Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries

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Ⓢ *Supporting Information*

ABSTRACT: In the pursuit of higher-energy-density lithium-ion batteries, one major challenge is the stability of high-capacity or high-voltage cathodes with electrolytes. An understanding of how different chemistries interact with high-energy cathodes is required to enable the rational design of coatings or solid electrolyte materials that offer long-term stability with the cathode. Here, we systematically evaluated the thermodynamic stability among a broad range of solid-state chemistries with common cathodes. Our thermodynamic analyses confirmed that the strong reactivity of lithiated and delithiated cathodes greatly limits the possible choice of materials that are stable with the cathode under voltage cycling. Our computation reaffirmed previously demonstrated coating and solid electrolyte chemistries and suggested several new stable chemistries. In particular, the lithium phosphates and lithium ternary fluorides, which have high oxidation limits, are promising solid-state chemistries stable with high-voltage cathodes. Our study provides guiding principles for selecting materials with long-term stability with high-energy cathodes for next-generation lithium-ion batteries.
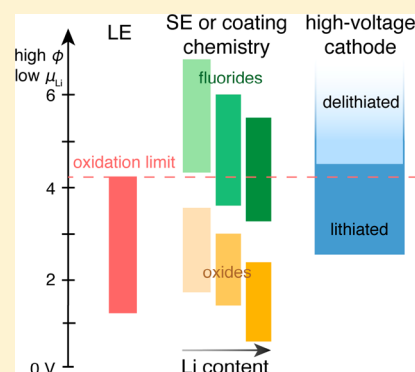
Strong demand for rechargeable energy storage requires further increase in the energy density of lithium-ion batteries. Currently pursued directions to achieve higher energy density include enabling Li metal anodes and increasing the capacity and voltage of cathode materials.[1,2] Ni-rich layered oxide materials such as $LiNi_{1−x−y}Mn_xCo_yO_2$ (NMC) and $LiNi_{1−x−y}Co_xAl_yO_2$ (NCA) have been widely adopted to increase cathode capacity and energy density compared to layered $LiCoO_2$.[2−4] In addition, increasing the operating voltage of cathode materials, by using high-voltage cathode materials such as spinel $LiNi_{0.5}Mn_{1.5}O_4$ and olivine $LiCoPO_4$, is another strategy to increase the energy density of the lithium-ion battery.[5,6] However, the key challenge in employing these high-energy cathode materials is their poor stability and strong reactivity with the electrolyte. The high operating voltages greater than 4.5 V for many cathodes are above the oxidation limit of the electrolyte, leading to deleterious side reactions between the cathode and electrolyte.[7,8] The application of coating layers on cathode surfaces blocks direct contact with the electrolyte and is an effective strategy for preventing undesirable side reactions with the electrolyte[9] or the dissolution of transition metal[10,11] from the cathode into the liquid electrolyte. Coating layers such as Al_2O_3,[12,13] TiO_2,[10] and SiO_2[14,15] on a cathode are demonstrated in improving the Coulombic efficiency, cyclability, and cycle life of the battery.[9,16] Recently, the use of solid electrolytes in all-solid-state batteries has also been proposed as a promising route for high-voltage cathodes and high-energy batteries,[17] but side

reactions between the cathode and solid electrolytes were reported.[18−21] In order to achieve long-term stable battery performance, materials such as coatings or solid electrolytes that exhibit good electrochemical stability with these high-energy-density cathodes during electrochemical cycling need to be developed.

In order to design and predict coating materials, computational techniques[21−23] powered by large materials databases[24,25] were proposed to investigate the thermodynamic stability of electrode and electrolyte materials and the interface stability between them.[26] Such computational studies were performed to identify novel coating layer materials for protecting the Li metal anode,[27] serving as scavengers for hydrogen fluoride,[28] and improving the compatibility between sulfide solid electrolytes and oxide cathodes in all-solid-state batteries.[21,29,30] Beyond direct computational screening, the rational design and prediction of materials that are stable with high-energy cathodes requires a comprehensive, systematic understanding of the interaction between different solid-state chemistries and cathodes.

Our study aims to provide a comprehensive theoretical understanding about how thermodynamic stability varies between different solid-state chemistries and cathode materials under voltage cycling. To assess long-term materials stability,

our evaluation criterion is the thermodynamic stability of the materials with the cathodes at charged (delithiated) and discharged (lithiated) states. When this criterion is not met, potential side reactions may happen, causing deterioration of the cathode and decline of the battery performance. In this study, we aim to answer the following questions: (1) what factors affect the stability of the materials in contact with the cathode and (2) what types of materials are stable with given cathodes under high-voltage cycling. This knowledge of solid-state chemistry can guide the selection, design, and discovery of novel coatings or solid electrolyte materials that have long-term stability with high-energy or high-voltage cathodes.

In this study, using high-throughput analyses of thermodynamic materials data, we illustrated the reaction and compatibility of a wide range of solid-state chemistries with common high-energy cathodes to guide future development of solid materials stable with cathodes under high-voltage cycling. We examined the interface stability and potential reactions between current common cathodes and contacting materials, such as lithium ternary oxides, binary oxides, lithium polyanion oxides, and lithium halides. Our calculations focus on the commercialized cathodes $LiCoO_2$ (LCO), layered $LiNiO_2$ (LNO) as a proxy for Ni-rich layered oxides such as NMC and NCA, and the high-voltage cathodes spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO) and olivine $LiCoPO_4$ (LCP). Both lithiated and delithiated cathodes were evaluated corresponding to the discharged and charged states of the battery, respectively (Figure 1). Using the thermodynamic scheme established in
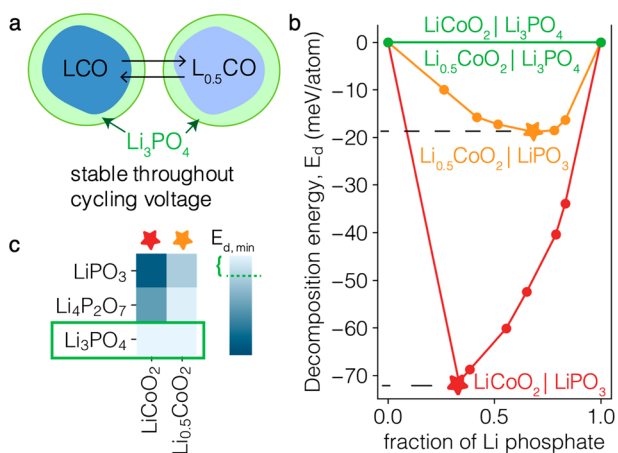

Figure 1. Thermodynamic analysis of the stability between cathode and contacting materials. (a) Illustration of cathode particles coated with Li_3PO_4 at lithiated and delithiated states. (b) Mutual reaction energy of $LiPO_3$–$LiCoO_2$ (red), $LiPO_3$–$Li_{0.5}CoO_2$ (orange), Li_3PO_4–$LiCoO_2$ (green), and Li_3PO_4–$Li_{0.5}CoO_2$ (green) as a function of the mixing fraction in the pseudobinary. The minimum mutual reaction energy (star) corresponds to the possible reaction with lowest energy. (c) Heatmap of the minimum mutual reaction energies of different compositions of lithium phosphates with lithiated and delithiated LCO.

previous studies, the interface of the contacting material (such as the coating or solid electrolyte) with the cathode was considered a pseudobinary mixture of the two materials.[21] Under this scheme, the reaction of the cathode and the contacting material to form the most favorable phase equilibria was identified (Figure 1b).[21,31] The decomposition energy, E_d, is defined as the minimum of the mutual decomposition energy between two phases, where the metastability (i.e., energy above
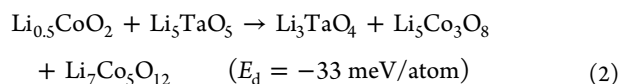
hull) of the reactant phases is excluded from the decomposition energy, as defined in a previous study,[21] and was evaluated using density functional theory (DFT) energies from the Materials Project database.[24] More details on the computation methods are provided in the Supporting Information (SI). This scheme has also been effectively demonstrated in the prediction of solid-state chemistries that are stable in highly reducing conditions against Li metal.[27]

Stability of Cathodes with Lithium Ternary Oxides. We first examined the lithium ternary oxides, many of which were demonstrated as coating layers[32−35] and investigated as solid electrolytes,[36,37] for their interface stability with cathodes (Figure 2). Different lithium ternary oxides exhibit different stabilities with cathodes. For example, Li_3PO_4 is stable with both lithiated LCO and delithiated $Li_{0.5}CoO_2$ ($L_{0.5}CO$), but $LiPO_3$ exhibits a favorable reaction of −71 meV/atom with LCO and −19 meV/atom with $L_{0.5}CO$ (Figure 1). In addition, within the Li−Ta−O materials, LCO is stable (i.e., no possible low energy reaction) with $LiTaO_3$, Li_3TaO_4, or Li_5TaO_5 but exhibits a low-energy phase equilibrium with $LiTa_3O_8$

$$LiCoO_2 + LiTa_3O_8 \rightarrow Co_3O_4 + Li_{0.5}CoO_2 + LiTaO_3$$
$$(E_d = -19 \text{ meV/atom}) \quad (1)$$
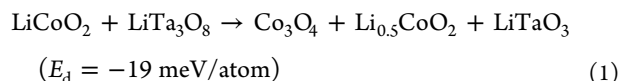
forming the delithiated phases $L_{0.5}CO$ and spinel Co_3O_4 due to the loss of Li from the cathode. In experiments, LCO particles were observed to form Co_3O_4 at the surface after cycling[38] or at high voltages,[39] an environment that corresponds to low Li chemical potential. Thus, a coating material that may potentially degrade the cathode should be avoided.

By contrast, the delithiated cathode $L_{0.5}CO$ has a tendency to react with the compounds with higher Li content, drawing Li out from the contacting material into the delithiated cathode. For example, Li_5TaO_5, which is stable with LCO, has a low-energy phase equilibrium with $L_{0.5}CO$

$$Li_{0.5}CoO_2 + Li_5TaO_5 \rightarrow Li_3TaO_4 + Li_5Co_3O_8$$
$$+ Li_7Co_5O_{12} \quad (E_d = -33 \text{ meV/atom}) \quad (2)$$

forming Li-rich lithium cobalt oxide phases and a lithium tantalum oxide with lower lithium content. In general, among all lithium ternary oxides, delithiated cathode $L_{0.5}CO$ is stable with fewer compounds and reacts with a greater magnitude of E_d than LCO (Figure S1), suggesting that the delithiated cathode or the charged state of the battery imposes greater stability problems on the cathode side. This stability trend is in agreement with theoretical calculations[40] and experimental thermal stability analysis.[41] In general, for ternary oxides, delithiated $L_{0.5}CO$ tends to react with materials with high Li content (Figure 2), and lithiated LCO tends to react with materials with low Li content, causing the loss of Li from the cathode. These opposite stability trends in the reactions of LCO and $L_{0.5}CO$ indicate the importance of finding a suitable material that is stable with both lithiated and delithiated states of the cathode in order to achieve long-term stability of the cathode with repeated cycling.

Ni-Rich Layered Oxide Cathodes. We studied Ni-based layered oxide cathodes using layered LNO as a proxy for commercial Ni-rich layered materials such as NMC and NCA. We found that LNO exhibits poorer stability with lithium ternary oxides compared to LCO, as shown by more favorable reaction energies E_d (Figure 2 and Table S1). For example, LNO mixed with $LiTa_3O_8$ shows a low-energy phase
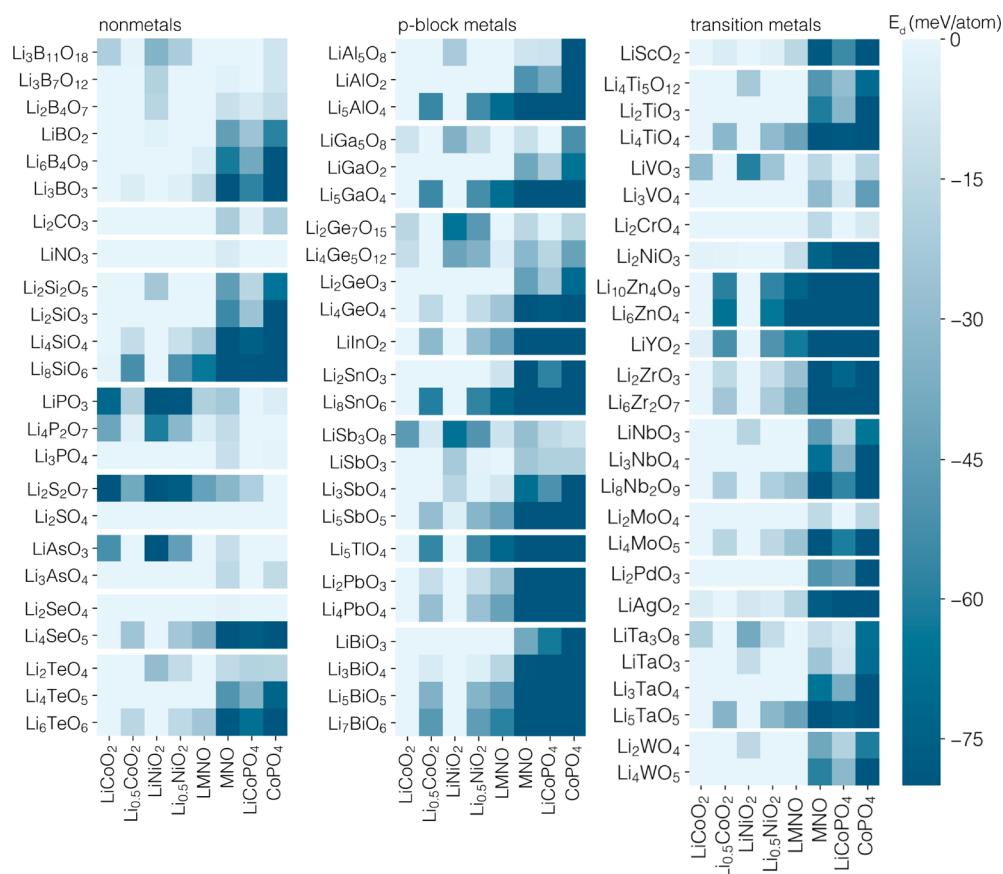
Figure 2. Decomposition energies of lithium ternary oxides with cathodes at lithiated and delithiated states. The color of each square in the heatmap corresponds to the minimum decomposition energy (E_d) of the cathode and contacting material. Groups of materials with the same elemental composition are ordered by increasing lithium content down the column. Only compositions where M is at its highest common oxidation state are considered.

equilibrium with a lower decomposition energy E_d of −39 meV/atom

$$LiNiO_2 + LiTa_3O_8 \rightarrow LiTaO_3 + Li_{0.5}NiO_2 + Ni_3O_4$$

$$(E_d = -39 \text{ meV/atom}) \tag{3}$$
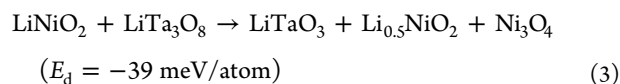
Similar to delithiated $L_{0.5}CO$ (eq 2), delithiated $Li_{0.5}NiO_2$ ($L_{0.5}NO$) tends to react with the oxides with higher Li content to form Li-rich nickel oxide phases such as Li_2NiO_3[42] and the rock salt phase NiO (Figure S2). For example, the low-energy phase equilibrium of $L_{0.5}NO$ with Li_5TaO_5 is

$$Li_{0.5}NiO_2 + Li_5TaO_5 \rightarrow Li_2NiO_3 + Li_3TaO_4 + NiO$$

$$(E_d = -32 \text{ meV/atom}) \tag{4}$$
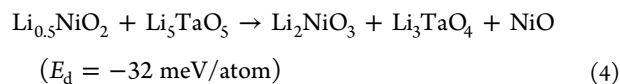
The formation of the rock salt NiO phase in delithiated Ni-rich cathodes is in agreement with experimental findings.[42−44] The greater reactivity of LNO than LCO may be attributed to the poorer stability of LNO than LCO in the layered structure and the stronger preference of LNO to form rock salt NiO compared to the preference of LCO to form cobalt oxides such as Co_3O_4. Ni-rich layered oxides, such as NCA and NMC, are expected to have the same behavior as LNO (Figure S3). The instability of the LNO and Ni-rich layered oxide cathodes compared to LCO is consistent with experimental reports[41] and indicates the challenge of finding suitable coating layers stable with Ni-rich cathode materials.

High-Voltage Cathodes. High-voltage cathodes such as LMNO and LCP were found to be even more unstable with the lithium ternary oxides compared to layered cathodes LCO and LNO, as shown by a greater magnitude of E_d with a greater number of materials. Similar to the delithiated layered cathodes, the delithiated high-voltage cathodes $CoPO_4$ (CP) and $Ni_{0.5}Mn_{1.5}O_4$ (MNO) are also less stable with lithium ternary oxides as the Li content of the oxide increases. The poor stability of the high-voltage cathodes is due to their stronger reactivity and tendency to attract Li at delithiated states. In the chemical space of lithium ternary oxides, few materials are stable with high-voltage cathodes.

General Trends among Cathodes. Among these lithium ternary oxides, we found that the lithium content of the material affects its stability with the cathode. In general, delithiated cathodes have the poorest stability with materials with high Li content because the oxidizing, Li-poor delithiated cathode has a tendency to extract Li from the contacting material. In contrast, lithiated cathodes, although generally more stable with lithium ternary oxides than delithiated cathodes, tend to be more stable with materials with higher Li content. These conflicting requirements illustrate the challenge of finding a single material that is stable with the cathode in both lithiated and delithiated states. Because delithiated cathodes are more reactive with a stronger driving force, protecting the delithiated cathode should be considered a priority.
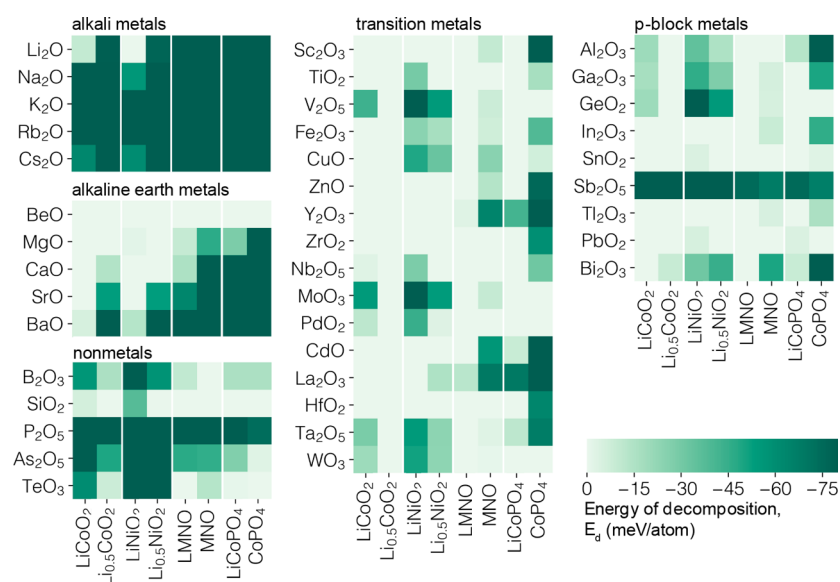
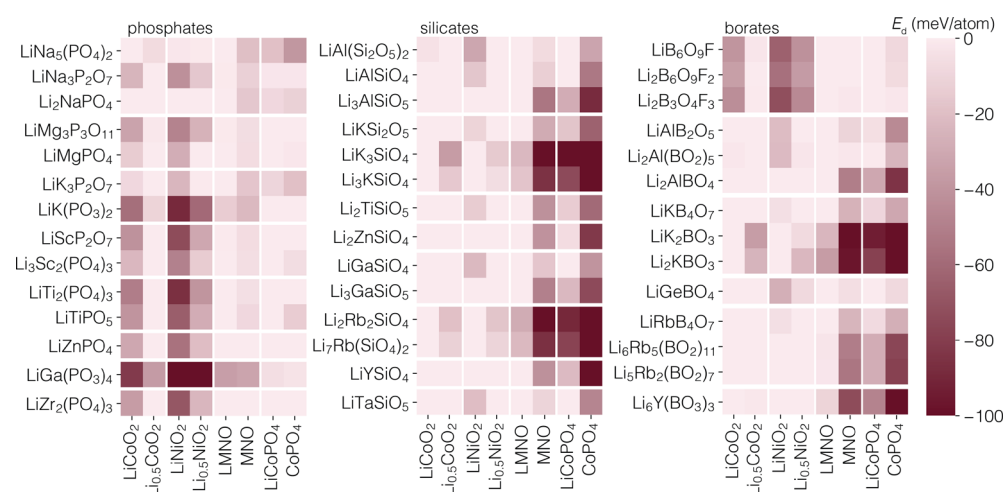Figure 3. Heatmap of decomposition energies E_d of binary oxides with cathodes, similar to Figure 2.

Figure 4. Heatmap of decomposition energies E_d of selected lithium polyanion compounds (composition Li−M−X−O, where X = B, Si, or P) with cathodes, similar to Figure 2.

Binary Oxides. To explore materials with better stability with delithiated cathodes, we next analyzed binary oxides, which do not contain Li (Figure 3). In agreement with the trend above about Li content, binary oxides in general are more stable with the delithiated layered cathodes ($L_{0.5}$CO and $L_{0.5}$NO) and the high-voltage cathodes (LMNO/MNO and LCP/CP) because they do not contain Li to be extracted. For example, some common oxide coatings, such as Al_2O_3, SiO_2, ZrO_2, MgO, and ZnO,[16] are observed to be stable with $L_{0.5}$CO. In addition, the stabilities of materials classes of the binary oxides were found to exhibit major differences (Figures S4 and S5). The binary oxides that contain alkali metals, alkaline earth metals, and nonmetals (except BeO, MgO, and SiO_2) are largely unstable with the cathodes (Figure S6). In contrast, many transition metal oxides and p-block binary oxides showed good stability with LMNO and LCP. Consistent with this computational result, many of these materials, such as Al_2O_3, SiO_2, and Ta_2O_5, were experimentally implemented as coating layers for LMNO[10,45−47] and LCP.[48] Although the binary oxides exhibit good stability, their lack of Li may cause them to have limited Li-ion conductivity. The conduction mechanism in these

materials may be mediated by Li^+ interstitials, which may have a high formation energy at high voltage.[49−52] As suggested by our thermodynamic computation, minor reactions may be favorable between some binary oxides (such as SiO_2 and Al_2O_3) and the cathode, which may beneficially introduce some Li into the material to improve Li-ion transport[53] and form strong chemical bonding between the coating and cathode. In experiments, an Al_2O_3 coating on LCO was found to form $LiAlO_2$ on LCO particle surfaces, consistent with our calculation.[54]

Polyanion Oxides. Polyanion chemistries, such as lithium borates, silicates, and phosphates, have been explored as promising materials classes for coatings and as solid electrolytes. We found that all of the polyanion chemistries exhibit better cathode stability with delithiated $L_{0.5}$CO and $L_{0.5}$NO cathodes (Figure S5) compared to the lithium ternary oxides. In particular, among all materials considered, the lithium phosphates exhibit the best stability with lithiated and delithiated high-voltage cathodes LMNO and LCP (Figures 4 and 5b). Consistent with our computation, lithium phosphate coatings have been reported to improve the cycle
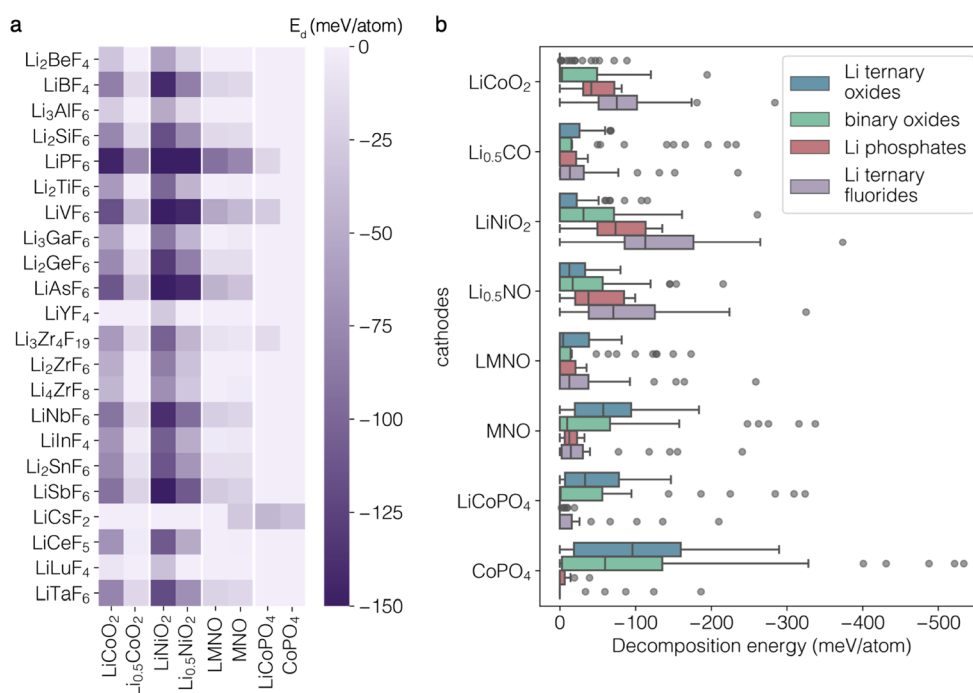
Figure 5. (a) Heatmap of decomposition energies E_d of lithium ternary fluorides with cathodes, similar to Figure 2. (b) Grouped boxplot of decomposition energies of all cathodes with lithium ternary oxides, binary oxides, lithium polyanion phosphates, and lithium ternary fluorides. The center line of each box indicates the median of the data set, the outer edges represent the first and third quartiles, and the end points are marked by either the most extreme value on either end or 1.5 times the interquartile range, whichever is smaller. Data outside of the end points are marked individually as gray circles.

life and capacity retention of both LNMO[55] and LCP[56,57] cathodes. In addition, some lithium phosphates such as NASICON are solid electrolyte materials[58,59] and are reported to exhibit excellent oxidation stability[31] and good cycling stability with oxide cathodes.[60−62] The stability of the phosphates may be attributed to their high oxidation limits matching those of delithiated high-voltage cathodes (Figure S7). Therefore, we find that lithium borates and silicates provide a large number of compounds stable with layered oxide cathodes, and lithium phosphates are promising coating or solid electrolyte chemistries for good stability with high-voltage cathodes.

Lithium Ternary Fluorides. Because materials with high oxidation limits tend to exhibit better cathode stability, we further explored and examined the stability of lithium fluoride compounds, which are known to have high oxidation limits.[23,63] We found reversed trends from those seen in the lithium ternary oxides (Figure 5a). A majority of lithium ternary fluorides exhibit better stability with high-voltage cathodes LMNO/MNO and LCP/CP than those with layered LNO and LCO. While many oxides have stability problems with delithiated $L_{0.5}CO$, fluorides generally exhibit better stability with delithiated $L_{0.5}CO$ but exhibit poorer stability with lithiated LCO. In addition, fluorides with high Li content still exhibit good stability with delithiated cathodes, in contrast to the tendency of delithiated cathodes and lithium ternary oxides to react as the Li content of the oxide increases. Therefore, lithium ternary fluorides are promising chemistries because they are stable with high-voltage cathodes while also containing sufficient Li carriers for transport at high voltages. In experiments, a number of fluorides such as CeF_3 and AlF_3 have been reported as cathode coating layers.[64,65] In addition, lithium chlorides such as Li_3YCl_6 were recently reported as

solid electrolytes with high Li+ conductivity and good stability with LCO cathodes.[63,66]

In this computational study, we investigated the thermodynamic stability between a broad range of solid-state chemistries and current cathode materials in Li-ion batteries. The thermodynamic analyses of high-energy and high-voltage cathodes quantified and emphasized their strong reactivity, in particular, at delithiated or charged states, which causes undesirable side reactions and deterioration in battery performance. Our results suggest that the thermodynamic stabilities of the lithiated and delithiated cathode with the contacting material are effective criteria for identifying promising coatings or solid electrolytes that can exhibit long-term stability with the cathode. Indeed, many experimentally demonstrated coating materials for oxide cathodes[16] such as ZrO_2,[39,67] Al_2O_3,[12] and SiO_2[15] on layered cathodes and Li_3PO_4, $LiNbO_3$, and $LiTaO_3$ in all-solid-state batteries[68] were confirmed by our thermodynamic criteria for their good stability with the cathode at all states of charge. For the binary oxides, minor reactions, for example, between Al_2O_3 and lithiated LCO, may provide enhanced interfacial binding between the coating and LCO and introduce lithium into the coating to provide Li+ transport.[53] The good agreement between experimental work and computation results suggests that the new chemistries identified in this study can guide future development of coatings or solid electrolytes stable with high-voltage cathodes.

Our thermodynamic analyses illustrated that the stability of the cathode and a given material varies with the Li content, cation, and anion chemistries of both the cathode and the contacting materials. Thus, the interface stability or compatibilities should be individually evaluated for each distinct pair of cathode and coating/solid electrolyte compositions. For

example, lithium phosphates are more stable with high voltage cathodes (LMNO and LCP) and less stable with layered oxide cathodes (LCO and LNO), and lithium borates and silicates by contrast are more stable with the layered oxide cathodes. While the type of metal cation in the cathodes and coatings greatly affects their stability, the poor stability between the coating layer and cathode can in general be attributed to the high oxidation potential of delithiated cathodes (4.5 V or greater), often beyond the oxidation limit (3.5−4 V) of most oxides (Figures S9 and S10). Therefore, many reported oxide coatings have low or no Li content and correspondingly high oxidation limits. Because Li content is desired for Li-ion transport, in order to simultaneously achieve good ionic conductivity and high-voltage stability, lithium polyanion phosphates, which have naturally high oxidation limits, are a promising chemistry for coatings or solid electrolytes. Recently, a NMC cathode coated with $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ phosphate, a well-known solid electrolyte, was demonstrated with improved rate capability and cycling stability.[62] In addition, lithium fluorides have high oxidation limits and can serve as a promising chemistry beyond oxides for stability with cathodes at high voltage.

Ion transport across the interface or interphase layer is known to be crucially important for battery performance. Poor chemical stability at the interface is indicative of the potential exchange of ions between the two materials and the formation of interphase layers, leading to higher interfacial resistance. While direct atomistic modeling of the ion transport at interfaces is challenging, Li-ion migration in the coating layer or solid electrolyte can be evaluated using the nudged-elastic-band method and molecular dynamics simulations.[23] In addition, the formation of Li-ion vacancies or interstitials within the materials is important for high ionic conductivity and can be evaluated by first-principles calculations for defect formation energies.[51,69] The effects of dopants and defects can be computationally assessed and leveraged to enhance the conductivity in materials.[70,71] Given the importance of Li-ion transport for battery performance, detailed computation may be performed to further evaluate Li-ion conduction in promising chemistries.

In summary, our study provides a thermodynamic scheme and guiding principles for selecting solid-state chemistries that are stable with highly reactive cathodes for Li-ion batteries. Our results provide guidance for the future selection of solid-state chemistries for cathode coatings or solid electrolyte materials that have good cathode stability over the cycling voltage range, states of charge, and operating lifetime. This thermodynamic scheme can be extended to investigating other solid-state devices, such as dielectric gates[72] or neuromorphic devices, where the interface stability and compatibility under applied voltage are relevant.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b01703.

> Computational methods; analysis of phase equilibria; additional stability analysis of Ni-rich layered cathodes NMC and NCA; oxidation and reduction limits of each materials class; additional analyses and comparisons between the pseudobinaries of different materials (PDF)

> Values of decomposition energies (E_d) and phase equilibria of all pseudobinaries of cathodes and contacting materials used to construct the heatmaps (XLSX)

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Notes
The authors declare no competing financial interest.

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