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# The origin of chemical inhomogeneity in garnet electrolytes and its impact on the electrochemical performance†

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The interface between solid electrolytes and lithium metal electrodes determines the performance of an all-solid-state battery in terms of the ability to demand high power densities and prevent the formation of lithium dendrites. This interface depends strongly on the nature of the solid electrolyte surface in contact with the metallic anode. In the garnet electrolyte/Li system, most papers have focused on the role of current inhomogeneities induced by void formation in the Li metal electrode and the presence of insulating reaction layers following air exposure. However, extended defects in the solid electrolyte induced by chemical and/or structural inhomogeneities can also lead to uneven current distribution, impacting the performance of these systems. In this work, we use complementary surface analysis techniques with varying analysis depths to probe chemical distribution within grains and grain boundaries at the surface and in the bulk of garnet-type electrolytes to explain their electrochemical performance. We show that morphology, post-treatments and storage conditions can greatly affect the surface chemical distribution of grains and grain boundaries. These properties are important to understand since they will dictate the ionic and electronic transport near the interfacial zone between metal and electrolyte which is key to determining chemo-mechanical stability.

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## 1. Introduction

The use of a metallic lithium electrode in place of the current state-of-the-art graphitic anode in Li-ion batteries is expected to enable cells with higher energy densities as a result of the large theoretical capacity of lithium metal (3860 mA h g<sup>-1</sup>). Unsolved problems with safety due to side reactions and dendritic lithium formation in flammable liquid-electrolyte-based cells have led to the search for a solid-electrolyte-based alternative in the form of an 'all-solid-state' battery. However, several problems remain for the interface between the solid electrolyte and Li metal anode.

The wide electrochemical stability window of fast-ionic conducting Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) garnets<sup>1</sup> means that they are

in principle compatible with Li metal as an electrode.<sup>2</sup> This, in combination with the mechanical hardness of the ceramic (hardness/yield strength of 6.3 GPa for LLZO compared to 0.655 GPa for metallic lithium),<sup>3</sup> was expected to suppress the Li dendrite formation<sup>4</sup> that commonly occurs with liquid or polymer electrolytes. However, poor electrode–electrolyte contact and resulting limited exchange current densities before dendrite formation have so far prevented the implementation of the garnets as viable solid electrolytes in Li metal battery applications.

To date, two areas of research have been explored in order to explain the performance of the Li|LLZO interface: (1) the role of the metallic Li in terms of its mechanical properties (creep and void formation during plating/stripping cycles) and (2) the surface chemistry of LLZO (especially in terms of reaction products forming at the surface).

Krauskopf *et al.* investigated the pressure-dependent electrode kinetics of the Li|LLZO interface,<sup>5</sup> in which they show that both contact geometry and ionic transport in the garnet electrolyte dominate the interfacial contribution for a clean interface under equilibrium. They found that by exerting pressures exceeding 100 MPa they could almost entirely remove the interfacial resistance. This was ascribed to plastic deformation of the lithium metal under the high pressures used which prevented void formation and the associated constriction

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LLZO were studied following two different mechanical polishing and thermal treatments of the sample.

### 3.1. Electrochemistry

Impedance spectra of the pellets (Fig. 1) show large differences in the interfacial resistance, depending on the surface treatment used, but little change in the bulk and grain boundary properties. Of note is the large decrease in the interfacial impedance following thermal etching of the sample to 900 °C (2 orders of magnitude lower area-normalized resistance compared to the polished sample). To quantify the spectra, three resistors in parallel with a constant phase element are used, with a high frequency inductance  $L$  (on the order  $10^{-6}$  H) and an internal resistance  $R_{\text{int}}$  fixed at 3  $\Omega$  (measured with a blank, or 'shorted' cell) in series. The resulting values are given in Table 1. The capacitance is calculated from the constant phase element using the Brug formula.<sup>19</sup>

Galvanostatic cycling of the cells (Fig. S3†) showed a substantial increase in the critical current density when comparing polished and thermally etched samples (0.03 mA  $\text{cm}^{-2}$  and 0.23 mA  $\text{cm}^{-2}$ , respectively).

### 3.2. Temperature-dependent XPS

XPS was used to observe the evolution of surface species such as corrosion layers on the LLZO surface following different surface treatments (polishing and thermally etching). *In situ* variable temperature XPS was carried out from room temperature (RT, grey line in Fig. 2) to 800 °C and back to RT (blue line) with 200 °C steps using a sample polished to 4000-grit with ethanol and with a final dry polish in the glove box that was then transferred under argon to the high vacuum XPS chamber. Energy calibration was carried out by using the O 1s peak for lattice oxygen as an internal standard and aligning this to a binding energy (BE) of 530.1 eV.<sup>14</sup> This is preferred over the

Table 1 Calculated values of normalized bulk, grain boundary and interfacial resistance,  $R$  and capacity,  $C$ , of Fig. 1 Nyquist plots

	Polished	Etched
$R_{\text{bulk}}$ [ $\Omega \text{ cm}^2$ ]	155.1	123.8
$C_{\text{bulk}}$ [F $\text{cm}^2$ ]	$7.8 \times 10^{-12}$	$8.3 \times 10^{-12}$
$R_{\text{gb}}$ [ $\Omega \text{ cm}^2$ ]	354.7	396.9
$C_{\text{gb}}$ [F $\text{cm}^2$ ]	$1.2 \times 10^{-11}$	$2.3 \times 10^{-11}$
$R_{\text{int}}$ [ $\Omega \text{ cm}^2$ ]	12 372.2	148.9
$C_{\text{int}}$ [F $\text{cm}^2$ ]	$1.1 \times 10^{-8}$	$1.2 \times 10^{-8}$

use of the C 1s peak from adventitious carbon,<sup>20</sup> which cannot be relied upon for BE referencing given that the peak position can vary with sample work function<sup>21</sup> and the adventitious carbon is likely to undergo chemical changes during *in situ* heating.<sup>22</sup> The Zr 3d peaks are also found to all align with this approach, indicating their chemical stability and that they could also be used for energy calibration. All spectra are normalised to the Zr 3d peak intensity. Full peak fitting is performed for RT spectra recorded before and after thermal etching and the assigned species can be seen in Fig. S4.†

Before thermal etching, the C 1s spectrum shows the presence of carbonate species at the surface with peaks located at  $\sim 289.9$  eV and  $\sim 291$  eV corresponding to  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , respectively, and adventitious carbon primarily associated with C–C and C–H species at  $\sim 286$  eV. The corresponding O 1s spectrum is dominated by a peak related to carbonate and hydroxide species at  $\sim 532.7$  eV, but lattice oxygen is still detectable through this corrosion layer. The Li 1s spectrum at room temperature is similarly dominated by a peak at  $\sim 56.2$  eV related to the presence of lithium carbonate and hydroxide.<sup>14</sup> By considering the relative intensity of the carbonate/hydroxide and lattice oxygen components and assuming the corrosion layer to be of uniform thickness, the corrosion layer thickness is estimated to be  $\sim 2.7$  nm based on the Strohmeier equation<sup>23</sup> and values of inelastic mean free path obtained using the Tanuma, Powell and Penn (TPP-2M) equation.<sup>24</sup> We note however that our current data are unable to determine whether the corrosion layer is uniform so this value should be treated with some caution.

During thermal etching, the C 1s, O 1s and Li 1s reveal the removal of the hydroxide/carbonate species and an increase in the lattice oxygen and lithium peaks found at binding energies of 529.8 eV and 55.2 eV, respectively. The carbonate peak is found to be completely removed for a thermal etching between 400 °C and 600 °C. This is in agreement with previous work by Zhu *et al.* which shows the loss of  $\text{Li}_2\text{CO}_3$  species for a temperature as low as 500 °C.<sup>2</sup> Furthermore, the fitted lattice Li component (with a peak at a binding energy of  $\sim 55.2$  eV) seems to weaken relative to the Zr 4s peak at  $\sim 53.1$  eV, indicating the possible loss of surface Li. Alongside the carbonate removal, the C 1s spectrum shows a significant shift in the position of the peak attributed to C–C, and C–H (*i.e.* adventitious carbon) to lower binding energies, consistent with graphitization and which remains after cooling back to RT. The formation and persistence of this graphitized



Fig. 1 Electrochemical impedance Nyquist plots of etched (orange squares) and polished (green circles) Ga-LLZO electrolyte in a symmetric Li|LLZO|Li coin cell, measured at 298 K across the frequency range 13 MHz to 1 Hz. The inset shows the low frequency data points.





Fig. 2 *In situ* variable temperature photoelectron spectra during the etching process starting from a freshly polished Ga-LLZO pellet (grey), heated to 800 °C under vacuum (orange-red), and cooled back down to room temperature (blue).

carbon could be important in determining the behaviour of the etched sample as a result of its increased electronic conductivity which might contribute to the observed low interfacial resistance with lithium metal. However, the uniformity of the coverage with carbonaceous species is unconfirmed in this case and so its effectiveness in promoting a homogeneous distribution of current is as yet unknown.

Alongside the removal of the carbonate species, the La 3d<sub>5/2</sub> core level also undergoes changes with the multiplet splitting increasing slightly from 4.4 eV to 4.6 eV, reaching a value more typical of La<sub>2</sub>O<sub>3</sub> (indicative of La in the LLZO lattice).<sup>14,21,25</sup> The lower initial value of 4.4 eV may correspond to the presence of some lanthanum oxycarbonate species,<sup>25</sup> which is removed by the etching process.

We finally note that the La 3p<sub>3/2</sub> and Ga 2p core level regions, which have the highest binding energies and thus lowest kinetic energies of the core levels measured, show a growth of the La and Ga signals at the surface as the carbonate/hydroxide layer is removed. This may seem surprising given the signals are normalised to the Zr 3d and thus might be expected to remain constant. However the low kinetic energies (~350 eV compared to ~1300 eV for Zr 3d) result in much shorter inelastic mean free paths for these photoelectrons and so the signal is much more surface sensitive and its intensity therefore varies with the thickness of carbonate/hydroxide layer.

### 3.3. ToF-SIMS depth profiling

As the XPS measurements have an information depth of up to 10 nm and average over a 300 × 700 μm spot size, we looked to the use of ToF-SIMS for depth profiling the samples to probe changes in cation species over a greater range of depths (several nanometers to several hundreds of nanometers).

SIMS analyses were performed using an Ar<sub>n</sub><sup>+</sup> (*n* ≈ 500) cluster sputter beam for gentle depth profiling of the samples, over an area spanning 200 × 200 μm. With this sputter beam, interaction of the ion beam with the sample is minimized, serving to preserve the nature of the surface under analysis better than other higher energy sputter beam species. For these set of experiments, vacuum transfer of the samples to the SIMS instrument was performed immediately following the surface treatment of each pellet, preventing the atmosphere of the glove box from interacting significantly with the surface. The ion counts are normalised to the sum of the total of all species under analysis here and plotted as a function of sputter ion fluence (proportional to sputter time and therefore depth). The <sup>6</sup>Li<sup>+</sup> minor isotope secondary ion species is chosen instead of <sup>7</sup>Li<sup>+</sup>, as the high yield of the latter leads to saturation of the SIMS detector which prevents all the <sup>7</sup>Li<sup>+</sup> secondary ion species being counted.

Fig. 3 shows the positive secondary ion profiles for two samples (etched and polished) using these conditions. The analysis area spans several grains, as seen in the ion maps in





(the pellet was fractured and each resulting piece subject to a different surface treatment). As we expected to have a thick corrosion layer, an  $O_2^+$  sputter beam (1 kV, 300 nA) was selected. Traditionally, the  $O_2^+$  ion beam is thought to enhance the ionization probability for positive secondary ions by a surface chemical effect and provide stable ion yields. The higher current of the  $O_2^+$  beam meant that the sputtering of the materials proceeds more quickly than the argon cluster, meaning greater depths could be reached in shorter times.

Fig. 4 shows the depth profiles over an analysis area of 200 by 200  $\mu\text{m}$ , spanning several grains and grain boundaries (see Fig. 9 and S7† for ion images of the areas under analysis). This time, both etched and polished samples show an initial region of changing counts in their depth profiles – again with a surface region rich in Li<sup>+</sup> and poor in LaO<sup>+</sup>, Ga<sup>+</sup>, Al<sup>+</sup> and ZrO<sup>+</sup> secondary ion yield, which here is more extended in the etched sample. We suggest that this region exists now even on the etched sample due to the presence of a corrosion layer following surface



Fig. 5 ToF-SIMS depth profiles of etched (a) and polished (b) LLZO pellets, showing positive secondary ion species. Regions of interest (ROI) were selected based on areas without grain boundaries and pores in the etched and polished samples, respectively. The analysis was performed using 25 keV  $Bi^+$  primary ions as the analytical beam and the sputtering was performed by 1 keV 300 nA  $O_2^+$  beam (burst mode).



Fig. 6 ToF-SIMS positive secondary ion maps and optical image (greyscale) of etched sample, corresponding to the depth profiles of the etched samples in Fig. 4a and 5a. The analysis was performed using 25 keV  $Bi^+$  primary ions as the analytical beam and the sputtering was performed by 1 keV  $O_2^+$  beam (burst mode).





Fig. 7 ToF-SIMS negative secondary ion maps and optical image (greyscale) of an etched LLZO sample. The analysis was performed using 25 keV  $\text{Bi}^+$  primary ions as the analytical beam and the sputtering was performed by 1 keV  $\text{O}_2^+$  beam (burst mode).

reaction inside the glove box by direct reaction with residual  $\text{CO}_2$  (also seen by Zhu *et al.*<sup>2</sup>). As the region is more extended in the etched sample, this could suggest that the etched sample surface is in some way more activated than the polished sample, making it more reactive and susceptible to facile physisorption of contaminants present in the glove box such as  $\text{CO}_2$ . Changes to the surface morphology (as seen in the SEM images of polished and etched samples in Fig. S2†), as well as chemical modification effects at the surface, might be responsible for this behavior.

To verify the presence of a corrosion layer, and to rule out beam-sample interaction effects which might lead to preferential and delayed sputtering of species, carbon and hydrogen-containing species were also followed in the depth profiles. Fig. S8† shows depth profiles containing multiple secondary ion species which could originate from a corrosion layer, such as

$\text{LiH}^+$ ,  $\text{CH}_3\text{O}^+$ ,  $\text{CH}_2\text{OLi}^+$ ,  $\text{CHOLi}^+$ ,  $\text{H}^+$  and  $\text{CH}_2^+$ . The profiles of these species correlate well with the profiles of  $^6\text{Li}^+$  in both etched and polished samples (and showing an anticorrelation with  $\text{ZrO}^+$ ,  $\text{LaO}^+$ ), agreeing with this hypothesis. In addition, *ex situ* room temperature XPS was performed on the samples. In agreement with the SIMS depth profiles, a thicker corrosion layer was found to have formed on the etched sample, with a higher at% of carbon-based species found on the etched sample (Table S1†). In order to assess the effect of this rapidly-formed corrosion layer on pellets left in the glove box after thermal etching, EIS was carried out on a cell assembled ~16 h after thermal etching (Fig. S9†), showing an increase in the interfacial resistance when compared with the impedance measured for a cell assembled immediately after thermal etching.

It can also be seen in Fig. 4 that the  $^6\text{Li}^+$  counts are eventually lower than the  $\text{LaO}^+$  counts at the end of each profile. This is in contrast with the depth profiles in Fig. 3, in which the  $\text{LaO}^+$  counts are always higher after the initial corrosion layer. We attribute this to two things. Firstly, to the more extensive formation of corrosion products during sample storage, which consumes more lithium from the bulk of the LLZO. Secondly, to the use of a different sputter gun which results in a change in the yield of secondary ion species. Given the high mobility of lithium in LLZO structure, these samples show a corresponding depletion of Li in the bulk of the samples probed by SIMS, indicating a slightly lithium-poor defective garnet.

It is also notable that in the polished sample, as well as having a thinner corrosion region, the relative intensities of the secondary ion species differ from those of the etched sample –  $\text{Al}^+$  has a higher number of counts than the etched sample. By ensuring the same side of the same mother pellet was measured, changes in cation concentrations due to differences in the chemistry of different pellet faces can be ruled out here. To elaborate: during sintering the formation of an  $\text{Al}_2\text{O}_3\text{-Li}_2\text{O}$  eutectic leads to an Al concentration gradient through the sample, coupled with Al loss from the top surface, with the concentration highest on the side of the pellet previously in contact with the alumina crucible during sintering. This is seen by LEIS depth profiles of both sides of a sintered Ga-LLZO pellet, in which the normalised Al content is higher on the bottom face of the pellet, as shown in Fig. S6b.†



Fig. 8 Three-dimensional reconstruction with negative secondary ions of the etched Ga-LLZO sample.  $\text{LaO}^-$  represents the bulk LLZO grains in dark green and  $\text{OH}^-$  at the grain boundary surface in brown (a and b). The grain boundaries also contain  $\text{AlO}^-$  in green (c).



The SIMS depth profiles were taken over an area consisting of multiple grains and grain boundaries, so a selected area analysis of the etched sample was performed in which the data was post-processed to include ion counts originating from the grains only (a region of interest, "ROI", in which grain boundary regions are excluded), to separate contributions from these two types of features. Fig. 5a shows the resulting depth profile, the main difference being the significant drop in  $\text{Al}^+$  counts (implying that the grain boundaries are Al-rich).

If a selected area analysis of the polished sample is performed, in which pores are eliminated from the analysis (Fig. 5b), the counts for  $\text{Al}^+$  also drop significantly. This could be due to segregation of Al species in the pores of the sample, perhaps forming as a result of the liquid-phase sintering process. (Fig. S10<sup>†</sup> shows a three-dimensional reconstructed image of the sample in Fig. 5b showing Al in the pores). Interestingly, the paper by Tian *et al.*<sup>28</sup> describes the electron-trapping properties of surfaces in LLZO materials, including pores in the structure, and how these might be important for dictating the nucleation of lithium dendrites through facile electron transfer. The different properties of pores (as well as grain boundaries) from the bulk LLZO material is thus likely to be important in understanding the performance of these solid electrolytes.

In addition to changes in ion species resulting from features such as pores and grain boundaries, the relative intensities of all the species inside the bulk garnet, in particular  $\text{Al}^+$ , vary from sample to sample, even following the same surface treatment. The changes in the  $\text{Al}^+$  counts is not intuitive – instead we

suggest that the concentration of  $\text{Al}^+$  is highly anisotropic and as such, from measurement to measurement on the same sample (or across the same batch of samples), the measured relative intensities of  $\text{Al}^+$  with other species varies widely, even when the same pellet face is being measured, and grain boundaries and pores are eliminated from the analysis, as is the case here. This was also reported by Wachter-Welzl *et al.*,<sup>29</sup> who saw inhomogeneous distribution of Al in 44 samples of Al-LLZO using a laser-ablation ICP-MS technique. Chemical mapping was thus performed here to further investigate the non-uniform distribution of species in different regions of the samples, as well as the role of grain boundaries and their chemical changes following different treatments.

### 3.4. ToF-SIMS mapping

Ion maps of the samples measured with an  $\text{O}_2^+$  sputter beam are shown in Fig. 6. A grain boundary feature can be seen in the images of the etched sample, which seems to consist predominantly of the fast-diffusing ion species Li and Ga. SIMS matrix effects prevent the quantification of concentrations of these species in the grains and grain boundaries; however, their presence in the grain boundaries is marked. Since  $\text{Ga}^{3+}$  acts as a donor dopant in the Li position of Ga-LLZO, its accumulation in the grain boundaries should be associated with a higher concentration of cation vacancies or electrons in the LLZO grains if the crystal structure is maintained, or a possible exchange of the lithium-substitution species ( $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ ). It is also possible that segregation leads to a secondary phase at grain boundaries. This may be important in terms of the ionic



Fig. 9 Schematic of proposed processes occurring on a LLZO pellet during various thermal and atmospheric treatments, including: the formation of an Al–Li–O eutectic during sintering leading to Al diffusion in the grains and pore formation, Al evaporation and pore contraction during thermal etching and OH-enrichment of surfaces and grain boundaries upon reaction with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which is more acute on the activated, etched LLZO surface.



and electronic conductivity as well as the chemical reactivity/stability of the grains and grain boundaries in these materials, with the possibility of tailoring the grain boundary composition to achieve a desired chemical stability and ionic transport behaviour.<sup>30</sup> In the etched sample, the counts for  $\text{Al}^+$  are too low (low yield of  $\text{Al}^+$  secondary ion species) to be able to compare its appearance within the grains and at grain boundaries in the image, so instead the negative ion species were followed (Fig. 7).

The polished sample, however, has a clear segregation of  $\text{Al}^+$  at pores (see Fig. S7<sup>†</sup>), which agrees with the depth profile results in which we saw a significant lowering of the  $\text{Al}^+$  counts when the pore regions were excluded from the analysis (Fig. 5). These Al-rich 'pockets' have been described by Doeff and co-workers,<sup>20</sup> and here may be more prominent in the SIMS maps as the Al might originate from a different Al-rich phase than that found in the grain boundaries or grains of the etched sample (resulting in different secondary ion yields).

Looking at the negative secondary ion maps of an etched sample (Fig. 7), the presence of Al in the grain boundaries (indicated by  $\text{AlO}^-$  secondary ions) is much clearer. It is likely that differences in intensities of detected Al secondary ions in the etched and polished samples originate from difference in the matrix from which they are created (the Al-containing species in the pores *versus* the grain boundaries likely differ in identity). The grain boundaries also appear rich in  $\text{OH}^-$ ,

suggesting a reaction to form corrosion products. In fact, three-dimensional reconstructed images show an accumulation of  $\text{OH}^-$  along the grain boundaries close to the surface only (Fig. 8). The significant reactivity of grain boundaries during proton–lithium exchange was previously reported, in which a significant increase in grain boundary resistance accompanying the exchange process in LLZO pellets was observed.<sup>11</sup> A schematic of the various proposed processes occurring following thermal and atmospheric treatment of the Ga-LLZO pellets as described in this work is given in Fig. 9.

It was previously noted that the relative intensities of some secondary ion species (especially  $\text{Ga}^+$  and  $\text{Al}^+$ ) collected in the SIMS depth profiles varied from measurement to measurement, even on different areas of the same sample. To investigate this, post-processing of depth profiles collected on a region of etched sample consisting of multiple grains was performed, and the resultant reconstructed depth profiles were compared. Two such regions are highlighted in Fig. 10 (for a complete comparison of all grains in the field of view, see Fig. S11<sup>†</sup>). Interestingly, a significant difference in the  $\text{Al}^+$  intensity can be seen across the two ROIs, with the relative intensity being much higher for  $\text{Al}^+$  in the smaller, central grain (ROI 1). This would indicate that the pellet microstructure influences the chemistry of grains and grain boundaries which could be the reason for the impact of grain size on electrochemical performance previously reported.<sup>20,31</sup>



Fig. 10 ToF-SIMS positive secondary ion depth profiles and corresponding region of interest (ROI) highlighted on optical images (greyscale) of an etched LLZO sample. The analysis was performed using 25 keV  $\text{Bi}^+$  primary ions as the analytical beam and the sputtering was performed by 1 keV  $\text{O}_2^+$  beam (burst mode).



We propose that during sintering, the formation of an  $\text{Al}_2\text{O}_3$ - $\text{Li}_2\text{O}$  eutectic along the grain boundaries due to Al contamination from the crucible leads to a concentration gradient of Al through the grain, caused by the diffusion of  $\text{Al}^{3+}$  ions. The formation of this eutectic has been previously reported<sup>32</sup> and during the sintering process would lead to a larger concentration of Al in smaller grains after a fixed sintering time (which is above the eutectic formation temperature of  $1055\text{ }^\circ\text{C}$ <sup>33</sup>). The effect of the grain size on Al content has been shown by Cheng *et al.*<sup>20</sup> who used XPS to show marked differences in surface Al and Li content in samples of Al-LLZO depending on the grain size (small grain samples with grains around 20 micrometers had larger Al content and smaller Li content).

Because the reactivity of LLZO will depend on its composition (especially the Li content), grains with differing Ga-, Al- and thus Li-contents may well interact differently when exposed to air,  $\text{H}_2\text{O}$  or  $\text{CO}_2$ , leading to a knock-on effect on interfacial resistance with a Li metal electrode. In fact, it has been suggested, based on density functional theory calculations, that Li-poor LLZO proceeds *via* a direct reaction with  $\text{CO}_2$  to form  $\text{Li}_2\text{CO}_3$ , rather than the faster two-step reaction involving a LiOH intermediate.<sup>20</sup>

## 4. Conclusions

Prior studies have reviewed the relationship between thermal treatment and surface chemistry in terms of accumulation and removal of corrosion layer species LiOH and  $\text{Li}_2\text{CO}_3$  present in large quantities on the surface of LLZO, and the subsequent change in interfacial resistance with a lithium metal electrode. It has also been acknowledged that the surfaces and defect properties of LLZO pellets are highly dependent on processing regimes which vary significantly across different research groups. However, no such detailed study exists on the characterization of these surfaces (including regions of non-uniformity). This work serves to provide a detailed picture of the nature of the often highly defective surfaces of LLZO solid electrolytes which may have a significant effect on the interface with Li metal which has not been previously considered.

Comparing two sample types of Ga-LLZO – polished and thermally etched, we see differences in interfacial impedance with a Li metal electrode and chemical characteristics of the surfaces following these treatments. Electrochemical impedance spectroscopy shows a reduction in interfacial resistance following etching of the polished sample at  $900\text{ }^\circ\text{C}$  in argon. In addition to cleaning of the LLZO surface that is observed in XPS (removal of  $\text{Li}_2\text{CO}_3$ - and LiOH-type species) which has been previously proposed in the literature, we use ToF-SIMS under two different operating conditions (using  $\text{Ar}_n^+$  and  $\text{O}_2^+$  sputter beams) to show that an additional process is occurring during the etching process, which results in an activation of the etched pellet surface. We notice that during heating, surface adventitious carbon is graphitized (as seen by the formation of lower BE C 1s peaks in XPS spectra). Additionally, loss of Ga and Li from the grains and accumulation of Al, Ga and Li at the grain boundaries indicate a chemical change in the surface of LLZO during etching. This activation process leads to lower interfacial

resistances with Li metal but also to rapid and extended formation of a corrosion layer if left in a glove box for some time, due to the direct reaction with residual  $\text{CO}_2$ . A combination of changes in surface morphology and chemical reactivity of the etched surface may be responsible for this activation process. Ion mapping of the etched and polished samples show segregation of Ga and Al species at the grain boundaries in the etched pellets, whilst the polished samples show enrichment of Al in pores. In addition, the non-uniform nature of these materials is highlighted, showing a dependency of the concentration and distribution of metal cations on the grain size as a result of the liquid phase sintering process involving a Li-Al eutectic.

The non-uniform nature of the LLZO electrolyte surfaces and segregation of cationic species in features such as grain boundaries could strongly affect the performance of the electrolyte. For example, segregation of donor dopant species in the grain boundaries could result in the build-up of electrons or cation vacancies in the grains, leading to electronic conductivity and uneven current distribution, as well as differences in their chemical stability which may be microstructure dependent. Accumulation of secondary phases or mobile cation species in the grain boundaries could also lead to changes in mechanical properties and stability of grain boundaries against *e.g.* Li metal. All these factors will in turn influence the viability of combining LLZO electrolytes with a Li metal electrode in an all-solid-state battery.

## Conflicts of interest

The authors declare no conflicts of interest.

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