Particle Morphology and Lithium Segregation to Surfaces of the Li$_7$La$_3$Zr$_2$O$_{12}$ Solid Electrolyte

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Abstract

Solid electrolytes for solid-state Li-ion batteries are stimulating considerable interest for next-generation energy storage applications. The Li$_7$La$_3$Zr$_2$O$_{12}$ garnet-type solid electrolyte has received appreciable attention as a result of its high ionic conductivity. However, several challenges for the successful application of solid-state devices based on Li$_7$La$_3$Zr$_2$O$_{12}$ remain, such as dendrite formation and maintaining physical contact at interfaces over many Li intercalation/extraction cycles. Here, we apply first-principles density functional theory to provide insights into the Li$_7$La$_3$Zr$_2$O$_{12}$ particle morphology under various physical and chemical conditions. Our findings indicate Li segregation at the surfaces, suggesting Li-rich grain boundaries at typical synthesis and sintering conditions. On the basis of our results, we propose practical strategies to curb Li segregation at the Li$_7$La$_3$Zr$_2$O$_{12}$ interfaces. This approach can be extended to other Li-ion conductors for the design of practical energy storage devices.
Introduction

The commercial Li-ion battery, which relies on liquid electrolytes, is now the workhorse behind the mobile electronics industry.\textsuperscript{1–5} Unfortunately, a practical limit of what can be achieved with the current Li-ion technology is encountered when the focus shifts to electric vehicles.\textsuperscript{2,4–6} One promising avenue to improve the energy and power densities of Li-ion batteries, while enhancing their safety, consists of replacing the flammable liquid electrolyte with a solid electrolyte capable of efficiently shuttling Li ions between electrodes.\textsuperscript{7–21}

To facilitate this transition, the Li-ion conductivity of solid electrolytes must be competitive to that of their liquid analogs.\textsuperscript{12,16} While significant attention is still devoted to intrinsic Li\textsuperscript{+} conductivity in solid electrolytes, many challenges remain for future solid-state applications.\textsuperscript{5,22–30} The most pressing challenges are finding solid electrolytes that are electrochemically stable against electrodes, maintaining physical contact between components over many Li intercalation/extraction cycles and suppressing Li-dendrite formation.

The Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} garnet-type electrolyte has received significant attention due to its high ionic conductivity ($10^{-6}$–$10^{-3}$ S cm$^{-1}$) achieved by a variety of doping strategies,\textsuperscript{7,8,10,11,31–36} but most importantly because of its perceived stability against the Li-metal anode.\textsuperscript{25,27,29,37–41}

However, the failure of polycrystalline Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} in solid-state battery prototypes comprised of Li-metal anodes has been the subject of several studies.\textsuperscript{25,28,38,40–43} It has been observed\textsuperscript{29} that once Li fills a crack in Li\textsubscript{6}La\textsubscript{3}ZrTaO\textsubscript{12}, fresh electro-deposited Li is extruded to the available surface. Tests with Li-metal/Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}/Li-metal cells showed that only small current densities of $\sim$ 0.5 mA cm$^{-2}$ could be tolerated before dendrite failure.\textsuperscript{27,44} Rationalising the mechanisms behind the propagation of dendrites in Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} is a major challenge.

In parallel, sintering strategies to maximise the bulk transport in ceramic materials are routinely applied. While high temperature densification enhances ion transport, the extent of morphological transformations of the electrolyte particles is still unclear. Kerman \textit{et al.}\textsuperscript{27} highlighted the connection between the processing conditions of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} and its particle
morphology and size. Kingon et al.45 demonstrated that ceramics containing volatile cations, such as Li7La3Zr2O12, become Li deficient upon sintering.

These experimental observations indicate that it is crucial to understand the variation of the Li7La3Zr2O12 morphology as a function of chemical and physical properties (composition and temperature).

In this study, we develop a phenomenological model based on first-principles calculations to determine the composition of Li7La3Zr2O12 particles, while the chemical environment of Li, La, Zr and O, voltage and/or the temperature are varied. Rationalising the particle morphology of solid electrolytes contributes towards a deeper understanding of several critical phenomena, including the Li+ conductivity at grain boundaries and the propagation of dendrites during battery operation. Indeed, our results predict significant Li accumulation at the exterior of the Li7La3Zr2O12 particles when we mimic reducing high-temperature synthesis conditions.

Based on our computational insights, we propose practical strategies to engineer the chemical compositions of the particles, providing a greater control of the complex chemistry of Li7La3Zr2O12. These general design strategies can be extended to other solid electrolytes and electrode materials.

Results

Phase stability and chemical domains

We first consider the relative stability of the Li7La3Zr2O12 tetragonal (space group I41/acd) and high-temperature cubic (Ia3d) polymorphs. The computed lattice constants (a = 13.204 and c = 12.704 Å) of the tetragonal phase compare well with the experimental data (a = 13.134 and c = 12.663 Å).46 Figure 1a shows the decomposition of Li7La3Zr2O12 into Li6Zr2O7 + La2O3 + Li8ZrO6, revealing the metastability of both the cubic (∼ 22 meV/atom above the stability line at 0 K) and tetragonal (∼ 7 meV/atom) polymorphs, in agreement with
The degree of metastability of the tetragonal phase is small enough that the compound can be stabilised by thermal effects, which explains the success of high-temperature (> 600 °C) phase-pure synthesis.\textsuperscript{8,11} It is assumed that the chemical decomposition of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} into Li\textsubscript{6}Zr\textsubscript{2}O\textsubscript{7} + La\textsubscript{2}O\textsubscript{3} + Li\textsubscript{8}ZrO\textsubscript{6} requires a major coordination rearrangement of Zr and La, thereby kinetically preventing Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} from decomposing. Therefore, we assume that Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} is thermodynamically stable (see phase diagram in Figure 1b).

Identifying the phases in equilibrium with Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (Figure 1b) allows us to set the bounds of chemical potentials of each element, thus providing a thermodynamic framework to calculate meaningful non-stoichiometric surface energies (see Method section). Figure 1b illustrates the phases in equilibrium with Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}, which show that only La\textsubscript{2}O\textsubscript{3},...
Li$_6$Zr$_2$O$_7$, Li$_2$O, O$_2$ and Zr are in direct equilibrium with the solid electrolyte. Experimentally, the binary compounds La$_2$O$_3$, Li$_2$CO$_3$ (LiOH or Li$_2$O)$^{29}$ and ZrO$_2$ are used as precursors for the synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$. In addition, when Li$_7$La$_3$Zr$_2$O$_{12}$ is assumed to be stable, Li$_8$ZrO$_6$ becomes metastable in the Li-La-Zr-O phase diagram (Figure 1b).

Our discussion moves to the definition of the relevant chemical potentials, which have to be rigorously defined to accurately calculate the energies of non-stoichiometric surface structures (see Eq. 1). From thermodynamic arguments, any combination of three compounds in equilibrium with Li$_7$La$_3$Zr$_2$O$_{12}$ define distinct chemical potentials ($\mu$) for the elements O, La, Li and Zr. In this study, we consider two different chemical regimes, i.e. oxidising and reducing. The tetrahedron composed of Li$_7$La$_3$Zr$_2$O$_{12}$, La$_2$O$_3$, Li$_2$O and O$_2$ mimics the oxidising and experimental synthesis conditions of Li$_7$La$_3$Zr$_2$O$_{12}$. In contrast, we consider a reducing environment as defined by Li$_7$La$_3$Zr$_2$O$_{12}$ being in equilibrium with Zr metal, La$_2$O$_3$ and Li$_2$O, which corresponds to experimental sintering conditions. A detailed derivation and the bounds of the chemical potential used for each species are summarised in Section 1 and Table S1 of the Supplementary Information (SI).

Although Zr forms oxides with multiple oxidation states, such as ZrO and Zr$_2$O as reported by Chen et al., Zr is not redox active in Li$_7$La$_3$Zr$_2$O$_{12}$. Therefore, Zr-metal and ZrO$_2$ represent valid reference states for the $\mu_{Zr}$ in reducing (Zr$^0$) and oxidising (Zr$^{4+}$) environments, respectively.

**Surface structures and energies**

Surfaces of solid electrolytes are important to their electrochemical properties, particularly due to the presence of active interfaces within intercalation batteries. The Li$_7$La$_3$Zr$_2$O$_{12}$ cubic polymorph provides the highest ionic conductivity.$^{11,47,51}$ However, accounting for the Li disorder presents a major computational complexity when creating representative surface structures. Thus, we consider the tetragonal polymorph, which constitutes a distinct ordering of Li sites, as the reference structure for creating our surface models.
Figure 2 depicts the atomic arrangement of the Li-terminated (010) surface of Li$_7$La$_3$Zr$_2$O$_{12}$, highlighting the significant reconstruction of the Li and O layers, respectively. The dotted lines in Figure 2 are a guide for the eye to illustrate the loss of symmetry of the Li environment at the surface compared to the bulk region. Figure 2 shows that La layers overlap with “rumpled” oxygen layers, which contribute to stabilise La-terminated surfaces, as discussed in the following paragraphs. In the case of Zr ions, the oxygen coordination environment in the surface slab show insignificant deviation from the octahedral coordination within bulk Li$_7$La$_3$Zr$_2$O$_{12}$, in qualitative agreement with the lack of surface reconstruction observed in
It is known that for a given Miller index several surface terminations may be possible since the bulk can be cleaved at different planes, as shown in Figure 2. The relative stability of each surface model is defined by their surface energy ($\gamma$, Eq. 1). Figure 3 depicts the computed $\gamma$ values of a number of stoichiometric and non-stoichiometric La, Li, O and Zr-terminated surfaces of Li$_7$La$_3$Zr$_2$O$_{12}$. Non-stoichiometric surfaces refer to surfaces where the stoichiometry deviates in composition from the bulk. The surface energies of symmetry-related Miller index surfaces (e.g., (100) $\approx$ (010) $\approx$ (001)) are detailed in Table S2. As introduced in Section , the chemical potentials, $\mu_i$, for calculating $\gamma$ of non-stoichiometric surfaces are set to reducing conditions (i.e., $\mu_{\text{La}} \approx \mu_{\text{La}}$ in La$_2$O$_3$, $\mu_{\text{Li}} \approx \mu_{\text{Li}}$ in Li$_2$O, and $\mu_{\text{Zr}} \approx \mu_{\text{Zr}}$ in Zr metal), see Figure 1b and Section 1 of the SI.

![Figure 3: Surface energies $\gamma$ (J m$^{-2}$) of La (blue), Li (red), O (green) and Zr (yellow) -terminated surfaces of Li$_7$La$_3$Zr$_2$O$_{12}$. Hatched bars indicate non-stoichiometric surfaces, whose surface energies are derived using the chemical potentials from Figure 1b. The chemical potentials of Li, La and Zr are fixed by Li$_2$O, La$_2$O$_3$ and Zr metal, respectively, corresponding to reducing conditions (details in Section ).](image-url)
Figure 3 shows three main features: i) Zr-terminated surfaces show the highest surface energy $\gamma$ (> 1.5 J m$^{-2}$), ii) certain Li-terminated surfaces possess significantly lower $\gamma$ ($\sim 0.87\pm0.02$ J m$^{-2}$ for the (010) surface), in good agreement with previous work. 48 iii) La- and O-terminated surfaces show similar surface energies, as indicated by $\gamma$ 0.98 J m$^{-2}$ and 0.99 J m$^{-2}$ for the La- and O-terminated (110) surfaces, respectively.

Although the surface structures are obtained from the tetragonal phase, we find identical surface energies for symmetry inequivalent surfaces (see Table S1 and Figure S1). For example, the surface energy ($\sim 1.77$ J m$^{-2}$) of the Zr-terminated (010) surface is identical to the (001) and (100) surfaces, which is typically not found for tetragonal structures. This suggests the similarity between the tetragonal and cubic phases of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and indicates that the Li ordering, which affects the relative stability of the bulk tetragonal and cubic phases, has only a negligible impact on the relative symmetry and energetics of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surfaces. Notably, the $c/a$ ratio exhibited by the tetragonal phase ($\sim 0.96$ from experimental lattice constants, see Section ) signifies the “small” tetragonal distortion in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.

**Effects of oxygen environment and temperature on surfaces**

With the aim of understanding the interplay between compositional and temperature effects on the morphology of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, we now move our attention to trends of surface energy as a function of temperature and oxygen composition. To include temperature dependence in our model, we apply a thermodynamic framework (detailed in the Method section) that connects changes in the O$_2$ chemical potential, $\mu_{O_2}$, directly to temperature. 53 This approximation is valid as the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ electrolyte is in contact with an oxygen environment during its synthesis and sintering.

With $\mu_O = \frac{1}{2}\mu_{O_2}$, $\mu_O$ sets the surface energy of non-stoichiometric surfaces, as indicated in Eq. 2. Note that under both oxidising and reducing conditions (Section ), the chemical potentials of La and Li are set by $\text{La}_2\text{O}_3$ and $\text{Li}_2\text{O}$, respectively. All the non-stoichiometric surfaces studied here are either oxygen rich or poor (see Method section). High $\mu_O$ (or $\mu_{O_2}$)
represents low-temperature situations and a highly oxidative environment, where oxygen molecules “condense” on the surfaces of Li$_7$La$_3$Zr$_2$O$_{12}$. In contrast, higher temperatures (i.e., more negative $\mu_O$) signify reducing conditions, where oxygen atoms become volatile and leave the surface as O$_2$ gas, which is equivalent to Li$_7$La$_3$Zr$_2$O$_{12}$ being in equilibrium with Zr metal.

Figure 4 shows the variation of the surface energy for a number of non-stoichiometric surfaces as a function of temperature, or its equivalent $\mu_O$, corresponding to an oxygen partial pressure of 1 atm.

A number of important observations can be drawn from Figure 4. i) The Li-terminated (010) surface has the lowest $\gamma$ (as in Figure 3) and the La-terminated (010) stoichiometric surface has the highest $\gamma$ for temperatures higher than 25 °C. The negative slope of each line signifies that all the surfaces are oxygen deficient. While studying non-stoichiometric surfaces, we have focused on La, Li and O deficient scenarios, as they are most likely to develop at high temperatures.$^{54,55}$ In order to maintain the electroneutrality of oxygen-terminated surfaces, oxygen vacancies were introduced to compensate the removal of cations (details are provided in the Method section). ii) The stability of the Li-terminated (010) surfaces in comparison to other terminations is significant. iii) At temperatures higher than 300 °C, the O-terminated (010) and (110) surfaces become more stable than the (110) Li-terminated surface. This result is also found for the (100), (001), (011) and (101) Li-terminated facets. iv) Above 750 °C, the negative $\gamma$ of (010) Li-terminated surface (as seen in Figure 4) is indicative of the instability of bulk Li$_7$La$_3$Zr$_2$O$_{12}$, and may be linked to the melting of Li$_7$La$_3$Zr$_2$O$_{12}$ particles.

**Environment dependent particle morphologies**

By combining our surface energies of various surface facets at distinct chemical compositions (Figures 3 and 4), we can implement the Wulff construction to derive the Li$_7$La$_3$Zr$_2$O$_{12}$ equilibrium particle morphology at synthesis conditions.
Figure 4: Surface energy $\gamma$ of La (blue), Li (red) and O (green) -terminated Li$_7$La$_3$Zr$_2$O$_{12}$ surfaces vs temperature and oxygen chemical potential $\mu_O$. The blue horizontal line indicates the stoichiometric La-terminated surface energy. The zero (eV) in the $\mu_O$ scale is normalised against the reference state $\mu^*_{O}$ and is detailed in the SI. $\mu_O$ near 0 eV relates to oxygen-rich (or oxidising) regimes, whereas more negative oxygen chemical potentials are oxygen-poor (or reducing) conditions. The grey shading marks the experimental temperature window for synthesis and sintering of Li$_7$La$_3$Zr$_2$O$_{12}$. The chemical potentials of Li and La are fixed by Li$_2$O and La$_2$O$_3$, respectively, while $\mu_O$ is allowed to vary.

Figure 5 depicts the change of the particle equilibrium morphology as a function of temperature.

At room temperature ($\sim 24 ^\circ$C), the equilibrium Li$_7$La$_3$Zr$_2$O$_{12}$ particle morphology is dominated by the (001), (101) and (110) surfaces. For temperatures greater than 600 $^\circ$C
(and < 750 °C), Li$_7$La$_3$Zr$_2$O$_{12}$ particles should assume a cubic shape dominated by the (100) and (010) surfaces, as seen in Figure 5.

At 24 °C and intermediate temperatures (\(\sim\) 180 °C), the (110) Li-terminated surface contributes to the overall particle shape. However, an increase in oxygen composition on the surface of the Li$_7$La$_3$Zr$_2$O$_{12}$ particles will be also observed, as shown by the increased stability of the (110) oxygen-terminated surfaces over (110) Li-terminations, as seen in Figure 4 at temperatures above 300 °C.

**Tuning the synthesis conditions of Li$_7$La$_3$Zr$_2$O$_{12}$**

We now discuss the surface phase diagram obtained by varying the chemical composition of Li$_7$La$_3$Zr$_2$O$_{12}$. This analysis contributes to understanding the experimental synthesis conditions to achieve the desired chemical composition of the particle surfaces.

Computing a complete surface phase diagram represents a formidable exercise given the large compositional space for the non-stoichiometric terminations accompanied by the large number of atomic arrangements of partially occupied terminating layers. Thus, we limit the discussion of the surface phase diagram to the Li$_7$La$_3$Zr$_2$O$_{12}$ surfaces in Figure 3. Li-rich and Li-poor conditions correspond to Li$_2$O (reducing conditions) and Li$_6$Zr$_2$O$_7$ (oxidising conditions), respectively, while Zr-rich is equivalent to Zr metal (reducing) and Zr-poor to
O₂ gas (oxidising).

Figure 6 shows the surface phase diagram at 0 K by varying the Li (µ_Li) and Zr (µ_Zr) composition. We find that regions of low µ_Li and µ_Zr are consistently dominated by the

![Figure 6: Surface phase diagram at 0 K of Li₇La₃Zr₂O₁₂ and schematic representations of particle morphologies at different chemical conditions. Stable surfaces and chemical terminations as a function of µ_Li and µ_Zr. The white square identifies the compositional Li–Zr conditions where Li₇La₃Zr₂O₁₂ is commonly synthesised. Zr-rich is equivalent to Zr metal (Zr-poor is O₂ gas), whereas Li-rich is Li metal (and Li-poor is Li₆Zr₂O₁₂). The voltage evolution vs Li/Li⁺ (with V = −µ_Li · e⁻) is also shown. The chemical potential scales are referenced against the reference states µ_{Li}^* (Li₂O) and µ_{Zr}^* (Zr metal).](image-url)

(010) O- and La-terminated surfaces. At more positive µ_Li and µ_Zr (near Li-rich and Zr-rich conditions), the (010) Li-terminated surfaces are stable. In fact, the (010) O- and La-terminated surfaces have similar surface energies ∼ 0.94 and ∼ 0.98 J m⁻², respectively (see Figure 3), as the La ions exposed are surrounded by a O sub-layer. The La/O or Li segregations at the surface of the particles of Li₇La₃Zr₂O₁₂ (at specific µ_Li and µ_Zr) are
schematically shown by the green and violet spheres of Figure 6.

Figure 6 also includes a voltage scale, which relates directly to the Li chemical potential \( V = -\mu_{\text{Li}} \cdot e^- \). Negative \( \mu_{\text{Li}} \) signify high voltages (vs Li/Li\(^+\)) and vice versa.

**Discussion**

To gain realistic insights into the design of solid electrolytes for solid-state batteries, we have performed a thorough first-principles calculation analysis of the \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) surfaces and its morphologies under various physical and chemical conditions.

**Morphology and composition of \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) particles** — Figure 1b shows that lower surface energies are found for surfaces terminated by cations with lower oxidation states, following the trend \( \text{Li}^+ < \text{La}^{3+} < \text{Zr}^{4+} \). This finding relates to electrostatic and geometric factors. By cleaving a cation-terminated surface, the large disruption of the ideal cation coordination environment results in a high-energy penalty, thus impacting significantly the relative stability of the surface.

Experimentally, \(^{56}\) it is found that \( \text{La}^{3+} \) and \( \text{Zr}^{4+} \) ions prefer high oxygen coordination (\( \geq 6 \) in the cubic and tetragonal \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) phases), whereas \( \text{Li}^+ \) can adjust to both octahedral and tetrahedral environments. \(^{11,57}\) Li ions can tolerate reduced coordination environments leading to lower surface energies compared to Zr-terminated surfaces, which undergo a reduction in coordination from 6–8 to 4. La-terminated surfaces show low surface energies (\( \sim 0.94 \text{ J m}^{-2} \)) compared to the Zr-terminated surface, which are explained by the oxygen sub-layer stabilising the partially uncoordinated La atoms and lowering the surface energy (see Figure S3).

We have identified that surfaces with low Miller indices, e.g. \((010)\) and \((110)\) with Li-rich textures, dominate across a wide range of temperatures and oxygen environments. Li segregation at the surfaces of \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) particles has been demonstrated by neutron depth profiling experiments. \(^{39}\) O-terminated surfaces are also possible, as shown in Figure 6. This
may be significant in relation to the recent report of oxygen migration in Li$_7$La$_3$Zr$_2$O$_{12}$.\textsuperscript{58}

The predicted room temperature morphology of Li$_7$La$_3$Zr$_2$O$_{12}$ is in excellent agreement with a scanning electron microscopy study of a single crystal,\textsuperscript{46} providing credibility to the computed morphologies of Figure 5. However, no specific surface facets were characterised, which we identified here.\textsuperscript{46} We can complement the experimental observations by extending our model beyond the shape of the particles. This is completed by ascertaining the dominant surface facets and the most likely chemical compositions under both reducing and oxidising conditions.

On the basis of these findings we speculate that small cations, such as Al$^{3+}$ and Ga$^{3+}$, doped at Li$^+$ sites may segregate at the surfaces of the particles. In agreement with our hypothesis, a number of experimental reports demonstrate that Al$^{3+}$ segregates to the grain boundaries of doped Li$_7$La$_3$Zr$_2$O$_{12}$\textsuperscript{55,59,60} We speculate that high-valent cations, such as Ta$^{5+}$ and Bi$^{5+}$ (introduced on the Zr lattice to increase the number of Li vacancies),\textsuperscript{11} will constitute the core of the Li$_7$La$_3$Zr$_2$O$_{12}$ particles.

**Densification and implications on ionic conductivity** – Densification of ceramic oxides via high-temperature (and spark-plasma) sintering is routinely employed to improve the electrolyte ionic conductivity.\textsuperscript{11,45,55} Typically, the interpretation of impedance measurements requires the deconvolution of the total ionic conductivity into three main contributions, namely,\textsuperscript{61–63} intrinsic bulk, grain boundary and interfacial electrolyte/blocking electrode. While bulk Li-ion transport has been emphasised by both experiment and computation,\textsuperscript{7–9,11,31,32,47,51} grain boundary Li-ion conductivity is much less examined, despite being crucial.\textsuperscript{7–9,11}

The seminal paper on Li$_7$La$_3$Zr$_2$O$_{12}$ by Murugan et al.\textsuperscript{8} showed significant Li-ion resistance at the grain boundaries (\textasciitilde 50\% of the total), thus suggesting the relevance of intergranular Li-ion transport.\textsuperscript{64} Ceramic oxides processed at high temperatures containing “volatile” cations, such as Li, including Li$_7$La$_3$Zr$_2$O$_{12}$, will produce Li deficient bulk materi-
als,\textsuperscript{27} and thus possible Li loss upon sintering treatments. For example, Antolini\textsuperscript{54} showed that sintering of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ ceramic electrodes can promote Li segregation at the particle exterior, thus altering the overall stoichiometry. Loss of Li$_2$O was observed in the synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12},$\textsuperscript{35,36,55,65} and additional Li$_2$O is routinely added during its preparation.

In agreement, our prediction in Figure 4 suggests that at high temperatures ($\geq 600$ °C in the sintering regime) and reducing conditions, the particle surfaces will show pronounced segregation of Li. Assuming that the stable surfaces computed in this study are representative of the grain boundaries in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, we speculate that the accumulation of Li ions can impact the Li transport involving grain boundaries.\textsuperscript{64}

**Engineering the particle morphology** – On the basis of our predictions, we can propose practical strategies to engineer particle morphologies of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.

For example, Figure 6 demonstrates that adding extra Zr and/or Li metals during synthesis may promote Li segregation at the grain boundaries.\textsuperscript{39} In addition, as indicated in Figure 4, routine high-temperature synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ promotes reducing conditions (i.e., oxygen-poor conditions) and Li terminated surfaces/particles. Hence low-temperature synthesis (and sintering) protocols should be sought.\textsuperscript{66}

From analysis of Figure 6, we speculate that O/La accumulation at the grains is also observed near the operating voltages of typical Li-ion cathode materials (e.g., LiCoO$_2$ $\sim$ 3.8 V vs. Li/Li$^+$ and LiFePO$_4$ $\sim$ 3.4 V). In this context, Miara \textit{et al.}\textsuperscript{67} have shown that $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ remains stable against LiCoO$_2$, whereas the analogous interface with LiFePO$_4$ decomposes forming a protecting Li$_3$PO$_4$ interface. Nevertheless, a more recent experimental investigation by Goodenough \textit{et al.}\textsuperscript{68} showed significant Al$^{3+}$ and La$^{3+}$ migration from Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ to LiCoO$_2$, and negligible Zr diffusion into LiCoO$_2$. In Figure 6, near 3 V we predict La segregation towards the particle surfaces corroborating these experimental findings.

The failure upon short-circuiting of polycrystalline $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ in solid-state devices,
utilising a Li-metal anode, has been linked to dendrite propagation.\textsuperscript{27} Near 0 V or at the potential of Li metal, we expect the Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} particles to be lithium terminated. In agreement with our results, Li segregation close to a Li-metal anode interface in Al-doped Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} has been recently observed by in situ transmission electron microscopy.\textsuperscript{38} We speculate that the occurrence of Li at the particle surface and at grain boundaries, could indeed set the ideal chemical environment required for Li-dendrite growth and propagation between Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} particles. In line with our results, Kerman \textit{et al.}\textsuperscript{27} proposed that once Li fills a crack in doped Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}, fresh electrodeposited Li extrudes to the existing grain boundaries.

Unsurprisingly, the process of dendrite propagation can originate from Li “stuffing” into grain boundaries.\textsuperscript{27} Thus, the significant accumulation of Li at the surfaces of the Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} particles may favour the initial stages of dendrite nucleation and growth along the existing grain boundaries. Further experimental studies are required to verify these hypotheses.

\section*{Conclusions}

Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} is an important solid electrolyte material, but its surfaces and particle morphologies under synthesis and sintering conditions are not fully characterised.

First, by studying the morphology and composition of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} particles from DFT-based calculations, we have demonstrated the spontaneous segregation of Li towards the particle exterior. Second, we map the compositional changes of the surfaces of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} as a function of temperature and of oxygen chemical pressure. Li segregation to surfaces is the dominant process over a range of temperatures, particularly during high-temperature synthesis and sintering. These findings are significant in relation to the initial stages of Li dendrite growth. Third, by studying the surface phase diagram of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}, we find that Li segregation can be curbed by tuning the ceramic synthesis conditions. We show that
synthesis in reducing environments (O-poor, Li-rich and/or Zr-rich) may promote Li segregation to the particle surfaces. Finally, we find that particle compositions of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> are altered upon voltage sweeps, with Li segregation at the exterior occurring at the Li-metal anode voltage.

These findings will contribute towards developing strategies for the optimisation of the synthesis and operation of promising solid electrolytes for solid-state batteries.

**Method**

**Surface energies and thermodynamic framework**

The physical quantity defining stable surface compositions and geometries is the surface free energy $\gamma$ (in J m<sup>-2</sup>):

$$\gamma = \frac{1}{2A} \left[ G_{\text{surface}} - G_{\text{bulk}} - \sum_{i} \Delta n_{i} \mu_{i} \right]$$  

(1)

where $A$ is the surface area (in m<sup>-2</sup>) and $G_{\text{surface}}$ and $G_{\text{bulk}}$ are the surface free energies of periodic surfaces and the reference bulk material, respectively. $G_{\text{surface}}$ and $G_{\text{bulk}}$ are approximated by the respective computed internal energies $E_{\text{surface}}$ and $E_{\text{bulk}}$, accessed by density functional theory (DFT) as described in the SI. In the case of non-stoichiometric surfaces, the final surface energy depends on the environment set by the chemical potential $\mu_{i}$ for species $i$ and amounting to an off-stoichiometry of $\Delta n_{i}$. Note that $\Delta n_{i}$ is negative (positive) if species $i$ is removed (added) to the surface. The chemical potential references $\mu_{i}$ were derived from the computed phase diagram (Figure 1b) at 0 K.

Eq. 1 provides $\gamma$ values at 0 K that are not representative for the operating conditions of solid electrolytes and the synthesis and sintering conditions. For non-stoichiometric surfaces, the approximation chosen to introduce the temperature dependence in the $\gamma$ values is based on the fact that the surrounding O<sub>2</sub> atmosphere forms an ideal-gas-like reservoir, which is in equilibrium with Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. The effect of temperature is introduced into the definition
of $\gamma$ as follows:

$$\gamma(T) = \frac{1}{2A} \left[ E_{\text{surface}} - E_{\text{bulk}} - \sum_{i} \Delta n_i \mu_i - \Delta n_O \mu_O(T) \right] \quad (2)$$

where $\mu_O$ is now a temperature dependent quantity and evaluated directly by combining DFT data with experimental values tabulated by NIST/JANAF as:

$$\mu_O(T) = \frac{1}{2} \mu_O(0 \text{ K, DFT}) + \frac{1}{2} \mu_O(0 \text{ K, Exp.}) + \frac{1}{2} \Delta G_{O_2}(T, \text{Exp.}) \quad (3)$$

where the $\mu_O(0 \text{ K, DFT})$ is the 0 K free energy of an isolated oxygen molecule evaluated with DFT, whereas $\mu_O(0 \text{ K, Exp.})$ is the 0 K experimental (tabulated) Gibbs energy for oxygen gas. $\Delta G_{O_2}(T, \text{Exp.})$ is the difference in the Gibbs energy defined at temperature, $T$, as $1/2[H(T, O_2) - H(0 \text{ K, O}_2)] - 1/2T[S(T, O_2)]$, respectively, as available in the NIST/JANAF tables. We omitted the partial pressure dependence of the $\mu_O$ term (i.e., we used $p_{O_2} = 1 \text{ atm}$) as we expect this contribution to be small, as demonstrated previously.

**Bulk surface models**

Because of the large number of possible chemical terminations, as a result of the quaternary nature of Li$_7$La$_3$Zr$_2$O$_{12}$, the selection of surfaces investigated was only limited to low-index surfaces, such as (100), (001), (101), (111) and (201). We note that some of these surfaces are related by the intrinsic tetragonal symmetry. For example, (100) = (010), as verified by the surface energies in the Supplementary Information (see Table S2).

In line with Tasker’s classification of oxide surfaces, only realistic type I surfaces were considered, which are characterised by zero charge and no electrical dipole moment. Nevertheless, these requirements are only satisfied by a limited number of stoichiometric Zr- or La-terminated surfaces with high surface energies.

Because our goal is to rationalise the chemical composition and morphology of the
Li$_7$La$_3$Zr$_2$O$_{12}$ particles, it is crucial to study the Li- and O-terminated surfaces. As a result, type I non-stoichiometric surfaces were generated by selectively removing layers of Zr and/or La and charge-compensated by O removal, as shown schematically in Figure 2. Upon cation removal, charge neutrally is maintained by introducing oxygen vacancies, resulting in the need to investigate a significant number of atomic orderings. We simplify this difficult task by computing with DFT only the 20 orderings with the lowest electrostatic energy, as obtained by minimising the Ewald energy of each surface using formal charges.$^{71}$ This results in the assessment of 420 non-stoichiometric surfaces using DFT. While performing this operation, we enforce symmetry between the two faces of the surfaces. Using this strategy, we identified 21 non-stoichiometric orderings and 11 stoichiometric surfaces that are O-, Li-, La- and Zr-terminated, respectively, whose surface energies are discussed in Figure 3 and Table S2.

**Acknowledgements**

The authors gratefully acknowledge the EPSRC Programme Grant (EP/M009521/1) and the MCC/Archer consortium (EP/L000202/1). PC is grateful to the Ramsey Memorial Trust and University of Bath for the provision of his Ramsey Fellowship. PC is thankful to Dr. Benjamin Morgan at the University of Bath for fruitful discussions. PC deeply indebted to Dr. yet to be Theodosios Famprikis at the LRCS, Amiens, France. We acknowledge fruitful discussion with Prof. Peter Bruce, Stefanie Zekoll and Dr. Jitti Kasemchainan at the University of Oxford.

**Supporting Information Available**

The following files are available free of charge. The Supporting Information is available free of charge on the ACS Publications website at DOI:
• Details of first-principles calculations.
• Chemical potentials bounds.
• Surface energies.
• Li$_7$La$_3$Zr$_2$O$_{12}$ particle morphologies.
• Li$_7$La$_3$Zr$_2$O$_{12}$ surface reconstruction.

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