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First-principles studies on cation dopants and electrolyte|cathode interphases for lithium garnets

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Abstract

Lithium garnet with the formula Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has many properties of an ideal electrolyte in all-solid state lithium batteries. However, internal resistance in batteries utilizing these electrolytes remains high. For widespread adoption, the LLZO’s internal resistance must be lowered by increasing its bulk conductivity, reducing grain boundary resistance, and/or pairing it with an appropriate cathode to minimize interfacial resistance. Cation doping has been shown to be crucial in LLZO to stabilize the higher conductivity cubic structure, yet there is still little understanding about which cations have high solubility in LLZO. In this work, we apply density functional theory (DFT) to calculate the defect energies and site preference of all possible dopants in these materials. Our findings suggest several novel dopants such as Zn$^{2+}$ and Mg$^{2+}$ predicted to be stable on the Li- and Zr-sites respectively. To understand the source of interfacial resistance between the electrolyte and the cathode, we investigate the thermodynamic stability of the electrolyte|cathode interphase, calculating the reaction energy for LLMO (M = Zr, Ta) against LiCoO$_2$, LiMnO$_2$, and LiFePO$_4$ (LCO, LMO, LFP respectively) cathodes over the voltage range seen in lithium ion battery operation. Our results suggest that for LLZO the LLZO|LCO is the most stable, showing only a low driving force for decomposition in the charged state into La$_2$O$_3$, LiLaZrO$_4$, and Li$_2$CoO$_3$, while the LLZO|LFP appears to be the most reactive, forming Li$_3$PO$_4$, La$_2$Zr$_2$O$_7$, La$_3$FeO$_6$, and LiFeO$_2$. These results provide a reference for use by researchers interested in bonding these electrolytes to cathodes.
1 Introduction

The lithium stuffed garnet with nominal composition \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) (LLZO) has garnered significant attention in recent years due to its stability towards lithium metal, wide electrochemical stability window, and modestly high ionic conductivity\(^1\text{-}^3\). However, the internal resistance of the garnet electrolyte is still too high for use in a practical battery, depending on the material type and synthesis conditions, this resistance can be dominated by the bulk resistivity (due to bulk Li-ion mobility), grain boundary resistance, or interfacial resistance between the electrodes and the electrolyte\(^4\text{-}^8\).

The highest lithium ion conductivity is found with the cubic phase, space group \( Ia-3d \), of \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) garnet\(^9\). However, at this concentration a low energy ordering of Li into the 8a (tetrahedral) and 16f, 32g (octahedral) sites of the tetragonal structure, can occur, reducing symmetry to \( I4_1/\text{acd} \). The room temperature ionic conductivity of the tetragonal structure is low, on the order of \( 10^{-6} \text{ S cm}^{-1} \), but the conductivity can be improved by over two orders of magnitude if the lithium ordering is broken and the cubic structure restored\(^10\). This is usually accomplished by creating Li vacancies through supervalent cation doping such as \( \text{Al}^{3+}, \text{Ga}^{3+} \), on the Li-site or \( \text{Ta}^{5+}, \text{Nb}^{5+} \) on the Zr-site. Bernstein et al., showed that beyond a critical vacancy concentration (\( x = 0.2 \) in \( \text{Li}_{7-x}\text{A}_x\text{La}_3\text{Zr}_2\text{O}_{12}, \text{A}= \text{Al}^{3+}, \text{Ga}^{3+} \)) the cubic structure is stabilized\(^11\).

Recently it was shown that \( \text{Ta}^{5+} \) (\( x \geq 0.4 \) in \( \text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \)) doped onto the Zr-site is also efficient in stabilizing the cubic structure\(^12\). Achieving a high enough vacancy concentration to disrupt the ordering significantly improves conductivity regardless of the specific dopant or doping site used. Another method to increase conductivity and stabilize the cubic structure is to break the ordering by stuffing lithium into the garnet beyond 7 Li per formula unit (pfu)\(^13\). Based on the available evidence, any dopant can lead to high conductivity if it has a high solubility within the host LLZO, and changes the lithium concentration away from 7 Li pfu. Many dopants have been tried by researchers (\( \text{Ta}^{5+}, \text{Nb}^{5+}, \text{Al}^{3+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Sn}^{4+}, \text{Sb}^{4+}, \text{Y}^{3+}, \text{Ge}^{4+}, \text{Si}^{4+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Hf}^{4+} \))\(^2,9,10,14\text{-}25\), and for some of these, significant effort has gone into determining on which host site these dopants substitute\(^26\text{-}30\). For example, NMR studies and first principles calculations have shown that \( \text{Al}^{3+} \) and \( \text{Ga}^{3+} \) reside on the Li-site\(^14,29,31,32\). However, for other dopants the most stable site in the LLZO structure has not been identified. In this work, we contribute to the body of knowledge on doped garnets by calculating the defect energy and site preference of these and many other potential dopants from first-principles.
Despite high bulk conductivity, any electrolyte is impractical if a large interfacial resistance is present, arising from decomposition products formed between cathode and electrolyte at high sintering temperatures, or from electrochemical decomposition at the interface during cycling. In this context it is the formation of a resistive interphase layer at the interface that leads to the observed resistance. Therefore, a careful analysis of the phases present may provide insight to those interested in reducing the observed interfacial resistance. Phase-decomposition arises from the unequal chemical potentials between the different atomic species across the interface. Rapid decomposition is seen for the sulfide electrolyte|oxide cathode combination, and thus a blocking layer is almost universally employed between the cathode and electrolyte. The problem of interfacial resistance has also been documented for the LLZO system. These researchers report poor performance in all-solid-state batteries with LLZO electrolyte and LCO cathodes caused by a co-diffusion of La, Zr, and Co leading to increased interfacial resistance, although it is unclear if this is from sintering or decomposition during charging.

In this work we use first-principles calculations to identify the thermodynamic driving forces for decomposition reactions between the electrolyte and electrode over the voltage range experienced during operation. We examine LLZO and the similar material, Li$_5$La$_3$Ta$_2$O$_{12}$ (LLTO), against three common cathodes: LCO, LMO, and LFP. We perform a careful thermodynamic assessment of the interphase equilibrium using a grand canonical ensemble open to lithium. As the lithium chemical potential is changed (i.e., simulating charge/discharge) the reaction energy for the formation of the lowest energy equilibrium of interphases from mixing of the cathode and electrolyte composition is determined. Together with the dopant stability analysis we provide valuable information when choosing a system for all-solid-state battery construction using LLZO or LLTO as an electrolyte.

2 Dopant Stability

2.1 Stability Calculation Methodology

In our dopant study, we consider 128 possible dopant species (Table 1) each of which can be placed at three cation sites (Li, La, Zr). Additionally, there are 3 lithium sites (24d, 96h, 48g) which must also be tested when a dopant is placed on the Li-site, leading to a total of 1152 structures to be calculated. Some cations are clearly less probable than others such as placing 6+ cations on the La-site or 1+ substitution on the Zr-site. Many can be ruled out simply in terms of
Table 1: Elements and oxidation states (in parentheses) of the dopant used in the calculations (128 total).

<table>
<thead>
<tr>
<th></th>
<th>H(1)</th>
<th>He</th>
<th>B(3)</th>
<th>C(4)</th>
<th>N(3,5)</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(1)</td>
<td>Be(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(1)</td>
<td>Mg(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(1)</td>
<td>Ca(2)</td>
<td>Sc(3)</td>
<td>Ti(4)</td>
<td>V(5)</td>
<td>Cr(3)</td>
<td>Mn(2,4)</td>
<td>Fe(2,3)</td>
<td>Co(2,3)</td>
</tr>
<tr>
<td>Rb(1)</td>
<td>Sr(2)</td>
<td>Y(3)</td>
<td>Zr(4)</td>
<td>Nb(5)</td>
<td>Mo(4)</td>
<td>Tc(4)</td>
<td>Ru(3,4)</td>
<td>Rh(3)</td>
</tr>
<tr>
<td>Cs(1)</td>
<td>Ba(2)</td>
<td>Lu(3)</td>
<td>Hf(4)</td>
<td>Ta(5)</td>
<td>W(4)</td>
<td>Re(4)</td>
<td>Os(4)</td>
<td>Ir(3,4)</td>
</tr>
<tr>
<td>Fr(1)</td>
<td>Ra(2)</td>
<td>Lr(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(3)</td>
<td>Ce(3,4)</td>
<td>Pr(3)</td>
<td>Nd(3)</td>
<td>Pm(3)</td>
<td>Sm(3)</td>
<td>Eu(2,3)</td>
<td>Gd(3)</td>
<td>Tb(3)</td>
</tr>
<tr>
<td>Ac(3)</td>
<td>Th(4)</td>
<td>Pa(5)</td>
<td>U</td>
<td>Np(5)</td>
<td>Pu(4)</td>
<td>Am(3)</td>
<td>Cm(3)</td>
<td>Bk(3)</td>
</tr>
</tbody>
</table>

Ionic radii or coordination number; however, they are included in this work for completeness.

For compounds in which the doping would lead to unbalanced charge, the Li concentration is adjusted to maintain charge neutrality. For example when Al$^{3+}$ is placed on a Li site, three Li$^+$ are removed. Lithium atoms are removed (as vacancies) from the highest energy sites or added (as interstitials) to the lowest energy sites according to an electrostatic energy criterion.

The oxidation states of the dopants range from 1$^+$ to 6$^+$ and are placed on the Li$^+$, La$^{3+}$, and Zr$^{4+}$ sites in LLZO creating structures with a range of Li concentration from Li$_{6.25}$A$_{0.125}$La$_3$Zr$_5$O$_{12}$ to Li$_{7.375}$La$_3$Zr$_{1.875}$M$_{0.125}$O$_{12}$ (A=6+ dopant on Li site, M = 1+ dopant on Zr-site, respectively). The defect formation energy is calculated as:

$$E_{\text{defect}} = E_{\text{pure}} - E_{\text{doped}} + \sum_{i}^{N} \Delta n_i \mu_i$$

Where $E_{\text{doped}}$ and $E_{\text{pure}}$ are the total energy of the supercell with and without the dopants respectively, $\Delta n_i$ is the number of atoms of element $i$ added to (or removed from) the supercell to create and charge balance the supercell, and $\mu_i$ is the chemical potential of element $i$. This is summed for all elements (N) which are added or removed during the doping reaction. The chemical potentials for each element $i$ are determined from the multi-phase equilibrium that contains the composition of the doped structure. This is calculated as the slope in the direction of element $i$ in the phase diagram. The software suite pymatgen is used to generate the phase diagram and calculate the chemical potentials of the elements added or removed during the reaction.

To compute the relevant phase diagrams, needed for obtaining the chemical potentials of defect species in the defect energy computations and the reaction products in the interfacial
stability calculations, we obtained relevant structures from the International Crystal Structure Database (ICSD)\textsuperscript{38}, and from our internal database of structures generated with data-mined substitution rules\textsuperscript{39}. All compounds in a given quintenary system Li-La-Zr-O-M (where M=dopant) were calculated.

We calculated the ground state of the garnet structure, starting with the disordered structure from the ICSD (CC: 422259) but adopted site occupancy factors (SOFs) of 0.417 for Li(1) and 0.479 for Li(2), for the 8 formula unit conventional supercell, which are more consistent with recent experimental and computational works\textsuperscript{3,40}. This structure with space group \textit{Ia-3d} (No. 230) is disordered on both the 24d Li(1) tetrahedral site and the 96h Li(2) octahedral sites. As the structure has partial occupancies for Li\textsuperscript{+}, we screened the possible arrangements of Li atoms by first applying an electrostatic energy criterion\textsuperscript{36}. Based on this criterion there were no occupied nearest neighbor 24d and 96h sites. We calculated the energies of the 100 orderings with the lowest electrostatic energy using DFT, taking the structure with the lowest DFT energy as the ground state structure.

All Density Functional Theory (DFT) calculations were performed in the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA)\textsuperscript{41}, implemented in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{42}. The projector augmented-wave (PAW)\textsuperscript{43} method is used for representation of core states. An energy cutoff of 500 eV and a \textit{k}-point density of at least 1000/(number of atoms in the unit cell) was used for all computations.

2.2 Stability Analysis Results

The most common dopant for LLZO is Al\textsuperscript{3+}, either intentionally or from the crucible during calcination\textsuperscript{32}, so we use Al\textsuperscript{3+} to illustrate our methods. The first step is to determine which cation site is most favorable for Al\textsuperscript{3+} doping. To do this we placed the Al\textsuperscript{3+} into each of the cation sites and charged balanced according to:

\[
\begin{align*}
\text{Al}^{3+} (\text{Li}) & : \quad \text{Li}_{56}\text{La}_{24}\text{Zr}_{16}\text{O}_{96} + \text{Al}^{3+} (\text{Li}) - 3\text{Li} \rightarrow \text{Li}_{53}\text{Al}_{2}\text{La}_{2}\text{Zr}_{16}\text{O}_{96} \\
\text{Al}^{3+} (\text{La}) & : \quad \text{Li}_{56}\text{La}_{24}\text{Zr}_{16}\text{O}_{96} + \text{Al}^{3+} (\text{La}) - \text{La} \rightarrow \text{Li}_{55}\text{La}_{22}\text{Al}_{1}\text{Zr}_{16}\text{O}_{96} \\
\text{Al}^{3+} (\text{Zr}) & : \quad \text{Li}_{56}\text{La}_{24}\text{Zr}_{16}\text{O}_{96} + \text{Al}^{3+} (\text{Zr}) + \text{Li} - \text{Zr} \rightarrow \text{Li}_{57}\text{La}_{24}\text{Zr}_{15}\text{AlO}_{96}
\end{align*}
\]

For convenience the notation adopted here is Al\textsuperscript{3+}(Li) indicating Al\textsuperscript{3+} doped on the Li-site, accordingly the other sites are Al\textsuperscript{3+}(La) and Al\textsuperscript{3+}(Zr). In the case of Al\textsuperscript{3+}(Li) substitution, the calculated quintenary phase diagram predicts the doped garnet to decompose into La\textsubscript{2}O\textsubscript{3},
Figure 1: A quaternary section of the quintenary phase diagram for Li-La-Al-Zr-O. The position of the new compound Li$_{53}$Al$_{23}$Zr$_{16}$O$_{96}$ is highlighted in green in the decomposition triangle. This particular substitution has a defect energy of 1.36 eV.

Li$_5$AlO$_4$, and La$_6$Zr$_2$O$_7$, as shown in Figure 1. The defect energies and decomposition products for all sites are:

- **Al$^{3+}$(Li):** $\text{Li}_{53}\text{Al}_{23}\text{Zr}_{16}\text{O}_{96} \rightarrow \text{Li}_5\text{AlO}_4 + 8\text{Li}_6\text{Zr}_2\text{O}_7 + 12\text{La}_2\text{O}_3$; \quad $E_{\text{defect}} = 1.36 \text{ eV}$
- **Al$^{3+}$(La):** $\text{Li}_{56}\text{La}_{6}\text{AlZr}_{10}\text{O}_{96} \rightarrow 0.6\text{Li}_6\text{Zr}_2\text{O}_7 + \text{Li}_5\text{AlO}_4 + 7.7\text{Li}_6\text{Zr}_2\text{O}_7 + 11.5\text{La}_2\text{O}_3$; \quad $E_{\text{defect}} = 3.16 \text{ eV}$
- **Al$^{3+}$(Zr):** $\text{Li}_{57}\text{La}_{24}\text{Zr}_{15}\text{AlO}_9 \rightarrow 1.4\text{Li}_6\text{Zr}_2\text{O}_7 + \text{Li}_5\text{AlO}_4 + 6.8\text{Li}_6\text{Zr}_2\text{O}_7 + 12\text{La}_2\text{O}_3$; \quad $E_{\text{defect}} = 1.87 \text{ eV}$

The lowest defect energy for Al$^{3+}$ incorporation is found for Al$^{3+}$(Li) which is in good agreement with magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy which locates the Al$^{3+}$ on the Li-sites$^{29,32,44}$. Furthermore, our work is in perfect agreement with a recent in depth computational analysis regarding the location of the Al$^{3+}$ in the cubic structure that showed the order of site preference was Li (24d tetrahedral site) $>$ Li (96h octahedral site) $>$ Zr (16a) $>$ La (24c)$^{45}$. The complete set of results for all dopants is provided in the supplemental information (Table S3), and is summarized in Figure 2. It is interesting to note that we predict that of the 3d transition metals, only Fe$^{3+}$(Li) has a lowest energy site on Li, the others all favor the Zr-site, in excellent agreement with recent findings$^{46}$.

The solubility of a dopant is primarily a function of its defect energy, with that defect energy compensated by the increased entropy due to Li disorder. Determination of the exact entropic contribution for each dopant is beyond the scope of this research, so as an
Figure 2: Site and oxidation state preference for the dopant elements studied. The color shows the most stable cation site (green for Li-site, red for La-site, and blue for Zr-site). The darker colors signify lower defect energy, such that Al\(^{3+}\)(Li) is darker than B\(^{3+}\)(Li). The box also shows the preferred oxidation state and the defect energy in eV.

approximation of what may be synthesized we determine the dopant that has been successfully synthesized with the highest calculated defect energy. According to our results and past literature we are aware of, Ce\(^{4+}\)(La) with \(E_{\text{defect}} = 1.60\) eV is the highest\(^{18}\) among the synthesized compounds, but to broaden our search we use Te\(^{6+}\)(Zr) with \(E_{\text{defect}} = 2\) eV as a reasonable defect energy cutoff. Although doping LLZO with Te has not been attempted in the past to the authors’ knowledge, solid solutions of Te compounds were successfully synthesized in the related Li\(_{3+x}\)Nb\(_{2-x}\)Te\(_2\)O\(_{12}\) (0.05 ≤ x ≤ 1.5) series\(^{47}\).

The number of possible defects on each site, after filtering with the 2 eV defect energy cutoff, is summarized in Table 2, and the list of dopants can be found in the supplementary materials (Table S2). In applying this filter, dopants are allowed to be stable on multiple sites and in multiple oxidation states. From this analysis there are 37 dopant(site) combinations which are isovalent with the doped site, and while they likely have high solubility, they will not modify the Li concentration and therefore are unlikely to stabilize the cubic structure (highlighted blue in Table S2). Of the remaining combinations, 25 contain 3\(d\) transition metals. Recent experimental work has demonstrated that Fe\(^{3+}\) doping is effective at stabilizing the cubic structure\(^{31,46}\), but 3\(d\)
Table 2: Number of dopant(site) combinations for LLZO with calculated defect energy lower than 2 eV. The results after excluding 3d transition metal dopants are shown in parenthesis.

<table>
<thead>
<tr>
<th>Site</th>
<th>Total</th>
<th>Subvalent</th>
<th>Isovalent</th>
<th>Supervalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li (1+)</td>
<td>15 (10)</td>
<td>0</td>
<td>0</td>
<td>15 (10)</td>
</tr>
<tr>
<td>La (3+)</td>
<td>27 (25)</td>
<td>7 (7)</td>
<td>18 (18)</td>
<td>2 (2)</td>
</tr>
<tr>
<td>Zr (4+)</td>
<td>66 (57)</td>
<td>36 (30)</td>
<td>19 (17)</td>
<td>11 (10)</td>
</tr>
</tbody>
</table>

Transition metals are generally not suitable for electrolytes since the 3d transition metal cations can be reduced against the lithium anode. After removing V, Cr, Mn, Fe, Co, and Ni, highlighted in red in Table S2, there remain 59 dopant(site) stable combinations which are not isovalent with the host site, marked as the numbers in parentheses in Table 2.

The highest conductivities are usually seen between 6 - 7 Li pfu\textsuperscript{25,48}. Supervalent dopants are required to achieve these concentrations in LLZO, and, as was mentioned in the introduction, the most common dopants are Al\textsuperscript{3+}(Li), Ga\textsuperscript{3+}(Li), Ta\textsuperscript{5+}(Zr), and Nb\textsuperscript{5+}(Zr). From our analysis we identify several more low energy dopants that are not 3d transition metals, and are relatively earth abundant. Perhaps the most interesting is Zn\textsuperscript{2+}(Li) with a defect energy of 1.32 eV which is slightly lower than Al\textsuperscript{3+}(Li). Zn is further attractive since it is a common component of solid electrolytes\textsuperscript{49–51}. Other possibilities include Mg\textsuperscript{2+}(Li), Sb\textsuperscript{5+}(Zr), W\textsuperscript{6+}(Zr), and Mo\textsuperscript{6+}(Zr), which all have defect energies below the 2 eV cutoff.

Subvalent dopants leading to compositions with Li above 7 pfu have typically been avoided in the past. However, we have previously shown that Rb\textsuperscript{1+}(La), with calculated defect energy of 1.29 eV, stabilizes the cubic structure and has high conductivity\textsuperscript{3}. From Table 2 it is seen that there are 30 subvalent non-3d transition metal dopants on the Zr-site below the threshold. Many of these dopants are earth abundant and have defect energies similar to or lower than Al\textsuperscript{3+}(Li). Some interesting dopants which do not appear to have been tried before include Mg\textsuperscript{2+}(Zr), which has a defect energy of 1.22 eV, Sc\textsuperscript{3+}(Zr), Ca\textsuperscript{2+}(Zr), and Ca\textsuperscript{2+}(La). Therefore, two strategies are to combine two dopants to achieve a concentration of ~6.5 Li pfu, or a renewed push to examine garnets with lithium content greater than 7 Li pfu may yield novel compounds.
3 Interphase Thermodynamics

3.1 Interphase Calculation Methodology

Reaction between the electrolyte and cathode is common and may create undesirable interphase products. The thermodynamic driving force for this reaction can come either from the reduction in interfacial energy, or by the thermodynamics of mixing the two compositions to create new phases with a lower bulk free energy. We find that for many electrolyte|cathode interfaces, the phase equilibrium thermodynamics of the bulk materials dominate any energy changes that could be expected from changes in interface energies. Thus, studying the interphases formed at the interface is accomplished by analyzing the phase diagram consisting of all the elements in the combined electrolyte + electrode materials. Since it is a priori not known in which ratio the electrolyte and electrode react, all compositions on the tie line between their relative compositions need to be evaluated. To determine the interphases in a Li-ion battery this equilibrium is complicated by the fact that there are sources and sinks for lithium, and all thermodynamic potentials have to be evaluated in open-system conditions for a specified Li chemical potential (μ\textsubscript{Li})\textsuperscript{37,52}. Hence we search for the composition on the tie line between the electrode and electrolyte composition which results in the largest driving force for reaction at a given μ\textsubscript{Li}.

For each composition \( c \) in a phase diagram the lowest energy \( E_{\text{hull}}(c) \) is obtained by evaluating the convex energy hull corresponding to the phase diagram at that composition. The convex hull gives at any composition \( c \) the linear combination of phases that corresponds to the lowest energy. Equilibrating this composition with a lithium reservoir leads to a grand potential \( \varphi_{\text{hull}} \):

\[
\varphi_{\text{hull}}(c, \mu_{\text{Li}}) = \min_{n_{\text{Li}}} [E_{\text{hull}}(c + n_{\text{Li}}) + n_{\text{Li}} \mu_{\text{Li}}] \tag{2}
\]

Where \( n_{\text{Li}} \) is the number of atoms transferred to/from the lithium reservoir. Then, at a constant \( \mu_{\text{Li}} \) we search for decomposition products along the tie line between electrolyte|cathode compositions, according to:

\[
\Delta \varphi(\mu_{\text{Li}}) = \min_{x \in [0, 1]} \left[ \varphi_{\text{hull}}(x \times c_{\text{electrolyte}} + (1-x)c_{\text{cathode}}, \mu_{\text{Li}}) - x \varphi_{\text{hull}}(c_{\text{electrolyte}}, \mu_{\text{Li}}) - (1-x) \varphi_{\text{hull}}(c_{\text{cathode}}, \mu_{\text{Li}}) \right] \tag{3}
\]

Where the reaction energy, \( \Delta \varphi(\mu_{\text{Li}}) \), is the driving force for reaction between electrolyte and cathode, and \( x \) is a mixing parameter corresponding to a point on the tie line between the electrolyte and electrode compositions. For each lithium chemical potential, the value of \( x \) is
varied to find the reaction with the largest reaction energy. This calculation is performed over the voltage range of 0 to 5.0V vs. lithium metal (corresponding to -5 eV < \( \mu_{\text{Li}} \) < 0 eV vs. lithium metal). We repeat this procedure for LLZO and LLTO electrolytes against three common cathode materials: LCO, LMO, and LFP.

To better understand the decomposition reactions, we also calculate the intrinsic stability windows of LLZO and LLTO garnets and cathodes. The intrinsic window is defined as the lithium chemical potential range over which the garnet phases are stable. One may think of this as the stability against ideal electrode material which would not decompose but only release or absorb Li. This is important since after electrolyte decomposition, the interface reactions occur between decomposed electrolyte and cathode. The process is similar to calculations made for Li_{10}GeP_{2}S_{12} found elsewhere\textsuperscript{53}. The procedure is to generate the lithium grand potential phase diagrams of Li-La-Zr-O and Li-La-Ta-O (and corresponding diagrams for the cathodes) from \( \mu_{\text{Li}} \) = 0 to -5 eV vs. lithium metal (see Ong \textit{et al.}\textsuperscript{52} for more details).

3.2 Interphase Calculation Results

To demonstrate these methods, we use the example of LLZO|LCO. The complete quintenary (Li-La-Zr-Co-O) grand canonical phase diagram at 3 V is shown in Figure S1, and the tie line between the two compounds is highlighted. It bears repeating that the stable phases will change with the voltage\textsuperscript{52}. The largest reaction energy, according to Equation 3, along this tie line represents the most likely decomposition phases. A pseudo-binary phase diagram for this interface at 3 V is shown in Figure 3, and the decomposition phase equilibria are labeled on the figure. It is seen that the reaction at \( x = 0.286 \) has the largest driving force, and the predicted decomposition products are: La\textsubscript{2}O\textsubscript{3}, LiLaZrO\textsubscript{4}, and Li\textsubscript{2}CoO\textsubscript{3}. The maximum reaction energy phases at 3 V for all cathodes and electrolytes studied are presented in Table 3, and the results at other voltages are presented in Table S1.

From Table 3 it is seen that at 3 V the reactivity of LLZO/LLTO with the cathodes is \( \Delta \varphi_{\text{LFP}} > \Delta \varphi_{\text{LMO}} > \Delta \varphi_{\text{LCO}} \), and for all cathodes LLZO is more reactive than LLTO. The main reaction involves lithium and oxygen loss from the electrolytes. For the reactions of LLZO/LLTO with LCO and LMO, the cathode gains lithium and is oxidized forming Li\textsubscript{2}MO\textsubscript{3} (M = Mn, Co). In LFP, the phosphorous has a strong tendency to gain lithium and form Li\textsubscript{3}PO\textsubscript{4}.

The above routine (generate a tie line on the grand canonical phase diagram and find the largest reaction energy) is repeated for voltages from 0 to 5.0V vs. lithium metal and the results
Figure 3: LLZO|LCO pseudo-binary phase diagram when Li is available at 3 V vs. lithium metal. The decomposition products along the tie line are marked, and the maximum driving force reaction is marked with a red star.

Table 3: The maximum reaction energies and decomposition products are shown for the electrolyte|cathode combinations studied, with Li available at 3 V.

<table>
<thead>
<tr>
<th>(x)Electrolyte</th>
<th>(1-x)Cathode</th>
<th>$\Delta \phi$ (eV/atom)</th>
<th>Normalized Decomposition Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29 LLZO</td>
<td>0.71 LCO</td>
<td>-0.207</td>
<td>0.143 La$_2$O$_3$ + 0.565 LiLaZrO$_4$ + 0.715 Li$_2$CoO$_3$</td>
</tr>
<tr>
<td>0.22 LLZO</td>
<td>0.78 LMO</td>
<td>-0.665</td>
<td>0.778 Li$_2$MnO$_3$ + 0.111 La$_2$O$_3$ + 0.221 La$_2$Zr$_2$O$_7$</td>
</tr>
<tr>
<td>0.35 LLZO</td>
<td>0.65 LFP</td>
<td>-1.735</td>
<td>0.53 LiFeO$_2$ + 0.65 Li$_3$PO$_4$ + 0.12 La$_2$FeO$_6$ + 0.35 La$_2$Zr$_2$O$_7$</td>
</tr>
<tr>
<td>0.50 LLTO</td>
<td>0.50 LCO</td>
<td>-0.105</td>
<td>0.50 La$_3$TaO$_7$ + 0.50 Li$_2$TaO$_4$ + 0.50 Li$_2$CoO$_3$</td>
</tr>
<tr>
<td>0.50 LLTO</td>
<td>0.50 LMO</td>
<td>-0.402</td>
<td>0.50 La$_3$TaO$_7$ + 0.50 Li$_2$TaO$_4$ + 0.50 Li$_2$MnO$_4$</td>
</tr>
<tr>
<td>0.38 LLTO</td>
<td>0.62 LFP</td>
<td>-1.161</td>
<td>0.375 LaFeO$_3$ + 0.625 Li$_3$PO$_4$ + 0.750 LaTaO$_4$ + 0.125 Fe$_2$O$_3$</td>
</tr>
</tbody>
</table>

are plotted in Figure 4. The calculated intrinsic stability windows of the electrolytes and cathodes are marked at the bottom of Figure 4. It is seen that the LLZO is more stable at low voltages, but both garnets are decomposed by 3.8V. Within the electrolyte stability window, the trends seen at 3 V largely hold. The biggest driving force for decomposition occurs at the edges of the intrinsic stability windows. LLTO is less reactive than the LLZO above 2 V against all cathodes. Above 3.8V the electrolyte decomposition products remain constant and so the lines are horizontal in Figure 4. Similarly at low voltages, in the cathode decomposition regime, the cathode decomposition products (i.e., metal and Li$_2$O) are stable against the electrolytes. The reaction energy is zero against LLZO. At voltages below 2 V the LLTO begins to decompose to form
Li$_2$O and metal alloys with the decomposing cathodes: TaCo$_3$, TaMn$_2$, TaFe$_2$ (see Table S3 for complete decomposition products). However, these low voltages are not normally accessed at the electrolyte|cathode interface during battery operation, especially since they are outside of the cathode stability range.

4 Discussion

Lithium stuffed garnets can accommodate a wide array of dopant elements on all three cation sites. Doping is a successful strategy for improving conductivity by stabilizing the cubic structure. Most experimental evidence suggests a lithium concentration around 6.5 Li pfu shows the highest conductivity$^{12}$. Thus, supervalent cations are typically used as dopants. The most commonly used dopant is Al$^{3+}$(Li), however, we find that the defect energy of Al$^{3+}$(Li) is higher than several others and that after a certain solubility limit formation of Li$_5$AlO$_4$, Li$_6$Zr$_2$O$_7$, and La$_2$O$_3$ is predicted. In contrast Sn$^{4+}$(Zr) has a defect energy of 0.31 eV and is known to form the stable garnet compound Li$_7$La$_3$Sn$_2$O$_{12}$$^{15}$, and a complete solid solution is expected. In this work
we find several promising subvalent dopants with similar or lower defect energies compared to Al\(^{3+}\)(Li) such as: Zn\(^{2+}\)(Li), and Mg\(^{2+}\)(Li). Moreover, recent molecular dynamics simulations and experimental work suggests that LLZO compounds with Li concentrations above 7 pfu can also exhibit high conductivities\(^{13,54-56}\). This suggests a new path for stabilizing the cubic structure since many of the low defect energy dopants from our calculations are subvalent dopants which increase the lithium concentration. In this group the dopant(site) combinations with relatively low defect energies are Sc\(^{3+}\)(Zr), Ca\(^{2+}\)(Zr), Bi\(^{3+}\)(Zr), Mg\(^{2+}\)(Zr), Ca\(^{2+}\)(La), Sr\(^{2+}\)(La), and Ba\(^{2+}\)(La), many of which have been used with LLTO, but not LLZO. The others are listed in Table S2.

In many cases interfacial resistance between the cathode and electrolyte dominates battery cell resistance and greatly reduces the cell power, but finding a compatible interface is a difficult and time-consuming experimental process. Electrolyte|cathode interfacial resistance arises by chemical and electrochemical means. In this work we propose a novel approach to study the electrochemical driving force for decomposition. By varying the voltage, the interphase formation between electrolyte|cathode are identified with the largest reaction energy (according to Equation 3). Our results indicate LCO is a good choice since it shows little reactivity towards the garnet electrolytes. On the other hand, the LFP cathode is highly reactive with the garnet electrolytes; the Fe is oxidized forming the higher oxidation state phases such as Fe\(_2\)O\(_3\) (against LLTO) and LiFeO\(_2\) (against LLZO) and Li\(_3\)PO\(_4\). In fact we have checked several other LiMPO\(_4\) (M=Ni, Cr, V) phases and this pattern holds. It is possible that in reality the Li\(_3\)PO\(_4\) could form at the cathode|electrolyte interphase as a protective barrier layer and prevent further decomposition reactions, though this would require that the balance of the reaction products containing iron oxides does not create percolating electronic pathways.

Experimentally there have been conflicting reports about the stability of the LLZO|LCO interface. Some reports show a large interfacial resistance with a heterogeneous layer at the interface containing Co, La and Zr\(^{34,57}\). However, other reports show no evidence of interfacial resistance even upon cycling\(^{58,59}\). From the information contained within Fig. 2 and Fig. 4 it is possible to resolve this conflict. Co, La, and Zr ions are relatively large, and highly charged ions that are unlikely to diffuse at room temperature. However, when co-sintered at elevated temperatures the thermodynamic driving forces lead to interdiffusion and decomposition. From the stability analysis (section 2.2) we predict decomposition of Co\(^{3+}\)(Zr) LLZO into La\(_2\)O\(_3\), Li\(_6\)Zr\(_2\)O\(_7\), and Li\(_8\)CoO\(_6\) (Table S3), in good agreement with Kim et al.\(^{57}\) who found evidence of
decomposition at the LLZO|LCO interface. On the other hand, low temperature PLD deposition of LCO on LLZO showed stable cycling. From Figure 4 this suggests a metastable interphase is formed. The stable cycling can be accounted for by the relatively low driving force for decomposition interphases between LLZO|LCO seen across the range of lithium chemical potentials studied in Figure 4, or the decomposed products act as a barrier layer preventing further decomposition as seen at high voltages. The effects on stability due to oxygen or lithium loss from the garnet during high temperature sintering is out of the scope of the current study, but will be considered in future work.

In general, our results support experimental findings that the electrolyte|cathode interphase is more sensitive to chemical decomposition at high sintering temperatures than it is to electrochemical decomposition during cycling. This shows the importance and difficulty of careful synthesis, but also the promise of lithium garnets for use in all solid-state batteries.

5 Conclusions

In summary, we investigate the potential for finding stable cation dopants and mitigating internal resistance of LLZO garnet through first-principles calculations. We examine all possible cation dopant elements for LLZO and their site preference (Li, La, or Zr) by comparing the calculated defect energies. Several novel dopants emerge such as subvalent Sc$^{3+}$ and Mg$^{2+}$ on the Zr-site. The interphase resistance is studied by examining LLZO and LLTO electrolyte reactions with LCO, LMO, and LFP cathodes. We find that at high voltages the LMO and LFP react rather strongly with the garnet electrolytes, while the LCO is relatively stable. These results are a valuable resource for researchers looking to find stable cation dopants and cathodes to improve all solid-state battery performance with LLZO electrolytes bonded to cathodes.
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Additional information

Supplementary information is available free of charge via the Internet at http://pubs.acs.org/. Correspondence and requests for materials should be addressed to L.J.M.
TOC Graphic

![Diagram of LiCoO$_2$ and LLZO interphases with Li$_2$CoO$_3$, La$_2$O$_3$, and LiLaZrO$_4$.]

$E_{\text{rec}}$ (eV/atom) vs. $x$ Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)

Interphases:

3V

Li reservoir

Li$_2$CoO$_3$

La$_2$O$_3$

LiLaZrO$_4$