***Elucidating the Role of Dopants on the Critical Current Density for Dendrites Formation in Garnet Electrolytes***

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***Abstract***

Garnet-type solid electrolytes have attracted great interest in Solid State Battery research thanks to their high ionic conductivity at room temperature (10-3 S cm-1) and their electrochemical stability against a lithium metal anode. However, the formation of lithium dendrites following charge/discharge limits their applicability and commercialisation. Although widely investigated, no clear explanation of dendrites formation has been previously reported. In this work, we employ cubic Al- and Ga-doped Li7La3Zr2O12, which represent two of the solid electrolytes with higher technological importance, to investigate the formation and chemical composition of dendrites. For the first time, this study elucidates the role that the dopants play in determining the critical current density for dendrites formation and highlights the importance of controlling the dopant distribution in the garnet structure. We use a combination of techniques including Secondary Electron Microscopy and Secondary Ion Mass Spectrometry in order to analyse the microstructure and chemical composition of dendrites in Li7La3Zr2O12. We show that, following electrochemical cycling, Li6.55Ga0.15La3Zr2O12 systematically displays a critical current density 60% higher than Li6.55Al0.15La3Zr2O12. Chemical analysis revealed that in Li6.55Al0.15La3Zr2O12 the dendritic features are composed of a mixture of Al and Li species, whereas in Li6.55Ga0.15La3Zr2O12 they are uniquely composed of Li. We also show that only in pristine Li6.55Al0.15La3Zr2O12, the dopant segregates at the grain boundaries suggesting that local chemical inhomogeneity can have a fundamental role in the nucleation and propagation of dendrites.

***Introduction***

In recent years, significant attention has been given to the development of All Solid State Batteries (ASSB) with the aim to improve the safety of current state of the art batteries based on flammable liquid electrolytes,1,2 and to develop batteries with higher power and energy densities which could be employed in large scale energy storage systems such as electric vehicles and grid storage.3,4 Several are the advantages in using a Solid State Electrolyte (SSE) over a liquid electrolyte, such as a higher thermodynamic stability of a SSE when compared with a liquid electrolyte, the possibility to directly use a lithium metal anode to replace commonly used graphite electrodes (Li metal represents one of the most attractive anodes due to its low density and high specific capacity), and a greater electrochemical stability window of ~5 V.5 Over the last few decades, a wide range of solid electrolytes with high ionic conductivity has been investigated, including LISICON,6 NASICON,7 sulphide glass/ceramic,8,9 and garnet-type electrolytes.10,11 Although sulphide based electrolytes have been reported to be excellent ionic conductors (10-2 S cm-1 at room temperature),12 they are not stable in contact with metallic lithium,13 limiting their application in ASSB. Garnet electrolytes such as cubic Li7La3Zr2O12 (LLZO) have also attracted increasing interest because of their high ionic conductivity at room temperature, up to 10-3 S cm-1,14 and their good theoretical electrochemical stability window against a metallic lithium anode.15 Tetragonal LLZO has much lower Li-ion conductivity (~10-6 S cm-1) compared with cubic LLZO (~10-3 S cm-1),16 therefore the stabilisation of cubic phase is desirable and has been achieved by donor-doping to optimise the content of lithium and subsequent Li vacancy concentration.17 The optimal lithium content for the highest conductivity has been defined to be ~ 6.5,18 therefore in this work we have employed the garnet nominal composition Li6.55M0.15La3Zr2O12 where M is either Al3+ or Ga3+, since Ga has been shown to deliver the highest Li conductivities to date and Al is a common impurity introduced through crucibles, making both dopants technologically relevant. Despite these advantages, substantial obstacles still remain in the use of solid electrolytes employed in lithium-metal batteries; among them, the formation of lithium dendrites have been reported by several groups, 19,20 and represents one of the primary challenge which need addressing in order to allow the commercialisation of ASSLB.

Considering a pressure-driven stability mechanism,21 the shear modulus of the solid electrolyte should be twice the modulus of lithium in order to prevent the formation of dendrites;21 however, despite the substantially higher shear modulus of LLZO compared to lithium metal (~60 GPa compared to ~4 GPa, respectively),22 dendrite formation has been observed at current densities >40 A cm-2 in Li metal/cubic LLZO/Li metal cells at room temperature.23 The critical current density can, however, be greatly enhanced by increasing the operational temperature of the cell;23 recently, Raj and Wolfenstine reported the current limit diagrams for dendrite formation in solid state electrolytes, confirming that a higher conductivity of the electrolyte, due to increased operational temperature, can reduce the formation of dendrites.24 Basappa *et al*. have recently shown a substantial increase in the critical current density for dendrite formation in Ta-doped LLZO where the grain boundaries were modified by the addition of Li2CO3 and LiOH.25 This led to a four-fold increase of the critical current density.

Further, the contact between the metallic lithium and the solid electrolyte plays a crucial role in dendrite formation, where a better contact between Li metal and SSE results in a smaller charge transfer resistance and increase in the critical current density for dendrite formation.23 Also dendrites are expected to develop as a consequence of the growth of a protuberance at the lithium-electrolyte interface due to a inhomogeneous distribution of current density and therefore ensuring a long lasting homogeneous interface is of vital importance.24

Although the formation of dendrites is one of the major causes of a short lifetime of solid state batteries, their mechanism of nucleation and propagation still remains unclear. Ren *et al.* directly observed lithium dendrites inside garnet-type lithium electrolytes (Ta-doped LLZO) which propagated through interconnected pores and along grain boundaries,19 suggesting that the electrolyte density is important in facilitating the formation of dendrites. More recently, Cheng *et al.* also showed evidence of intergranular lithium metal propagation in polycrystalline Al-doped LLZO, which leads to short-circuiting of the cell.26 They observed a web-like structure which extended across the full width of the pellet, forming hexagonal–like features, suggesting that dendrite propagation occurs at the boundaries between LLZO grains. Aguesse *et al.* have reported dendrite formation in Ga-doped LLZO after ~20 charge/discharge cycles which leads to cell failure, proposing three mechanisms of degradation of the LLZO, including penetration of dendrites through the ceramic electrolyte during lithium plating.20 They observed both inter- and intra-granular dendrites, suggesting that the dendrites can grow and propagate both across the grain boundaries and through pores within the grains, respectively.

Despite several efforts to understand the mechanism of dendrite formation, the literature is still full of inconsistencies in reporting values of current densities and numerous questions remain unanswered. One of the main problems is the lack of reproducibility and control of the chemical composition along the polycrystalline pellets, due to several factors, including the use of different dopants, the presence of impurities, moisture reactivity and lithium content. In this paper we focus on the analysis of the role of local chemical inhomogeneity in the dendrite nucleation and composition with a particular focus on the role of dopant species distributions. In order to do this, we have chemically, microstructurally and electrochemically characterised Al- and Ga- doped Li6.55M0.15La3Zr2O12 to correlate the local chemical environments in the Li/LLZO interfaces to the electrochemical performance of Li metal/LLZO/Li metal cells in terms of the critical current density for dendrite formation. In order to try to isolate the effect of the dopant, samples with similar microstructure were synthesised and chemical degradation due to moisture reactivity was avoided during the synthesis and processing.27 The chemical distribution of the different elements on the surface and cross section of cycled pellets was analysed using a unique Focused Ion Beam – Secondary Ions Mass Spectrometer (FIB –SIMS) with depth-resolved simultaneous dual detection of positive and negative secondary ions and a high lateral resolution of 10 nm, to obtain a comprehensive analysis of the chemical composition of grains and grain boundaries prior and after dendrite formation.28–30

***Results and Discussion***

Al- and Ga-doped LLZO (Al-LLZO and Ga-LLZO, respectively) pellets with nominal composition Li6.55M0.15La3Zr2O12 were prepared using a modified sol-gel technique as previously reported in the literature14 and characterised by X-ray diffraction (XRD), Figure 1. Rietveld refinements of the XRD patterns evidence that both Al-LLZO and Ga-LLZO pellets have a cubic crystal structure with the *Ia-3d* space group.10,14 The stabilisation of the cubic phase is due to donor doping (either Al3+ or Ga3+) in the Li position that leads to the creation of two Li vacancies following the charge neutrality condition expressed by the Kröger-Vink notation below:

Where M indicates the dopant atom, in this work either Al3+ or Ga3+.



Figure 1. X-ray powder diffraction patterns and Rietveld refinement fittings (dotted black line) of Ga-LLZO (orange line) and Al-LLZO (blue line); \* indicates reflections from Li2ZrO3 secondary phase.

The XRD patterns also show the presence of a minor quantity (<10 %) of Li2ZrO3 as a secondary phase (indicated by \* in Figure 1) in both materials. It is important to notice that the amount of Li2ZrO3 is similar in both Al-LLZO and Ga-LLZO. Secondary Electron Microscopy (SEM) images, Figure 2, show a smooth surface as the result of fine polishing and also show a bi-modal distribution of grain size for both Al-LLZO and Ga-LLZO, with grain sizes ranging from 20 m to a few m. The grains were revealed by using thermal etching as described in the experimental section. Density calculations from geometrical measurements, result in an average relative density of >95% for both Al-LLZO and Ga-LLZO pellets and the high density is confirmed by cross sectional SEM micrographs which show a low amount of interstitial pores, Figure 2 (right). A relative density >93% has been recently reported as the critical density to prevent dendrite formation.24,31,32



Figure 2. Plane (left) and cross-sectional (right) SEM micrographs recorded at 5 kV for thermally-etched (a) Ga-LLZO and (b) Al-LLZO pellets.

It has been widely observed that the moisture reactivity of fast Li-conducting LLZO which leads to Li+/H+ exchange in the lattice, also causes the formation of secondary phases such as LiOH and Li2CO3.33,34 Recently, we have demonstrated that this Li+/H+ exchange greatly affects the electrochemical properties of LLZO, 35 leading to a substantial detrimental effect on the lithium transport properties in the grain, grain boundaries and Li/electrolyte interface. This is an important parameter to control, since current flux distribution can have very important effect in the critical current for the nucleation of dendrites. In this regard, the synthesis and processing of LLZO was carried out in an Ar-filled glove box with O2 and H2O levels <0.3 ppm to prevent Li+/H+ exchange.

FIB-SIMS depth profile analysis of both positive and negative secondary ions in the pristine (as prepared) samples of Al-LLZO and Ga-LLZO also show clean grains with a high content of lithium (7Li) and lanthanum (detected as 155(LaO)+), Figure 3 (b-c) and (e-f), respectively. Positive secondary ion signals are normalised to the 69Ga+ secondary ion intensity, originating from the primary ion beam, to correct for changes in sputter rate. In this work we used a primary ion source of 69Ga with 99% isotopic purity in order to follow the 71Ga secondary ion intensity resulting from the Ga dopant. The FIB-SIMS signals of lithium positive secondary ions in both Al- and Ga-LLZO appear to decrease within the first thirty points of the measurement, whereas the signals of the other species (155(LaO), 106(ZrO), 27Al and 71Ga) appear to increase in the same time scale. This is attributed to a thin layer of LiOH formed upon contact of the LLZO with air during the transfer of the samples from the glove box to the FIB-SIMS chamber.35 Negative secondary ion depth profiles also shows a decreasing 17OH signal in the initial stages of the measurement, confirming the presence of a LiOH layer on top of the sample. Once the first LiOH layer has been removed by ion sputtering, the signals of all the garnet components appears to be constant and stable, indicating an even concentration.



Figure 3: Secondary electron micrographs and positive and negative secondary ion depth profiles for (a), (b) and (c) an Al-LLZO pristine sample and (d), (e) and (f) a Ga-LLZO pristine sample. The pellets were thermally etched prior to SIMS analysis in order to reveal the grains. Positive secondary ion intensities are divided by the 69Ga intensity.

FIB-SIMS mapping of large areas of the pristine samples reveals Al segregation at the grain boundaries in Al-LLZO, whereas the Ga is homogeneously distributed across grain and grain boundaries in Ga-LLZO as shown in Figure 4. The darker areas in the 71Ga map can be attributed to the presence of Li2ZrO3. Aluminium segregation in the grain boundaries has been previously observed in Al-substituted LLZO using EDX and have been attributed to the presence of Al impurities.36,37 The difference in the spatial distribution between Al and Ga could therefore have a great impact in the formation and propagation of the dendrites following electrochemical cycling.



Figure 4: FIB-SIMS elemental maps for (a) 27Al in a pristine Al-LLZO pellet and (b) 71Ga in a pristine Ga-LLZO pellet.

Symmetric lithium cells were assembled by hot pressing the lithium foil on both sides of the 1 mm thick LLZO pellets following the procedure described in the method section. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range 0.1 Hz – 13 MHz prior to cycling of the cells and the spectra are reported in Figure 5(a). The spectra were fitted with a model circuit composed of a series of three resistances in parallel to three constant phase elements to take into account the depressed shape of the semicircles, inset Figure 5(a).



Figure 5: (a) EIS spectra of Al-LLZO (blue circles) and Ga-LLZO (orange circles) with relative fittings (dotted lines) and equivalent circuit used for fitting (inset) of a Li/LLZO/Li symmetrical cell; Li plating/stripping graph for (b) Al-LLZO and (c) Ga-LLZO; (d) I vs R graph for Al-LLZO (blue circles) and Ga-LLZO (orange circles).

From the fitting of the EIS data (dotted lines, Figure 5(a)) it was possible to extrapolate the total conductivity of the pellets by combining the grain (bulk) and grain boundary contributions. The calculated values of conductivity, capacitance and Area Specific Resistance (ASR) associated with the electrode/electrolyte interface are reported in Table 1.

Table 1. Capacitance (C), conductivity (σ) and Area Specific Resistance (ASR) values extrapolated from the fittings of EIS data for Ga-LLZO and Al-LLZO cells with symmetric Li electrodes.

|  |  |  |
| --- | --- | --- |
|  | Ga-LLZO | Al-LLZO |
| **Cbulk (F cm-1)** | 3.95x10-11 | 1.4x10-11 |
| **bulk (S cm-1)** | 1.1x10-3 | 7.7x10-4 |
| **Cgrain boundary (F cm-1)** | 5.05x10-9 | 1.7x10-10 |
| **grain boundary (S cm-1)** | 2.4x10-3 | 6.4x10-4 |
| **total (S cm-1)** | 7.5x10-4 | 3.5x10-4 |
| **Celectrode (F cm-1)** | 1.94x10-5 | 3.2x10-5 |
| **ASR ( cm2)** | 16.7 | 12.1 |

The total conductivities of the Al-LLZO and Ga-LLZO pellets are 3.5x10-4 S cm-1 and 7.5 x10-4 S cm-1, respectively. The charge transfer resistance values are 16.7  cm2 and 12.1  cm2 for Al-LLZO and Ga-LLZO respectively. The low values of charge transfer resistance are amongst the lowest values reported in the literature,38,39 confirming an intimate contact between the metallic lithium and the solid electrolyte, achieved without the use of any inter-layer. This could be related to the lack of a corrosion layer due to sample processing in an Ar-filled glove box in order to minimise the contact with moisture.

The symmetric cells containing pellets were cycled at room temperature at various current densities, starting from 10 A cm-2 with increasing steps of 10 A. Details on the experimental conditions can be found in the method section of the manuscript. The Li/Al-LLZO/Li cells follow an Ohmic current-voltage behaviour up to 0.1 mA cm-2, after which a decrease of the cell voltage output is observed, indicating short-circuiting of the cells which is ascribed to dendrite formation, Figure 5(b). 0.1 mA cm-2 is therefore considered as the critical current density (CCD) for Al-LLZO, which is almost two times greater than the CCD reported by Sharafi *et al.* for a comparable Al-doped LLZO cycled at room temperature.23 On the other hand, Li/Ga-LLZO/Li cells could be consistently cycled up to 0.16 mA cm-2 (Figure 5(c)), with a significantly higher critical current density (~60% greater) than the CCD of Al-LLZO. The higher current density for Ga-LLZO was repeatedly observed in this study, always obtaining CCD of 0.1 mA cm-2 for AL-LLZO and 0.16 mA cm-2 for Ga-LLZO as shown in figure S1 of the Supporting Information. It is also important to notice that the drop in the cell voltage is much sharper in Ga-LLZO then Al-LLZO, suggesting a different mechanism in cell short-circuiting due to lithium dendrite formation. This could also be assumed from the observation of a different behaviour of the cells before short circuit (Figure 5(d)): while for the Ga-LLZO cell, the resistance decreases slightly and linearly before cell short circuit, the Al-LLZO cell shows a sharp increase of resistance at ~0.05 mA cm-2 before short circuit. The causes of the erratic behaviour of Al-LLZO are still not clear but under investigation. The difference in critical current density suggests that the dopant used to stabilise the LLZO cubic phase could also play a significant role in the formation of dendrites which leads to the short-circuiting of the cell. Figure 5(d) also shows a higher resistance associated to the dendrites formed in Al-LLZO following the short-circuit event, and a different resistance transition in Ga-LLZO, suggesting a possible different chemical composition and mechanism of formation.

Following electrochemical cycling, EIS was carried out on the cells containing dendrites, showing the data to be clustered near the origin and suggesting electrical short circuit of the cells which confirms the formation of dendrites, Figure 6(a). Further evidence of dendrite formation was clear by visual inspection of the cycled LLZO pellets; black spots were visible by eye on the surface of the pellets (Figure 6(b)) after opening the cells following electrochemical cycling, in accordance to what has been observed in previous reports.20,23,26 XRD diffractograms (see supporting information, Figure S2) were also repeated on the cycled pellets and they do not show substantial differences from the XRD diffractograms of the pristine pellets (Figure 1(a)), suggesting that the formation of dendrites does not lead to decomposition of the garnet structure within the resolution of the equipment employed in this study.

SEM micrographs also show the presence of dendritic features on the surface of the pellets in both Al-LLZO (Figure 6(c)) and Ga-LLZO (Figure 6(e)). A closer analysis of the cross section of the Al-LLZO pellet reveals the appearance of dendritic features in the middle of the grains (Figure 6(d)), which spread through the pellet with a web-like structure (Figure 6(f)). This has also been observed for the Ga-LLZO samples and SEM images are reported in the Supporting Information, Figure S3, which also shows a higher magnification image of the dendritic feature reported in Figure 6(f). Both intra- and inter-granular dendrite formation has also been recently described by Aguesse *et al.*20 It is important to note that, if the cells are cycled at a current density lower than the CCD, no short circuiting is observed (Figure S4 in the Supporting Information)



Figure 6: (a) EIS spectra of Al-LLZO (blue data points) and Ga-LLZO (orange data points) recorded after electrochemical cycling; (b) disassembled Al-LLZO cell following electrochemical cycling, showing the appearance of dendritic features visible by the naked eye; (c) and (e) surface SEM images recorded for Al-LLZO and Ga-LLZO pellets, respectively; (d) high magnification SEM image of the cross section of an Al-LLZO pellet following electrochemical cycling, showing inter-grain dendritic features; (f) cross sectional SEM image of an Al-LLZO pellet showing a large dendritic feature extending through the cross section of the pellet in a web-like manner.

These features appear darker in backscattered electron images, suggesting that they contain lighter elements when compared with the grains. Energy dispersive X-ray spectroscopy (EDX) analysis (Supporting Information, Figure S5) reveals these dendritic like-features in the surface of the pellet to be aluminium rich. Both Al-LLZO and Ga-LLZO show large features between the grains, extending through the thickness of the pellets, indicating the formation of inter-granular dendritic features which leads to the short circuiting of the cells (Figure 6(f) and S3).

In order to investigate in more detail the chemical composition of the dendrites in the Al-LLZO and Ga-LLZO, FIB-SIMS analysis in positive secondary ion mode was performed, (Figure 7).



Figure 7: (a) Secondary electron image of an Al-LLZO pellet following depth profiling on surface dendritic features (red circles); (b) positive ion SIMS depth profile of dendritic features in Al-LLZO; (c) secondary electron image of a dendritic feature on the surface of a Ga-LLZO pellet following depth profiling; (d) positive ion SIMS depth profile of dendritic feature in Ga-LLZO

Figure 7 shows the secondary electron images and the positive secondary ion depth profiles for Al-LLZO (a) and Ga-LLZO (c). As it can be seen from the positive ion depth profiles (Figure 7(b)), in Al-LLZO the dominant signal is for 7Li, and the 27Al signal has increased in number of counts when compared with the pristine sample (Figure 3(b)), indicating that these dendritic-like features are mostly composed of a mixture of Li and Al. The features analysed for Al-LLZO were both intra- and inter-grain. It is worth noting that the flatness of the SIMS profiles is due to an initial FIB cleaning of the surface in order to rule out the possibility that the features observed were superficial features.

On the other hand, the Ga-LLZO positive secondary ion depth profile of intra-grain dendritic features (Figure 7

(d)) shows them to be mostly composed of lithium, whose counts dominate the profile, whereas the counts of all other positive ions are relatively low. This has been confirmed by analysing several dendritic features which provided consistent results. The different nature of the dendritic features in Al-LLZO and Ga-LLZO suggests that the dopant used to stabilise the LLZO cubic phase could also play a pivotal role in the formation and propagation of the dendrites, and in effect leading to different critical current densities. In order to elucidate this, we carried out SIMS elemental mapping on a cross section of the LLZO/Li metal interface prepared by FIB following electrochemical cycling with the aim of highlighting any clear preferential paths for the dendrites to propagate in. Figure 8 shows the secondary electron image and the SIMS elemental maps for 7Li, 27Al and 155(LaO) positive secondary ion species of the cross section of a cycled Al-LLZO pellet. From the elemental maps it is possible to see regions of the cross section which are rich in both lithium and aluminium species (brighter areas in Figure 8 (b) and (c)), which appear to be interconnected and are ascribed to the presence of dendritic features growing through the pellet, preferentially forming along the grain boundaries. On the other hand, 155(LaO) mapping confirms that these regions are poor in lanthanum. Recently, Han et al. have demonstrated that by coating LLTO with a thin layer of Al2O3, the wettability of the garnet increases resulting in a low interfacial resistance and in the formation of a fast Li conducting Li-aluminate phase.40 Similarly, in the Al-LLZO used in this work, the Al rich grain boundaries might act as fast pathways for Li dendrites, resulting in a lower critical current density. To the best of our knowledge, this is the first example of chemical analysis of dendritic features in garnet-type electrolytes and contributes the fundamental understanding of dendrites formation and propagation.



Figure 8. (a) Secondary electron micrograph of a gallium FIB-milled surface perpendicular to the pellet surface of an Al-LLZO sample following electrochemical cycling; SIMS elemental mapping for (b) 7Li, (c) 27Al and (d) 155(LaO) secondary positive ions.

We suggest that the differences in critical current densities highlighted in Figure 5 and the chemical inhomogeneity of the pristine materials showed in Figure 4 are directly related. As shown in Figures 7 (d) and (f), the dendrites mostly propagate along the grain boundaries and, in Al-LLZO are composed of Li and Al species (Figure 8 (b and c)). Hence, we propose that a segregation of Al at the grain boundaries facilitates the dendrite propagation, leading to a faster short-circuiting of the cells, corresponding to lower critical current density values (0.10 mA cm-2) when compared with Ga-LLZO (0.16 mA cm-2). The fact that the dendrites in the middle of the grains are also Al-rich (as shown by SIMS analysis) suggests that the lower current density in this system could be related to a lower electrochemical potential required for the formation of Li-Al alloys and to a potential fast Al-diffusion in this materials under polarisation conditions. Further studies are under way to elucidate this.

***Conclusions***

In conclusion, we have shown for the first time that the dopant utilised to stabilise the cubic phase of Li7La3Zr2O12 (LLZO) also plays a pivotal role in the formation and propagation of dendrites, and therefore it is directly related to the critical current density for dendrite formation in LLZO/Li metal-based cells. By using FIB-SIMS, the chemical composition of the dendritic-like features in both Al-LLZO and Ga-LLZO was analysed, revealing them to be Al- and Li-rich in Al-LLZO, whereas in Ga-LLZO they are uniquely composed of Li species. This could be ascribed to the fact that, unlike the Ga, the Al segregates between the grains in Al-LLZO and may facilitate the initial propagation of lithium in the grain boundaries leading to a critical current density as low as 0.1 mA cm-2 . This has a critical impact in the choice of dopants for the stabilisation of cubic garnet electrolytes with high Li-conductivity and their processing to avoid Al-contamination representing an important step forward towards understanding dendrite formation and its suppression.

***Experimental***

*LLZO preparation*

Li6.55Al0.15La3Zr2O12 (AL-LLZO) and Li6.55Ga0.15La3Zr2O12 (Ga-LLZO) were prepared via sol-gel method using as starting materials: LiNO3 anhydrous (99.0%, Alfa Aesar), La(NO3)3∙6H2O (99.9%, Alfa Aesar), Zr(C5H7O2)4 (Alfa Aesar). Al(NO3)3∙9H2O (98%, Alfa Aesar) and Ga2O3 (99.999%, Alfa Aesar) were employed as dopant precursors. The precursors were weighted in the desired stoichiometry and dissolved in a 9:1 mixture of 0.5M citric acid (ACS reagent, ≥99.5%, Sigma-Aldrich) and nitric acid (68%, VWR). After gel formation, combustion was carried out at 600⁰C for 12h with a heating ramp of 2⁰C/min and a cooling ramp of 10⁰C/min, holding at 100⁰C to prevent uptake of water. After milling of the combusted powders in an argon-filled glove box, calcination was carried out in Al2O3 crucibles in a tubular furnace under a dry O2 (BOC high purity grade N6.0) atmosphere at 800⁰C for 12 h with a heating ramp of 5⁰C/min and a cooling ramp of 5 to 10⁰C/min. Pellets of the calcined and milled powders were prepared by using 0.5 g of powder pressed using a circular dye (13 mm diameter) under 2 tons for 1 minute in the glove box. The as prepared pellets were sintered at 1175⁰C and 1150⁰C for Al- and Ga-doped LLZO respectively in an Ar atmosphere in alumina crucibles. During sintering, the pellet were covered by mother powder in order to take in account possible lithium losses. After sintering, the pellets were polished using different grit SiC sanding paper (in sequence 240 (58 µm), 800 (21 µm), 1200 (15 µm), 2500 (8 µm) and 4000 (5 µm)). The pellets prepared in this way have an average sintered diameter of 10 mm and a thickness of 1 mm. In order to reveal the grains, the polished pellets were etched in an Ar atmosphere at 900⁰C for 30 minutes with a heating and cooling ramp of 10⁰C/min. During etching the pellets were placed in enclosed alumina crucibles on top of a Pt foil. The density of the pellets was geometrically calculated.

*Physical Characterisation pre- and post-cycling*

Polished and etched Al-LLZO and Ga-LLZO pellets were characterised by XRD (using a Bruker D2 Phaser instrument with a 2θ range of 10° to 80° 2θ, with a step size of 0.034° 2θ, and a time per step of 2 s step-1) in order to confirm the transition between tetragonal and cubic phases and in order to define any possible secondary crystalline phase. SEM and EDX images were recorded using a Zeiss electron microscope (Sigma 300, Leo Gemini 1525 field emission gun) with accelerating voltages varying from 5 to 1.5 eV.

*Symmetrical cell assembly*

Symmetrical Li/LLZO/Li cells were prepared by hot pressing Li metal foils on both sides of polished LLZO pellets in an Ar filled glove box. Lithium foils were cut with a smaller diameter (9.5 mm) than the diameter of the LLZO pellets (10 mm) in order to avoid short-circuit during cell assembly. Each side of the cell was heated at 150 ⁰C for 30 minutes under a constant pressure. After cooling the Li/LLZO/Li pellet was assembled in a commercial 2032 coin cell case using spacers (either 1mm or 0.5mm) and a spring in order to secure the sample inside the cell case.

*Electrochemical Characterisation*

Symmetric Li/LLZO/Li cells were electrochemically cycled at room temperature using a commercial battery tester (580 Battery Test System (Alvatek) and BCycle software)at various current densities for 30 minutes for each charging or discharging cycle, with a 5 minutes rest period between charging/discharging cycles, until the cell showed short-circuit. Electrochemical impedance spectroscopy was conducted in a frequency range between 0.1 Hz to 13 MHz at 100 mV signal amplitude prior and after electrochemical characterisation using a Solatron 1260 Impedance Analyser. The impedance was measured at room temperature with a 2-contact rig using a HFS600E-P Linkam stage and plotted in Nyquist-type plots with the response fitted to equivalent circuits using Z-view software.

*FIB SIMS*

A FEI FIB200-SIMS ion microscope was used for imaging and mapping and recording mass spectra from the surface of the materials, as well as being used in depth profiling mode to obtain chemical information as a function of depth. A Ga+ primary ion source (69Ga 99 % isotopically pure) at 30 keV was used as the primary beam (spot size 7-10 nm) which is incident at 30° to the normal of the ceramic surface using a current from 30 pA for imaging and up to 1 nA for depth profiling. Simultaneous negative and positive secondary ions were detected in dynamic SIMS mode using both FEI and Hiden EQS quadrupole detectors, respectively. The FIB-SIMS instrument is equipped with detectors for secondary electrons, positive ions and negative ions to allow an asynchronous semi-simultaneous signal acquisition,29 and for imaging in secondary electron and ion modes.

Transfer of the pre-mounted samples was done by sealing the samples in a container in the glove box, and transferring to the SIMS chamber before immediately pumping down to high vacuum (<10-5 mbar). This meant that the samples for analysis were exposed to ambient air for a matter of no more than a few minutes.

***Conflicts of interest***

The author declare no conflicts of interest.

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