

In conventional Li$^+$ batteries, properly formed SEIs have negligible electrical conductivity and high lithium ion selectivity and permeability, and they can enhance the long-term performance of Li$^+$ batteries. Contrary to the advantageous properties of SEIs in conventional batteries, most solid-solid interphases are highly resistive to ionic transport with continuous thickness growth, which contributes to the increased impedance of charge transfer in all-solid Li$^+$ batteries. Along the progression of knowledge regarding the SEI from its discovery in 1979, several models of the morphology and self-passivation mechanism have been proposed. The “mosaic structure” and the inorganic/organic bilayer model of the SEI are the most widely accepted models. They both describe the SEI as a two-layer film composed of multiple organic and inorganic heterogeneous layers. The apparent SEI ionic impedance depends on the properties of SEI sub-layers. Analogous to the mosaic microphase model of SEI, a complicated heterogeneous multi-component interphase is expected at the solid-solid interface.

Recent research has provided insights into the character of solid-solid interphases. At the interface between an LiCoO$_2$ electrode and Li$_2$S–P$_2$S$_5$, mutual diffusion of Co, P, and S was identified at the noncoated interface by transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy. At the LiCoO$_2$/LGPS interface, a wide variety of decomposition products have been suggested by X-ray photoelectron spectroscopy, including GeS$_2$ and polysulfide species with different chain lengths. The total impedance at this interface increases by a factor of 5 after 100 cycles. These results indicate that the spontaneously formed interphase is typically heterogeneous and the product phases exhibit a wide range of ionic conductivities. Due to the high complexity of cathode/solid electrolyte region (typically five or more elements are present) and the limited resolution of experimental measurement, it is very challenging to characterize the exact composition of the phases present at the interface. Despite the extensive studies on the origin of reactivity at the electrolyte/electrode interface, the microstructure and composition of product phases at the interface are still not fully understood.
Although the exact composition and size of the phases in the interphase remain unknown, the possible distribution of phases at equilibrium can be extracted from an ab initio phase diagram. The system reaches local thermodynamic equilibrium if a pair of contacting phases corresponds to a tie-line on the phase diagram. For example, at the interface between a metallic Li anode and the electrolyte LiPON, the possible reaction products include $\beta$-Li$_3$PO$_4$, Li$_2$O, Li$_3$N, and Li$_3$P. (Here we use Li$_2$PNO$_2$ as a representative of the LiPON electrolytes.) As can be seen from the Li-P-O-N phase diagram in Figure 1a, Li$_3$P is connected by tie-lines with Li$_3$N, Li$_3$PNO$_2$ and Li, which means Li/Li$_3$P/LiPON can coexist with each interface (indicated by the forward slashes) in local thermodynamic equilibrium, as can Li/Li$_3$N/Li$_3$P/LiPON. Since Li$_3$N and Li$_3$P are known to be good ionic conductors, the lithium ions are likely to diffuse along interphase segments of Li$_3$P and Li$_3$N (Figure 1c). The rate capability degradation caused by interphase formation in this case is expected to be minimal despite the formation of poor ionic conductors Li$_2$O and $\beta$-Li$_3$PO$_4$, which agrees with the good cyclability verified by experiment. On the other hand, if Li$_6$PS$_5$Br were used as the solid electrolyte as shown in Figure 1b, it would react and would not locally co-exist (share an interface) with Li$_3$P, as they are not connected by a tie line. This interface could be stabilized by the formation of Li$_2$S between Li$_3$P and Li$_6$PS$_5$Br as illustrated in Figure 1d, but this degrades the interfacial properties as Li$_2$S is a poor lithium-ion conductor. These examples suggest that relatively fast Li$^+$ transfer through the electrode-electrolyte interphase can be expected with the presence of a percolating interphase segment in which the product phases all exhibit acceptable Li$^+$ diffusion rates. We will use the term “product phases” to refer to the new phases that form as products of the reaction between the electrode and electrolyte.
Figure 1. Quaternary phase diagram defined by the half cell of Li anode and the solid electrolyte a) LiPON and b) Li$_6$PS$_5$Br. The stable phases and tie-lines most relevant to solid electrolyte-anode interfacial reaction are highlighted in blue. c) and d) Schematic diagram of phase equilibria at the interface between Li anode and solid electrolyte. Any two phases in contact are in local thermodynamic equilibrium corresponding to a tie-line on phase diagrams a) and b), respectively.

In this work, to search for viable diffusion pathways, we developed a systematic algorithm that identifies Li-containing product phases likely to form and pathways through the interphase for which all solid-solid interfaces are likely to be in local thermodynamic equilibrium (we will refer to these as “stable pathways”). We have used this algorithm to evaluate the interfaces of 32 electrolyte/cathode pairs and 24 electrolyte/anode pairs. Of these, only one combination, LLZO/Li, is predicted to establish a stable interface without any reaction products. For the remaining interfaces, it can be expected that an interphase will form to bridge the chemical potential gap between the solid electrolyte and the electrode. To estimate the rate of lithium ion transfer through the interphase we evaluate the ionic conductivity of all sub-phases with molecular dynamics using a recently developed active learning interatomic potential scheme.\textsuperscript{22} Owing to the higher polarization ability of S$^2^-$ than O$^{2^-}$, higher ionic conductivity is anticipated in the sulfides than the oxides.\textsuperscript{23} As confirmed by the molecular dynamics simulations, the
oxide (including the phosphate and sulfate) components of the interphases tend to be the rate-limiting step for Li⁺ transfer and significantly contribute to the increase of impedance. Among the reactive interfaces, only the LiPON/Li interface develops a stable pathway for ionic transfer in which the Li⁺ transfer time is predicted to be comparable to that through the solid electrolyte itself. At other interfaces the predicted ionic conductivity through the stable pathways that could form is more than five orders of magnitude lower than that in the state-of-the-art solid electrolytes, which indicates that interphase growth of a few nanometers could significantly diminish the fast ionic conduction in the solid electrolyte material, which is typically hundreds of microns in thickness.

**METHODOLOGY**

2.1 Identifying stable interfaces between reaction products

To determine the stability of the interfaces, we used the convex hull method.²⁴-²⁶ Two phases can coexist in local thermodynamic equilibrium if they are connected by a tie-line on the phase diagram. Under this condition, no phase decomposition or additional interfacial reaction is predicted to happen. For each combination of electrode and solid electrolyte, we obtained DFT-calculated energies for the materials in the chemical space spanned by the two compounds from the Materials Project database²⁷ and used the qmpy Python package²⁸ to calculate convex hulls of 0 K phase diagram. The tie-lines on these convex hulls were used to identify stable pathways, and pathways consisting of lithium-containing materials were further evaluated for lithium-ion conductivity as described below. We evaluated pathways containing up to three components, as we found that the rate-limiting materials for three-component pathways were the same as for two-component pathways.

The composition and energy of the electrode material depends on the state of charge of the battery. To ensure stability across the chemical potential range spanned by the different states of charge, a material connected by a tie line to the charged state of an electrode was only considered to form a locally stable interface if it was also connected to the discharged state, and vice versa. In situations in which where a phase in contact with the electrode is electronically conductive the lithium chemical potential in this phase can also be expected to vary with the state of charge. Here we conservatively consider a material to be potentially electrically conductive if its GGA bandgap is less than 1 eV. In this case, we evaluated the electrochemical stability of adjacent interphase components on the electrolyte side using the grand-potential phase diagram method²⁹ as implemented in pymatgen.³⁰ If the electrochemical stability window is not wide enough to span the electrode operating voltage, the pathway does not qualify as a stable pathway.

2.2 Monte-Carlo sampling of phase diagrams
Figure 2. A hypothetical pseudo-binary phase diagram where the vertical and horizontal axes correspond to formation energy and composition, respectively. Formation energies phase are shown with an inherent error bar of 31 meV/atom. With originally calculated (unperturbed) energies in (a), phase A forms between the electrolyte and the cathode. The shape and composition of convex hull evolves during the sampling. The phase diagram in (b) shows an example of the energy-perturbed sample in Monte Carlo sampling, where formation of a double-layer interphase (with both A and B phases) is predicted.

Thermodynamic stability of materials can be estimated by constructing a convex hull of DFT-calculated formation energies with respect to composition. Phases that are on the convex hull are predicted to be stable at 0 K. However, many phases with formation energies above the calculated 0 K convex hull exist in nature for extended periods of time, as a result of either DFT error, entropic stabilization, or phase metastability preserved by a high kinetic barrier of decomposition. Quite a few state-of-the-art solid electrolyte materials such as Li₁₀Ge(PS₆)₂, Li₁₀Sn(PS₆)₂ and Li₇P₂S₆ have been determined to be metastable theoretically and experimentally. Local phase equilibria cannot be directly established for an interface containing a metastable phase, as the phase is not by itself thermodynamically stable. One way to conduct stability analysis on these materials is to manually place the metastable electrolyte exactly on the 0 K convex hull, but the manual adjustment of one phase might bias the relative stability of other phases unphysically.

To take phases above convex hull into consideration systematically, we combined ab initio phase diagrams with Monte Carlo sampling. We applied 20,000 normally distributed perturbations to the energies of each material in the phase diagram, where the standard deviation (σ) of the normal distribution was assumed to be the sum of the reported average DFT reaction energy error (24 meV/atom) and average error due to ignoring finite temperature effects (7 meV/atom). The statistical analysis of the phase diagram is illustrated by a hypothetical pseudo-binary phase diagram in Figure 2. This approach gives phases originally above the hull a chance to be stable with a probability that is inversely related to the magnitude
of their energy above the convex hull. Similarly, it also allows us to identify phases at the interface that may not be able to coexist in thermodynamic equilibrium but, due to a small reaction energy, are relatively likely to become kinetically stable. During the statistical sampling of the phase diagrams, we counted the occurrence of Li-containing pathways, and we evaluated the Li-ion conductivity of all pathways that appear in more than 50% of the samples in which both electrolyte and electrode are on the statistically sampled convex hull.

2.3 Calculating ionic conductivity

DFT calculations

The training data for machine-learned potentials were ab-initio molecular dynamics (AIMD) simulations obtained using the Vienna Ab-initio Simulation Package (VASP) and the projector augmented wave approach. In line with previous reports, the calculation parameters were selected to balance accuracy versus computational cost. We used a plane wave energy cut-off of 400 eV and a minimal Γ-point-only k-point mesh. Computations were performed with spin polarization and with magnetic ions initialized in a high-spin ferromagnetic state for materials containing transition metal atom(s). Non-spin-polarized calculations were performed otherwise. A time step of 2 fs was adopted. The supercell sizes were constructed to ensure there was at least a 9 Å separation between neighboring images to avoid periodic boundary effects. The lattice parameter was fixed at that of the cell fully relaxed at 0 K.

MTP learning on-the-fly molecular dynamics (LOTF-MD)

The ionic conductivity of each component in the interphase was computed using a scheme we developed recently that is based on learning-on-the-fly molecular dynamics (LOTF-MD) and moment tensor potentials (MTP). The use of this scheme allows us to gather orders of magnitude more data than can be achieved using AIMD with little loss of accuracy in the calculated energies, resulting in more accurate estimates of ionic conductivity. For each structure the MTP was initially trained on 15 ps (2 fs per time step) of an AIMD simulation at 1000 K. The molecular dynamics simulations used to evaluate ionic conductivity were performed with the trained MTP in LAMMPS. The interface between moment tensor potential molecular dynamics and DFT geometry optimization was carried out by the Machine Learning of Interatomic Potentials (MLIP) software package. Details of the active learning criteria as well as experimental benchmark results can be found in our previous report. In this study, we used the following automated workflow to calculate the ionic conductivity of different phases that may be present at the interface. The simulation temperature was initialized at 1000 K for each material and decremented by 50 K until the diffusivity was so low that the total mean squared displacement did not reach 2000 Å² within 200 ns. To identify the onset of possible melting, we calculated the mean squared displacement of species other than lithium. We determined that melting occurred if the mean squared displacement of non-lithium species
exceeded 3 Å². If melting was detected, we decreased the simulation temperature until the structure remained intact during the molecular dynamics run. We performed molecular dynamics for 4 nanoseconds at 1000 K for all interphase components as an initial screening. Using a typical hopping distance of 3 Å between neighboring Li sites and an activation energy of 0.5 eV, we estimate that the room-temperature diffusivity would be \(5.06 \times 10^{-14} \text{ cm}^2/\text{sec}\) or lower if no Li diffusion is observed in 4 ns at 1000 K (see Supplementary Information S1 for derivation). Thus if no Li⁺ hopping was observed at 1000 K for 4 ns, the phase was considered to be ionically insulating at room temperature and no additional molecular dynamics simulations were run on it. For structures in which Li⁺ exhibited a mean squared displacement larger than 9 square angstroms at 1000 K, multi-temperature MD simulations were performed below the melting point for at least 4 ns each until the total mean square displacement of Li⁺ reached 2000 square angstroms, which has been reported by He, X. F., et al. to be a sufficient sample size for accurate statistical analysis. The lowest five qualifying temperatures were used to fit an Arrhenius relationship to determine the activation energy for diffusion and estimate the room-temperature diffusivity. The room-temperature conductivity \(\sigma_{300K}\) was calculated using the Nernst–Einstein relation under the assumption that the Haven ratio is equal to one:

\[
\sigma_{300K} = \frac{n e^2 z^2}{k_B T} D_{300K}
\]  

(1)

where \(n\) is the volume density of the diffusing species, \(e\) is the unit electron charge, \(z\) is the charge of the ionic conductor (here 1 for Li⁺), and \(D_{300K}\) is the extrapolated room-temperature tracer diffusivity.

RESULTS AND DISCUSSION

We investigated the interfaces between eight solid electrolytes and seven representative electrode materials, listed in Table 1 for cathodes and Table 2 for anodes. In each of the 32 pairs of solid electrolyte/cathode half cells in Table 1, lithium ions have to pass through at least one product phase when shuttling between the solid electrolyte and the electrode. This is also the case for 24 pairs of solid electrolyte/anode listed in Table 2, except for LLZO/Li which establishes a stable interface without any interfacial chemical reaction.
Table 1. Li-containing stable pathways between different pairs of cathode materials and solid electrolytes.

| Solid electrolyte | Cathode | LiFePO4 / FePO4 | LiMn2O4 / MnO2 | Li2NiCoMnO6 / LiNiCoMnO6 |
|-------------------|---------|-----------------|----------------|-------------------------|
| Li2Zr2O12 (LLZO) | LiCoO2 / LiC2O4 (LCO) | LiFePO4 / FePO4 | LiMn2O4 / MnO2 | Li2NiCoMnO6 / LiNiCoMnO6 |
| Li2PSi11 | Li3PO4 | Li2PO3 | Li3PO4 | Li2PO4 |
| Li10GeP2S12 (LGPS) | Li3PO4 | Li3PO4 | Li3PO4 | Li3PO4 |
| Li10SiP2S12 | Li3PO4 | Li3PO4 | Li3PO4 | Li3PO4 |
| Li6PS4Br | Li3PO4 | Li3PO4 | Li3PO4 | Li3PO4 |
Table 2. Li-containing stable pathways between different pairs of anode materials and solid electrolytes.

| Oxide-based Solid electrolyte | Anode                        | Li    | Li$_2$Ti$_3$O$_{12}$ / Li$_2$Ti$_3$O$_{12}$ (LTO) |
|--------------------------------|------------------------------|-------|--------------------------------------------------|
| Li$_6$PS$_3$Cl                 | Li$_2$S/Li$_2$SO$_4$         | LiCl  | Li$_2$S/Li$_2$SO$_4$                             |
|                                | Li$_3$PO$_4$                 | LiCl  | Li$_2$S/Li$_2$Cl                                |
|                                | Li$_2$S/LiCl                 | LiCl  | Li$_2$PO$_4$/Li$_2$SO$_4$                        |
|                                | LiCl                         | LiCl  | Li$_2$PO$_4$                                    |
|                                | LiCl                         | LiCl  | Li$_3$PO$_4$                                    |
| Li$_2$O$_3$/Li$_2$O             | Li$_2$O                      | LiCl  | Li$_2$O/Li$_2$TiO$_3$                           |
| Li$_2$O$_3$/Li$_2$CO$_3$        | Li$_2$O                      | Stable| Li$_2$ZrO$_3$/Li$_2$TiO$_3$                      |
| Li$_2$O                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$PO$_4$/Li$_2$O            | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$N$_3$/Li$_2$O             | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$N$_3$/Li$_2$PO$_4$/Li$_2$O | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$P$_3$S$_11$               | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
| Li$_2$S                        | Li$_2$PO$_4$/Li$_2$O          | Li$_2$PO$_4$/Li$_2$TiO$_3$ |
The stable pathways identified by our analysis include 21 lithium-containing materials. Of these, no site-to-site $\text{Li}^+$ hop was observed during 4 ns for $\beta$-$\text{Li}_3\text{PO}_4$, $\text{Li}_2\text{MnO}_3$, $\text{Li}_2\text{O}$, $\text{Li}_2\text{CoO}_3$, $\text{Li}_9\text{Co}_7\text{O}_{16}$, $\text{Li}_9\text{Mn}_{14}\text{O}_{32}$, $\text{LiN}_3$, $\text{Li}_2\text{TiO}_3$, $\text{Li}_2\text{CO}_3$ and $\text{Li}_{11}\text{Mn}_{13}\text{O}_{32}$ at 1000 K. Therefore these product phases are regarded as ionic insulators at operating temperature. Lithium ion diffusivities for the remaining materials are shown on the Arrhenius plot in Figure 3 with activation energies listed in Table 3. The computed activation energies for diffusion agree well with the experimentally characterized values except for $\text{Li}_2\text{O}_2$, for which we overestimate the activation energy by 0.7 eV. This might be explained by defects present in experimental samples that are not included in the simulation of the stoichiometric single crystal. As both experiments and calculations indicate that $\text{Li}_2\text{O}_2$ is a poor ionic conductor, this discrepancy does not affect our analysis of stable pathways.

Most all-solid $\text{Li}^+$ batteries to date use an inorganic solid electrolyte thicker than 200 µm whereas the reported thicknesses of the interphase region range from a few tens to a few hundreds of nanometers. As ionic conductivities for leading solid-state electrolytes are in the range of roughly $10^{-4}$ to $10^{-2}$ S/cm, we estimate that the ionic conductivity of the phase products need to be at least $10^{-8}$ S/cm to achieve a time frame for $\text{Li}^+$ transfer through the interphase region that is similar to that through the solid electrolyte layer. The only materials in our conductivity screen that exceed this value are $\text{Li}_3\text{PS}_4$, $\text{Li}_4\text{SnS}_4$, $\text{Li}_4\text{GeS}_4$, $\text{LiZr}_2\text{P}_2\text{O}_{12}$ and $\text{Li}_3\text{P}$, each of which have been employed as ionic conductor materials.
Figure 3. Arrhenius plot of diffusivity of interphase components obtained from molecular dynamics simulations using learning on-the-fly moment tensor potentials and the extrapolation diffusivities at room temperature denoted by dashed lines.
Table 3. Calculated activation energies and room-temperature ionic conductivities for Li⁺ diffusion through interphase components.

| MP entry id | Composition | $E_a$ (eV) | Ionic conductivity at 300K (S/cm) | Experimental value of $E_a$ and ionic conductivity at 300K |
|-------------|-------------|------------|-----------------------------------|-------------------------------------------------|
| mp-985583   | Li₃PS₄      | 0.23±0.02  | 0.0156                            | 0.16 eV⁴⁸                                      |
| mp-1195718  | Li₃SnS₄     | 0.30±0.03  | 0.0021                            | 0.4 eV⁵¹                                       |
| mp-30249    | Li₃GeS₄     | 0.53±0.03  | 2.05×10⁻⁶                        | 0.52 eV⁴⁹                                     |
| mp-10499    | LiZr₂P₃O₁₂  | 0.50±0.01  | 1.2×10⁻⁴                         | 0.59⁵²                                        |
| mp-736      | Li₃P        | 0.63±0.07  | 2.14×10⁻⁸                        | 0.44 eV⁵⁰                                     |
| mp-1153     | Li₂S        | 0.99±0.15  | 1.99×10⁻¹³                       | 0.70 eV (T < 800K), 1.52 eV (T > 800K)⁵³       |
| mp-4556     | Li₂SO₄      | 0.96±0.05  | 1.75×10⁻¹⁰                       | 1.1 eV⁵⁴                                      |
| mp-841      | Li₂O₂       | 1.59±0.05  | 2.11×10⁻¹⁸                       | microcrystalline: 0.89 eV, 3.4×10⁻¹³ S/cm      |
|             |             |            |                                   | nanocrystalline: 0.82 eV, 1.1×10⁻¹⁰ S/cm       |
| mp-554577   | Li₄P₂O₇     | 0.98±0.07  | 7.61×10⁻¹²                       | 0.95 eV⁵⁵                                     |
| mp-976280   | LiBr        | 1.02±0.05  | 1.92×10⁻¹⁰                       | -                                              |
| mp-1185319  | LiCl        | 1.17±0.11  | 1.32×10⁻¹²                       | 0.83 eV⁵⁶                                     |

The oxide electrolytes LLZO and LiPON are regarded as promising solid electrolyte materials for their wider electrochemical stability windows compared with sulfide electrolytes.¹¹ The LLZO/Li interface is predicted to be stable in 60% of the sampled phase diagrams. However this is the only one of the 14 oxide-based interfaces to exhibit such stability; in the remaining 13 electrolyte/electrode pairs, the interface between electrode material and electrolyte is predicted to be stable in less than 6% of the generated samples.

The reactivity between LLZO and high-voltage cathodes agrees with the previously-reported DFT-calculated oxidation limits of 2.9 V²⁹ or 3.2 V¹³ and the experimental observation of the formation of secondary phases form during heat treatment of LCO with LLZO.⁵⁷ From phase equilibria analysis, we predict that along the stable pathway between LLZO and each of the cathodes, Li ions encounter at least one poorly conductive oxide which degrades rate performance of the battery. On the anode side, LLZO is likely to form a stable interface with metallic Li, which is considered to be a highly promising anode material due to its low redox potential and high capacity. Our prediction agrees with the stability between LLZO and molten
Li observed in experiment as well as the marginal reaction driving force from previous DFT calculations. If graphite or LTO is used as the anode, direct contact with LLZO leads to the formation of highly resistive interphase components Li$_2$O, Li$_2$O$_2$, Li$_2$CO$_3$, Li$_2$TiO$_3$ and Li$_2$ZrO$_3$.

For the solid electrolyte LiPON, $\beta$-Li$_3$PO$_4$ is the dominant decomposition product at the interface with each of the cathode materials. Although the ionic conductor Li$_3$P is likely to form on the electrolyte surface, it is unlikely to share tie-lines with the cathode. As the ionic conductivity of $\beta$-Li$_3$PO$_4$ is more than six orders of magnitude lower than LiPON, rate capability degradation is anticipated at the LiPON/cathode interface. It should be noted that Li$_3$PO$_4$ produced at the surface of LiPON could be amorphous or $\gamma$-Li$_3$PO$_4$, both of which exhibit higher ionic conductivity than $\beta$-Li$_3$PO$_4$. On the anode side, Li$_3$P frequently shares tie-lines with both LiPON and metallic Li during phase diagram sampling, forming a stable Li$^+$-conducting pathway. This suggests that good cycling performance can be achieved by the spontaneous interface reaction of this half-cell. Increased impedance is predicted at the interface between LiPON and graphite or LTO due to the formation of poor ionic conductors $\beta$-Li$_3$PO$_4$, Li$_2$O or LiTiO$_3$.

Sulfide-based solid electrolytes are known for their high ionic conductivity and superior processability compared to oxide-based electrolytes but are comparatively unstable when in contact with active electrode materials. For all interfaces between cathodes and sulfide electrolytes, we predict that Li$_3$PO$_4$ is very likely to share tie-lines with both the sulfide-based electrolyte and the oxide-based cathode. This is consistent with the experimental observation of transition metal sulfides and $\beta$-Li$_3$PO$_4$ crystalline phases at the interface between a 75Li$_2$S–25P$_2$S$_5$ glass and the cathode LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. Similarly, the formation of LiX (X=Cl, Br) can effectively eliminate the driving force for additional interface reaction between argyrodites Li$_6$PS$_3$X (X = Cl, Br) and the cathode materials. Based on the large bandgap predicted by DFT, Li$_3$PO$_4$ and LiX (X=Cl, Br) are electronically insulating and thus protect the solid electrolyte well. However, they are poor lithium ion conductors.

We find that double-layer sulfide/sulfate pathways can sometimes bridge the chemical potential gaps between the sulfide electrolytes and the oxide cathode materials. Using the LGPS-LCO system as an example, we illustrate the need for a two-component pathway by plotting the chemical stability windows for all reactant and product phases with respect to sulfur and phosphorus (Figure 4). Li$_3$PO$_4$ has a wide stability window with respect to both S and P, which is why it shows up as a single-component pathway. The electrochemical stability window of Li$_2$SO$_4$ with respect to sulfur overlaps with that of both the LGPS electrolyte and the LCO cathode. However, the stability of the Li$_2$SO$_4$-LGPS interface is limited by the stability windows of the phosphorous ions, which do not overlap. The gap can be eliminated by the formation of another sulfide layer, such as Li$_4$GeS$_4$ or Li$_2$S, between the solid electrolyte and Li$_2$SO$_4$. According to our ionic conductivity evaluation, Li$_2$SO$_4$, Li$_4$GeS$_4$ and Li$_2$S are all better
ionic conductors than β-Li₃PO₄ (the thermodynamically stable polymorph of Li₃PO₄), so these double-layer pathways potentially allow for faster Li⁺ conduction through the interphase.

Figure 4. Electrochemical stability windows with respect to elements S and P within which solid electrolytes, cathode materials, and interphase components are stable.

On the anode side, when a sulfide-based electrolyte is paired with graphite or metallic lithium, the increased impedance is mainly attributed to the formation of Li₂S or LiX (X=Cl, Br). Our result agrees with the in-situ composition analysis at the Li₇P₃S₁₁/Li interface indicating that Li₂S is the main component that contributes to interfacial impedance. In this system, a slowly-growing interphase layer only a few nanometers wide increased the total resistance from 280 Ω to 325 Ω. When a sulfide-based electrolyte is paired with the LTO anode, the poor ionic conductor Li₂TiO₃ may be formed in addition to Li₂S or LiX (X=Cl, Br), greatly increasing the internal resistance to charge transfer.

Poor conductivity through the bulk phases likely to form in the interphase suggest that an alternative approach, such as the application of a protective coating, may be necessary to stabilize nearly all electrode/electrolyte interfaces. Some of the materials we have examined, such as Li₃PO₄,63-66 Li₂TiO₃,67,68 Li₂CO₃,69 and Li₂O,70 have been employed as cathode coatings despite being predicted to be poor Li⁺ conductors with our calculation method. This suggests that conductivity through these materials does not occur through stoichiometric single-crystals as modeled here, as the presence of defects, grain boundaries, and/or disorder in the synthesized materials could lead to higher conductivity.71 Defect structures in these ionic materials largely depend on the processing conditions, which can result in orders of magnitude variation in the experimentally-determined conductivities for the same phase.72,73 Some of these materials may exist in an amorphous form if the coating is sufficiently thin, as the amorphous form can be stabilized by interfacial energy.74,75 We do not examine amorphous or polycrystalline materials in depth here, as their structure and properties can be difficult to
predict with current computational approaches. There are also differences between an artificial coating and a spontaneously formed interphase in terms of the thickness and interfacial contact. Artificial surface coatings can be controlled between 1 and 10 nm\textsuperscript{76} which is generally thinner than the interphases formed in reactions, which typically have thickness ranging from a few tens to a few hundreds of nanometers.\textsuperscript{18, 47} On the other hand, interphases formed in situ potentially achieve better physical contact and more coherent interfaces with both the electrode and the electrolyte, which limits the degree to which additional resistance or mechanical failure is introduced by poor contact.\textsuperscript{77}

CONCLUSIONS
Based on the calculated ionic conductivities of interphase components along pathways through the interphase that are likely to contain stable interfaces, we find that the bulk ionic conduction rate between the solid electrolyte and the electrode is primarily limited by poorly conductive oxide (phosphate, sulfate) phases despite the presence of several good ionic conductors such as Li\textsubscript{3}PS\textsubscript{4}, Li\textsubscript{3}SnS\textsubscript{4}, Li\textsubscript{4}GeS\textsubscript{4}, LiZr\textsubscript{2}P\textsubscript{2}O\textsubscript{12} and Li\textsubscript{3}P. Across 55 pairs of reactive electrode/electrolyte interfaces, Li/LiPON is the only pair where an interphase is predicted to form that prevents further interfacial reactions without significantly compromising ionic conductivity. Although it is possible that sufficient ionic conductivity may be achieved through alternative diffusion mechanisms (such as diffusion along the interfaces between product phases) and/or interface-driven stabilization of amorphous phases, these results suggest that in nearly all cases the long-term performance of solid-state batteries may be best achieved by applying a protective coating between the electrode and electrolyte.

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S1: Estimation of room temperature diffusivity

If no diffusive hops have been observed in the first 4 nanoseconds of the molecular dynamics simulation, we estimate the upper limit of diffusivity by assuming that each Li\(^+\) undergoes site-to-site hopping exactly every 4 nanoseconds. The materials in this study have a typical hopping distance between adjacent Li sites of about 3 Å. Using

\[
D = \frac{\text{MSD}(\Delta t)}{6\Delta t},
\]

where \(\text{MSD}(\Delta t)\) is the mean squared displacement of lithium ions after time \(\Delta t\), we estimate the upper limit of Li diffusivity at 1000K as \(D = \frac{1}{6} \times \frac{(3\text{Å})^2}{4\text{ns}} = 3.75 \times 10^{-8}\) cm\(^2\)/sec. Supposing the material has an intermediate activation barrier of 0.5 eV, we extrapolate the diffusivity at 1000K down to 300K assuming Arrhenius scaling by a factor of \(\frac{D(300K)}{D(1000K)} = e^{\frac{0.5}{0.5}} = 1.35 \times 10^{-6}\), which gives room-temperature diffusivity of \(5.06 \times 10^{-14}\) cm\(^2\)/sec. We note that if we had assumed a higher activation energy, which is likely if no hops have been observed in 4 ns, then the room-temperature diffusivity would be even lower.
