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Perspective

The role of grain boundaries in solid-state Li-metal batteries

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Abstract

Despite the potential advantages promised by solid-state batteries, the success of solid-state electrolytes has not yet been fully realised. This is due in part to the lower ionic conductivity of solid electrolytes. In many solid superionic conductors, grain boundaries are found to be ionically resistive and hence contribute to this lower ionic conductivity. Additionally, in spite of the hope that solid electrolytes would inhibit lithium filaments, in most scenarios their growth is still observed, and in some polycrystalline systems this is suggested to occur along grain boundaries. It is apparent that grain boundaries affect the performance of solid-state electrolytes, however a deeper understanding is lacking. In this perspective, the current theories relating to grain boundaries in solid-state electrolytes are explored, as well as addressing some of the challenges which arise when trying to investigate their role. Glasses are presented as a possible solution to reduce the effect of grain boundaries in electrolytes. Future research directions are suggested which will aid in both understanding the role of grain boundaries, and diminishing their contribution in cases where they are detrimental.

Keywords: solid electrolytes, grain boundaries, lithium growth, glasses

1. Introduction

Current state-of-the-art solid electrolytes are inorganic ceramics, typically made from powders by sintering or pressing. The nature of this synthesis route means that the electrolytes produced are polycrystalline and contain a high density of grain boundaries, which can be expected to have consequences on the performance of the electrolyte. Two prominent material systems that fall into this category are oxide electrolytes, for example garnet $Li_7La_3Zr_2O_{12}$ (LLZO), and sulphide electrolytes, such as Li_2S-P_2S_5 (LPS).

When referring to a grain, we allude to a region in which the atoms have a periodic arrangement. The grain boundaries are the interfaces between grains of differing orientation, and so have a locally different structure. The presence of grain boundaries are established to have far-reaching effects on materials, such as the mechanical, electrical, corrosion and thermal properties. The degree of misorientation between grains controls the grain boundary structure and so can also have effects on the performance of materials. It is generally the case that higher angles result in higher associated grain boundary energies, which can make them preferential sites for reactions, or can control the grain growth, for example.

It is believed that the ionic conductivities of grain boundaries are inferior to the bulk for many solid electrolyte materials, lowering the total ionic conductivity,

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and as such making grain boundaries undesirable. Additionally, it appears that lithium filament growth occurs intergranularly in polycrystalline samples [1], suggesting grain boundaries play a role in failure by short-circuiting which needs to be understood further. In this work we will look into both the present understanding of the impact of grain boundaries on electrolyte performance and acknowledge some of the difficulties which exist in conducting studies investigating their effect.

Glasses are a class of material which are of interest in this research area thanks to the absence of grain boundaries. Existing work on glassy electrolytes shall be touched on briefly, before finally considering some directions which may be useful for future work to take regarding grain boundaries in solid-state electrolytes.

2. The role of grain boundaries on ionic conductivity

Although diffusion along grain boundaries is often faster than the bulk in polycrystalline solids [2, 3], it has long been believed that grain boundaries act as a bottleneck to ionic conductivity in solid-state electrolytes in which the bulk is a superionic conductor [4–7]. Various mechanisms explaining this ion-blocking effect of grain boundaries have been suggested, such as distortions due to grain misalignment [4] and grain boundaries acting as sinks of ionically-blocking impurities [8]. However, not much experimental work looking into the effect of grain boundaries on ionic conductivity exists in the solid-state battery field.

Wu and Go synthesised $Li_{3x}La_{0.67-x}TiO_3$ (LLTO) with grain sizes varying from 25 nm to 3.11 μm through annealing heat treatments of sintered compacts at temperatures between 900 °C and 1100 °C at 80 MPa pressure under vacuum. Not only were they able to observe the dramatically lower grain boundary conductivity ($\sim$4 orders of magnitude), but also an increase in grain boundary resistance with decreasing grain size, despite the grain boundaries being apparently crystallographically the same [9]. They proposed a space-charge model in which the cores of the grain boundaries are positively charged and so repel the mobile cations. They use this concept to define an ‘electrical grain boundary’ which has greater thickness than the corresponding crystallographic grain boundary. This is an idea which has been well-established in fuel cell literature where extensive research already exists [10–14]. It is worth noting that no comparison of density variations between samples were provided other than that they were all greater than 94% relative density, meaning the impact of porosity variations cannot be eliminated with certainty. This is an important consideration in experimental research on grain boundaries, which shall be addressed in section 3.3.

A number of studies using molecular dynamics to calculate ionic conductivities and activation energies of cation migration across different low-energy grain boundaries confirm the reduced grain boundary conductivity in various oxides [4, 15, 16]. A good demonstration of the large impact that grain boundary resistance can have macroscopically is provided by the antiperovskite oxide, Li_3OCl. Activation energies of 0.3–0.4 eV are predicted by density functional theory (DFT) studies [17–20], yet activation energies as high as $\sim$0.6 eV have been reported experimentally [5, 6], which is suspected to be a result of grain boundaries. Dawson *et al* [4] constructed four symmetric tilt grain boundaries commonly observed in other perovskite oxides using the coincidence site lattice theory. The corresponding grain boundary energies, and the components of lithium-ion conductivity parallel and perpendicular to the grain boundary were calculated, and from this, the variation of ionic conductivity in samples with different average grain sizes was modelled [4]. The grain boundary density is found to be high as a result of their low energy, and to have high

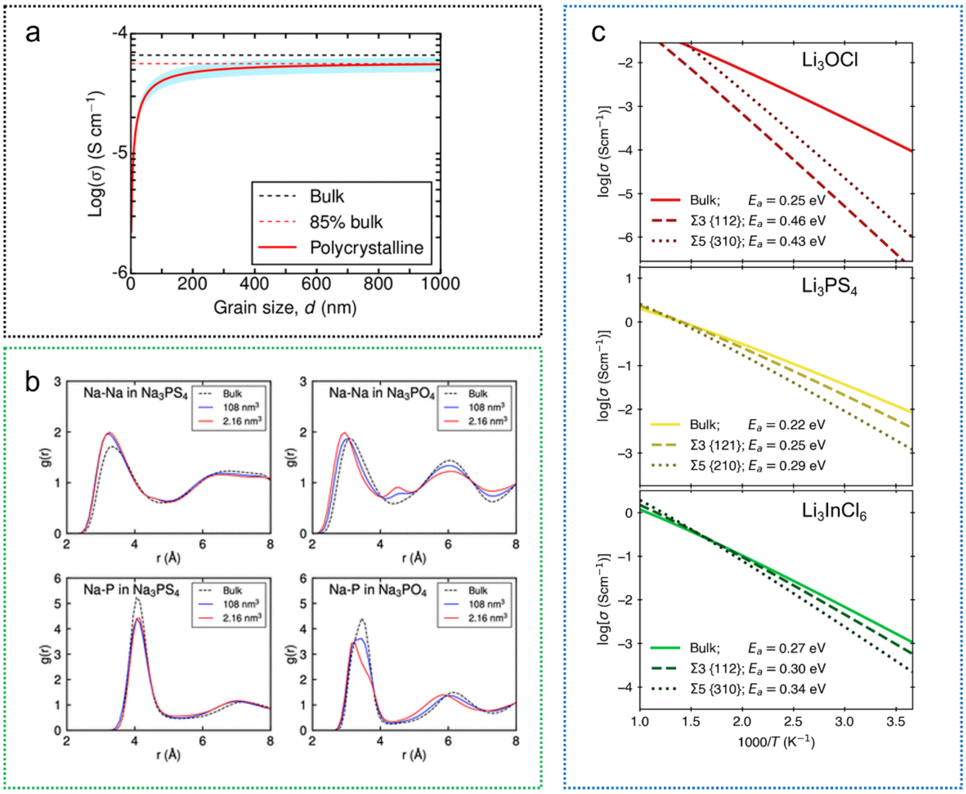

Figure 1. (a) The calculated polycrystalline (red solid line) and bulk (black dashed line) conductivity of Li_3OCl at 300 K as a function of grain size. The blue band represents the polycrystalline upper and lower limits based on different densification behaviours. Reprinted with permission from [4]. Copyright (2018) American Chemical Society. (b) Na–Na and Na–P Radial Distribution Functions calculated for bulk and polycrystalline (grain volumes of 108 and 2.16 nm^3) Na_3PS_4 (left) and Na_3PO_4 (right) at 400 K. Reprinted with permission from [16]. Copyright (2019) American Chemical Society. (c) Ionic conductivities for the bulk and grain boundaries of Li_3OCl (top), Li_3PS_4 (middle) and Li_3InCl_6 (bottom). Corresponding activation energies, E_a, for each system are also shown. Reproduced from [21]. CC BY 4.0.

resistance to Li-ion motion, resulting in low total conductivities. As presented in figure 1(a), this work predicts that the polycrystalline Li_3OCl system is unable to achieve conductivities greater than 85% of the theoretical bulk, indicating that higher conductivities can be accessed by elimination of grain boundaries, such as by creation of single crystals.

Unlike candidate oxide electrolytes, sulphides appear to have low grain boundary resistances which are comparable to the bulk, making grain boundaries less detrimental to performance [22–25]. Dawson *et al* modelled a homologous oxide and sulphide (Na_3PO_4 and Na_3PS_4) to directly compare the effect grain boundaries had on each structure. Radial distribution functions (RDFs) which show the average distribution of atoms around a given atom were calculated (figure 1(b)). It was observed that in the case of the oxide, the grain boundary was over-coordinated, whereas in the sulphide the RDFs calculated for single crystal and polycrystalline simulations were essentially the same, implying the conduction mechanism in the grain boundary is the same as the bulk crystal [16]. They suggested that small differences in conductivity which do occur can be credited to the composition changes and higher concentration of point defects that exist in the grain boundary region.

Quirk and Dawson looked at modelling three Li-ion conductors—an anti-perovskite oxide (Li_3OCl), a thiophosphate (Li_3PS_4), and a halide (Li_3InCl_6) [21]. They demonstrated the oxide to have worse ionic conduction across grain boundaries than within the bulk, as expected, but found the effect to be less severe in the halide, much like in sulphides (figure 1(c)). Electrostatic perturbations in grain boundary regions were shown to be much higher in the case of the oxide, which is attributed to be the reason behind its increased activation energy.

These results indicate that grain boundaries may not always be limiting from the viewpoint of ionic conductivity. It may be sufficient to instead pursue materials with a combination of high grain boundary energies (such that the density of grain boundaries is low) and low grain boundary resistances.

3. The role of grain boundaries in lithium filament growth

3.1. *Intergranular lithium growth*

The avoidance of filamentary lithium growth was a key motivator in initial investigations into solid-state electrolytes. Monroe and Newman proposed that lithium dendrite growth can be prevented with use of a solid electrolyte with a shear modulus greater than twice that of lithium [26], which is satisfied by most inorganic electrolytes. In spite of this, lithium growth is largely still a problem. The growth of these filaments is dependent on the rate of electrodeposition, and so critical current density (CCD) is often used as a convenient measure of resistance to failure by filament short-circuiting. Targets of 3–10 mA cm^{-2} for competitive Li-metal batteries are a long way from realisation [27, 28].

Cheng *et al* claimed to demonstrate that lithium filaments propagate intergranularly in polycrystalline samples by providing scanning electron microscopy (SEM) images displaying a web-like structure of lithium on an LLZO surface fractured post cycling (figure 2(a)) [1]. Another study used x-ray computed tomography to show lithium filaments often take tortuous paths through LLZO which are concordant with expected intergranular pathways for the grain size of the sample [29]. These results indicate that grain boundaries may be detrimental even in material systems where their effect on ionic conductivity is negligible.

Several theories have been suggested to explain the occurrence of intergranular lithium deposition. Much of this existing work into CCD is based on LLZO electrolytes, deemed a good choice thanks to its high bulk conductivity and relatively good chemical stability with lithium metal [30, 31]. As has been demonstrated in computational work looking at grain boundary ionic conductivities and structures, the behaviour of different material systems varies greatly. Consequently, it could be beneficial to study lithium-growth behaviour across other candidate electrolyte materials as well. It might be of particular interest to consider systems in which the negative impact of grain boundaries is less clear, such as sulphides, unlike oxides which are already established to have a detrimental effect on ionic conductivity. Yu and Siegel proposed that the lower shear modulus of grain boundaries allows for accumulation of lithium in these elastically softer regions, which consequently generates a stronger local electric field and hence promotes subsequent deposition (figure 2(b)) [32]. If grain boundaries act as fast diffusion pathways such that the rate of lithium arriving at the electrolyte-electrode interface exceeds the lateral diffusion away, the resulting lithium ‘pile-up’ might lead to deposition of filaments along the grain boundaries (figure 2(c)). This idea has been disproved using DFT calculations of the grain boundary ionic conductivity for the case of LLZO [15], and many other material systems show high grain boundary resistances as was discussed in section 2.

Han *et al* proposed an electronic leakage mechanism in which electrons tunnel into the electrolyte and reduce Li^+ ions [34]. This is able to explain the occurrence of both interface-controlled growth and direct lithium deposition inside of the solid electrolyte. For high ionic conductivity oxide and sulphide electrolytes such as LLZO and Li_2S-P_2S_5, the electronic conductivity is of the order 10^{-9}–10^{-7} Scm^{-1} [35–37]. This was used to explain why lithium

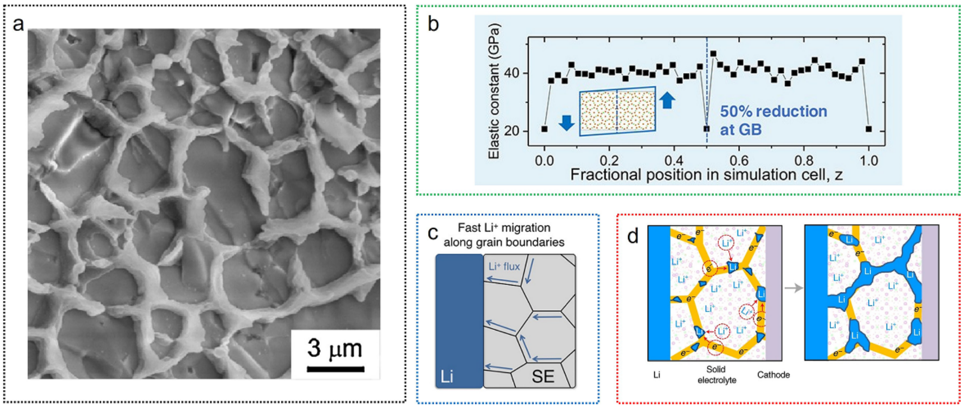

Figure 2. (a) SEM image of the fractured surface of cycled LLZO, showing apparent lithium deposition along grain boundaries. Reprinted from [1], Copyright (2017), with permission from Elsevier. (b) Example calculation of the elastic modulus across a grain boundary in LLZO carried out by Yu and Siegel and used to explain why lithium accumulates along grain boundaries. Reprinted with permission from [32]. Copyright (2018) American Chemical Society. (c) Suggested mechanism of intergranular lithium deposition in which grain boundaries act as fast-diffusion pathways, resulting in a 'pile up' of lithium at the anode-electrolyte interface. Reprinted with permission from [32]. Copyright (2018) American Chemical Society. (d) Schematic showing how electrons tunnelling into the solid electrolyte can reduce lithium ions and result in lithium deposits which interconnect over time. This is proposed to occur preferentially along grain boundaries thanks to their reduced band gaps. Reproduced from [33], with permission from Springer Nature.

phosphorous oxynitride (LiPON), which has very low electronic conductivities between 10^{-15} and 10^{-12} Scm^{-1}, performs better at resisting lithium growth than other solid electrolytes, including those with much higher shear moduli and ionic conductivities [34]. This work was extended further with the postulation that grain boundaries act as preferential routes for electron leakage [33]. The greatly affected atomic arrangements at grain boundaries can reduce their band gaps relative to the bulk, and when the local potential at grain boundaries exceeds this narrow bandgap, the resulting leakage current acts as a source of electrons for lithium reduction. These isolated deposits grow with cycling, eventually interconnecting and leading to short-circuits, as demonstrated schematically in figure 2(d). LiPON is deposited as an amorphous film free from grain boundaries and so may also perform well for this reason. Quirk and Dawson obtained insights into the electronic structures of grain boundaries in an oxide, sulphide and halide electrolyte material using atomistic modelling [21]. Projected density of states were plotted using the hybrid-DFT functional HSE06. In all scenarios, band gap narrowing was found to occur (by an average of 0.73 eV across the studied materials [21]), indicating higher electronic conduction and supporting this argument for intergranular lithium plating. Not only does this increased leakage current potentially play a role in their failure by lithium-growth-induced short-circuiting, but also has negative consequences on the efficiency of the cell.

Another explanation for grain-boundary plating was proposed by Li and Monroe. This theory suggests grain boundary deposition may be due to the capacitive nature of the electrolyte-electrode interface, which can sustain a space-charge layer under pressure when there is a current [38]. Their chemical deposition energetics argument states that when the compressive stress at the electrolyte-electrode interface exceeds a critical value, it becomes more favourable for lithium to deposit along grain boundaries than the electrolyte-electrode interface. This condition is more likely to occur at high-energy grain boundaries which lead to a less negative critical pressure [38]. The work assumes that the strain energy associated with depositing along the grain boundary is small. Precipitation along grain boundaries is a commonly observed phenomenon, and so it seems reasonable to expect that this strain term would not

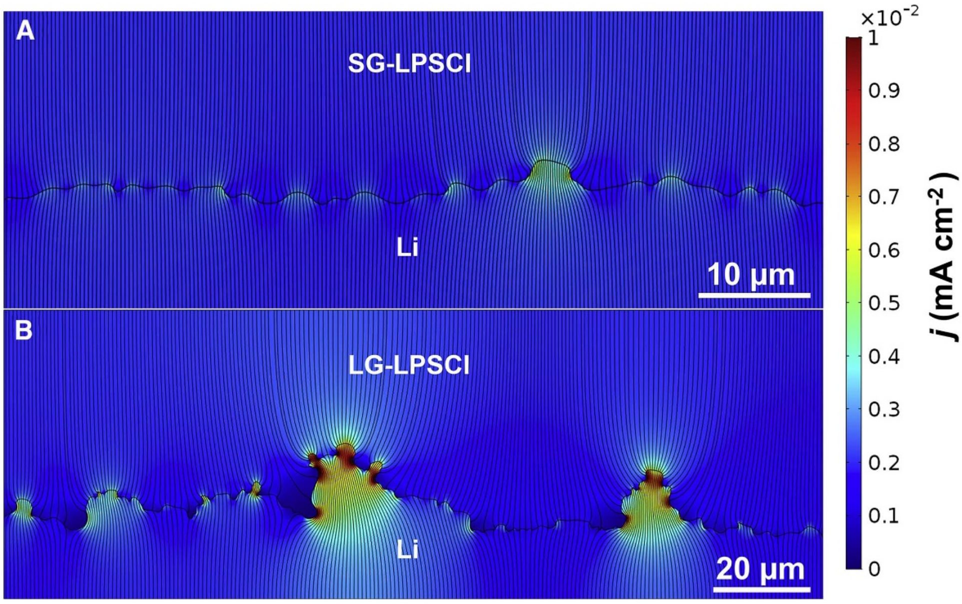

Figure 3. Finite element analysis of the current density distribution at Li|SG-LPSCl and Li|LG-LPSCl interfaces obtained via digitisation of FIB-SEM images. Sharper and deeper flaws are observed in the LG case. (SG—small grain, LG—large grain). Reprinted from [41], Copyright (2022), with permission from Elsevier.

massively change the excess energy required for grain-boundary plating such that it becomes unfeasible. This theory still requires a source of electrons to reduce the lithium in conjunction with satisfaction of the free energy requirements, and so does not contradict the theory proposed by Han *et al*.

3.2. The effect of grain size on CCD

Cheng *et al* reported perhaps counterintuitive findings of an improved CCD with smaller grain size for sintered LLZO samples. This was attributed to the three-times higher interfacial resistance measured in the case of the large-grained samples [39], which might be explained by noting that control of grain size was obtained through the sintering of different sized particles [40]. Singh *et al* carried out a study which also used variation of particle size to produce cold-pressed Li_6PS_5Cl pellets (referred to in the study as ‘small-grain’ and ‘large-grain’ samples) demonstrating the same trend in CCD [41]. Their work showed the samples made from larger particles to have a higher surface roughness, which was used to explain their worse resistance to lithium filament growth [41]. Firstly, the current focusing will be enhanced in the case of increased surface roughness, as is demonstrated in figure 3 showing finite element analysis of the current density distribution at the interfaces between small- and large-grained samples with the lithium metal anode [41]. Various studies have considered non-uniform current distributions at the lithium anode-solid electrolyte interface, such as these, to be important in lithium filament nucleation [30, 42, 43]. Secondly, when conformal contact is made between the lithium anode and solid electrolyte, the lithium which fills the pits in the solid electrolyte surface exerts a force on the electrolyte. This can be considered as a crack in a mode I opening geometry. Hence, the higher the surface roughness, the larger the effective crack size, the higher the stress concentration factor (K_c) at the ‘crack’ tip, and the lower the loads required to propagate the ‘crack’. In the case of both of these papers, the interfacial properties attributed to control the lithium growth are not strictly a result of the grain boundaries, but the synthesis approach used to control the grain size. This is an important distinction, and some of the experimental challenges which exist in

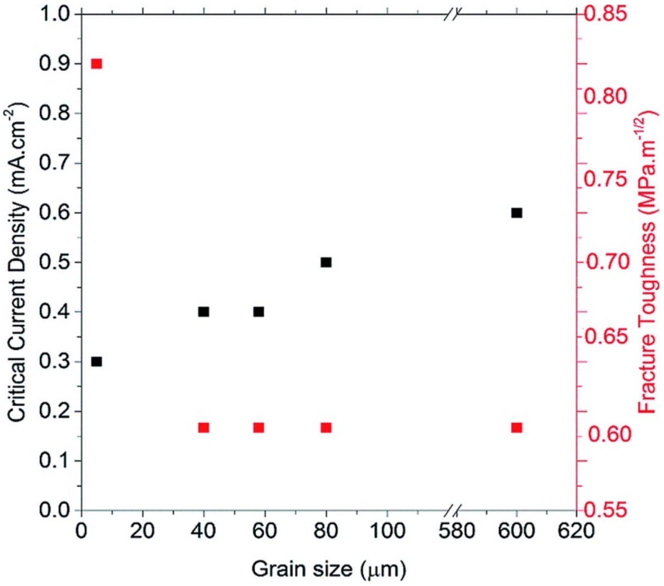

Figure 4. CCD and fracture toughness of LLZO samples as a function of grain size. Reprinted from [44] with permission from the Royal Society of Chemistry.

deconvoluting the effects of different microstructural features shall be addressed in section 3.3. In addition to improving the CCD through decreased surface roughness, Singh *et al* propose that resistance to lithium propagation is also improved in small-grained samples thanks to a stress-shielding effect. They argue that the high density of grain boundary triple junctions in samples with smaller grains results in continuous deflection of the lithium protrusion such that it takes a more tortuous path and hence increases the fracture toughness, K_{IC}, of the material [41].

Other work carried out by Sharafi *et al* used hot pressing to yield samples with very small interfacial resistances. A CCD increasing with grain size was demonstrated in this research, unlike the above findings from Sharafi *et al* [44]. Supporting characterisation allowing for a dependency on fracture toughness to be eliminated was provided (figure 4, table 1). Although the relative density and average grain misorientation angle were found to increase in conjunction with grain size in their samples synthesised through different temperatures of hot-pressing, a further sample with yet larger grains was produced through an additional annealing step (50 h, 1300 °C) carried out post-hot press (1100 °C). This material exhibited the same relative density and a similar misorientation as the sample hot-pressed at 1300 °C (table 1), indicating that the observed differences between these two measurements are indeed a result of the grain size. Sharafi *et al* postulate that the contradicting findings by Cheng *et al* could be a result of the nature of the grain boundaries produced in a sintered compared to hot-pressed pellet.

3.3. Decoupling the effects of grain boundaries from other microstructural features

In the case of most inorganic solid-state electrolyte candidates, the melting temperatures of the materials are too high for processing to be carried out by melt-casting such that the grain growth and grain boundary density cannot be controlled by varying the cooling rate [45].

Instead, nanoscale powders are often synthesised which can then be sintered or pressed into pellets. These powder particles can constitute of single crystals, polycrystals, amorphous materials or even multiple materials. Differing sinter temperatures or subsequent heat treatments can then be used to control the grain

Table 1. Summary of microstructural, mechanical and electrochemical properties of different LLZO samples investigated by Sharafi *et al* A-1300 °C refers to a HP-1100 °C sample which was subsequently annealed at 1300 °C for 50 h. Reprinted from [44] with permission from the Royal Society of Chemistry.

	Microstructural properties				Mechanical properties		Electrochemical properties	
Pellet	Phase purity	Relative density (%)	d_{ave} (μm)	Misorientation angle (°)	H (GPa)	K_{IC} (MPa $m^{-1/2}$)	σ_{total} (mS cm^{-1})	CCD (mA cm^{-2})
HP-1100 °C	Cubic LLZO	96.0 ± 0.5	5 ± 2	20	9.88 ± 0.49	0.82 ± 0.07	0.46	0.3
HP-1200 °C	3 vol% pyrochlore	97.7 ± 0.5	40 ± 13	35	8.05 ± 0.52	0.61 ± 0.05	0.52	0.4
HP-1250 °C	1 vol% pyrochlore	98.1 ± 0.5	60 ± 20	40	7.74 ± 0.46	0.60 ± 0.06	0.54	0.4
HP-1300 °C	Cubic LLZO	99.4 ± 0.5	80 ± 20	40	7.42 ± 0.48	0.61 ± 0.04	0.56	0.5
A-1300 °C	Cubic LLZO	99.4 ± 0.5	600 ± 200	41	6.80 ± 0.49	0.60 ± 0.05	0.57	0.6

size. During sintering, various diffusion mechanisms take place, the relative importance of which can be visualised using sintering maps, and some of which contribute to densification to a greater extent than others. As such, the conditions chosen for sintering (temperature, time, particle size) have effects on the densification of the final sample as well as the grain coarsening behaviour. Additionally, depending on the rate of grain growth, the pores which remain may be either isolated inside of grains, or interconnected along grain boundaries. This could be expected to have an impact on electrolyte performance. For example, in a sample with a high degree of associated grain boundary porosity, it is conceivable that plating lithium would deposit along the boundaries with significantly less stress than in a ‘perfect’ grain boundary with a much sharper interface and less steric space. These considerations bring into question whether studies investigating the effect of grain boundaries, which often dismiss the small density variations arising from the different synthesis conditions, can be taken at face value, or whether it is in fact the porosity which is responsible for observations. Prudence is especially important in scenarios where sintering has been utilised: in instances of different sized particles being used to control grain size [40, 46], there will also be implications on the sinter quality resulting from a combination of different diffusion distances, initial packing efficiency and driving forces for densification.

Many mechanisms explaining the nucleation and growth of lithium have been proposed, but the reality is probably a complex interplay of factors. In order to separate the impacts of grain boundaries from porosity, interfacial contact and other microstructural features, we need a model system with 100% relative density, controllable grain size and stability with lithium metal. Lithium hydroxyhalide antiperovskites have low melting points (<300 °C) meaning they can be synthesised into dense pellets through melt-solidification. Control of grain size has been demonstrated through variation of the cooling rate used in this process [45], and so this may be an ideal material system for future studies.

In addition to the intrinsic difficulties with controlling grain size, it is sometimes the case that minimal microstructural characterisation is provided in literature. SEM is an essential tool for gaining insight into the microstructure of a solid electrolyte, but care must be taken not to mistake ‘particle’ size for ‘grain’ size. Cross-sectional images should be taken to determine uniformity of the grain structure and porosity since surface images may not be representative. This should ideally be used in conjunction with electron backscatter diffraction (EBSD) mapping such that the crystal orientation, and so the degree of misorientation between grains, can be ascertained. For EBSD, very flat surfaces are required. This can make sample preparation challenging, but can be achieved by polishing with an ion beam, for example. Energy-dispersive x-ray spectroscopy can be used to observe segregation of elements to or from grain boundaries, such as impurities which might block ion motion. Techniques such as transmission electron microscopy and atomic force microscopy may additionally be useful in gathering more details on the grain boundaries, such as thicknesses.

This information might be useful in understanding observed phenomena, especially in instances where contradictory findings have been reported elsewhere. The impact of grain boundaries extends beyond simply the grain boundary density (i.e. grain size) and will depend on other factors such as grain boundary energies, thicknesses, grain shapes and texture. This in turn will depend on the synthesis routes used to produce them, and is not something which has been sufficiently addressed in literature. For example, applying pressure during sintering, known as hot pressing, adds an additional driving force for densification without impacting the grain coarsening behaviour. It is also shown to produce mechanically stronger grain boundaries, evident from transgranular rather than intergranular fracture of $Li_{6.19}Al_{0.27}La_3Zr_2O_{12}$ (LLZO) hot-pressed when compared to traditional sintering [47].

When navigating research on the role of grain size in solid-state electrolytes, it is therefore important to consider whether the effects of grain size can be isolated from other variables.

4. Glasses

While solid electrolyte research to date is largely focused on crystalline inorganic materials, the amorphous equivalents of these systems (referred to as the glassy form) often have higher ionic conductivity than their homologues. No single agreed definition of a glass exists, but a stringent definition as proposed in the Springer Handbook of Glass is that *'Glasses are dense (non-fractal) isotropic and homogeneous non-crystalline solids characterised by the absence of any internal phase boundaries'* [48]. From a thermodynamic perspective, glasses are the liquid structure 'frozen-in' metastably by supercooling, although they can be produced by alternative routes. Glasses do not contain resistive grain boundaries, which eliminates them as possible sites of lithium filament growth and crack formation, as well as allowing for isotropic conduction pathways.

In spite of the possibilities offered by glasses, they are not a prominent research area in the recent literature. Two of the more widely studied systems are lithium phosphorous oxynitride (LiPON) and lithium thiophosphates (LPS) which shall be briefly introduced in the following section. For a comprehensive discussion on glassy electrolytes more generally, the reader is directed to existing reviews in the area [49–51].

4.1. Lithium phosphorous oxynitride

Lithium phosphorous oxynitride (LiPON) is an example of an amorphous electrolyte material produced in thin film form. It is typically fabricated by radio-frequency sputtering of a Li_3PO_4 target in a nitrogen-based atmosphere to produce a material with a $Li_xPO_{4-y}N_y$ composition [52, 53]. This sputtering process enables the production of films with high interfacial contact [54].

A key advantage of LiPON is its resistance to Li filament growth [55]: current densities of up to 10 mA cm^{-2} [56] and thousands of cycles [57] have been demonstrated. This excellent performance may in part be due to its low electronic conductivity, which is 3–5 orders of magnitude lower than other prominent solid-state electrolyte candidates, as was discussed in section 3.1. Additionally, LiPON has been determined to have excellent fracture toughness, K_{IC}. A nanoindentation study on LiPON was unable to produce cracks in the surface, instead finding the strain could be accommodated by densification and plastic flow [58]. Typical crystalline electrolytes have much lower fracture toughnesses between 0.5 and 1 MPa $m^{-1/2}$ [58–61], and so their worse resistance to lithium-filament growth could also be explained by this figure of merit. The good mechanical properties of the sputtered interface [62], high relative density, absence of grain boundaries and few defects may also contribute to the CCD.

A reverse-engineering approach to understanding the excellent performance of LiPON could aid in designing new lithium-growth-resistant electrolytes. The presence of a substrate underneath LiPON can make obtaining measurements with good signal-to-noise ratios, for example by nuclear magnetic resonance spectroscopy, very challenging. The substrate also hinders carrying out other mechanical testing of the films, such as bend testing. Filling these holes in the characterisation of LiPON may allow further insights. The reported synthesis of 'freestanding' LiPON may be a step toward achieving this [63].

In spite of performing well in lithium-growth suppression, LiPON electrolytes are not suitable for application outside of microbatteries due to their low conductivities ($\sim 10^{-6}$ Scm^{-1}) [50], limiting their use to thin films. They could also potentially be used as a protective layer on the anode of lithium-metal batteries [64].

4.2. Lithium thiophosphate glasses

Early work on glassy sulphide electrolytes involved melt-quenching samples to liquid nitrogen temperatures [65–72]. Greater concentrations of modifiers containing lithium ions can be incorporated into glasses when using mechanical milling instead of melt-quenching, and hence greater conductivities achieved. Consequently, most current research uses extended periods of ball milling to produce an amorphous powder which must then be pressed into a pellet [72–75]. This provides scope for deconvoluting the effect of porosity from grain boundaries.

It is found that a metastable superionic phase which cannot be directly synthesised, of composition $Li_7P_3S_{11}$ and conductivity $>10^{-3}$ Scm^{-1}, can be precipitated from the glass phase by carrying out a heat treatment just above the glass's crystallisation temperature [76]. Glasses which have undergone crystallisation in this way are known as glass-ceramics. Generally, crystallisation produces phases with lower conductivity than the glassy state, but the production of this superionic phase is an exception. As such, a lot of work on sulphides deals with glass-ceramics rather than pure glasses, and hence not truly grain-boundary-free systems. Seino *et al* looked at improving the 'unification' of a $70Li_2S$-$30P_2S_5$ glass-ceramic powder, and were able to increase the conductivity from $1.4\ \times 10^{-3}$ Scm^{-1} for a pellet cold-pressed at 94 MPa to $1.7\ \times 10^{-2}$ Scm^{-1} for a pellet which subsequently underwent a 2 h heat treatment at 280 °C, determined as being just above the glass's crystallisation temperature from differential scanning calorimetry measurements [75].

Wang *et al* carried out an investigation comparing the cycling and rate performance of crystalline versus glassy lithium thiophosphate (LPS) electrolytes for three different compositions using In/LiIn | SE | $LiNb_{0.5}Ta_{0.5}O_3$ coated $LiCoO_2$ cells [77]. In all cases, the coulombic efficiency, capacity retention and rate performance were better for the glassy counterparts. The authors suggested the improved capacity retention and rate performance might be a result of the cathode-electrolyte interfacial resistance which is shown to develop more slowly in electrochemical impedance spectra taken on the glassy systems than the crystalline homologues. From analysis of the x-ray photoelectron spectroscopy measurements and impedance spectra, they conclude that this is a result of contact loss in the composite cathode. The greater degradation of the crystalline counterpart is attributed to its higher electronic conductivity when compared to the equivalent glass [77].

5. Critical research fronts

5.1. Porosity

Whether grain boundaries are detrimental to the CCD of an electrolyte is still not fully understood. In order to address this, it will be necessary to deconvolute the effects of porosity and grain boundaries, rather than dismissing small density variations which occur when using different sintering and heat treatment conditions to control grain growth. An effective method of producing very dense samples will be required to do this, such as melt-casting. Lithium hydroxyhalide antiperovskites (Li_2OHX, X = Cl, Br) may be an ideal model system for this thanks to their low melting points (<300 °C), which allows for both easy synthesis and control of grain size through cooling rate [45]. Another potential method of investigation might be controlled nucleation and growth of crystals from a glassy matrix through heat treatments. Typically, crystal nucleation and crystal growth dominate at different temperatures [78], and so the number of nucleated grains (and consequently grain size) can be controlled through the time held in the nucleation temperature range [79].

5.2. Mechanical properties

The importance of the electrolyte's mechanical properties in determining the CCD of a battery is also of interest—and within this, whether lithium-filament growth fills existing cracks, or is the cause of crack propagation itself [62, 80]. If the former, factors such as electronic leakage along grain boundaries may mean that it is preferable to reduce the grain boundary density by creating large-grained samples. However, in the latter case, smaller grain sizes might be desirable thanks to the increased fracture toughness associated with smaller grains.

A more thorough understanding of the impact that different synthesis approaches have on the mechanical properties of grain boundaries may also help in the mission to create filament-resistant electrolytes.

5.3. Electronic properties

An improved understanding of the electronic properties of grain boundaries and the consequences of this on the CCD needs to be gained through both modelling and experimental studies. Atomistic calculations will be useful in computational investigations, however novel approaches may be necessary to experimentally acquire information regarding the electronic conductivity of grain boundaries.

5.4. Ionic conductivity

In future computational studies, it may be beneficial to predict total conductivity of bulk electrolytes using models accounting for both conductivity between grains and along the grain boundaries, such as done on Li_3OCl [4]. This is particularly important in systems with high grain boundary conductivity, such as sulphides, in which the migration along grain boundaries will be significant. To do this, it would be good for studies to consider the tortuosity of the conduction pathways in calculations. The consequences that conduction along grain boundaries, if any, have on CCD may also be of interest in sulphides.

5.5. Glasses

In spite of an incomplete understanding of the mechanisms governing grain boundary behaviour, early indications of increased electronic leakage and the reduced ionic conductivity in some systems imply that the removal of grain boundaries may benefit the performance of electrolytes regardless. As has been mentioned, one approach to eliminating grain boundaries is the creation of glasses. A lot of the work in this area has been focused on sulphide glasses. However, in view of the low grain boundary resistances exhibited by crystalline sulphides [75], they may not be a material system in which a particularly large benefit is gained from amorphisation. Additionally, the preference of glass-ceramics over glasses in sulphide work means that the focus in research is not actually on grain-boundary-free systems. The potential performance improvements which could be gained from amorphisation should be investigated for other material systems. This is not limited to established solid electrolyte candidates, but could also encompass new chemistries such as borate glasses

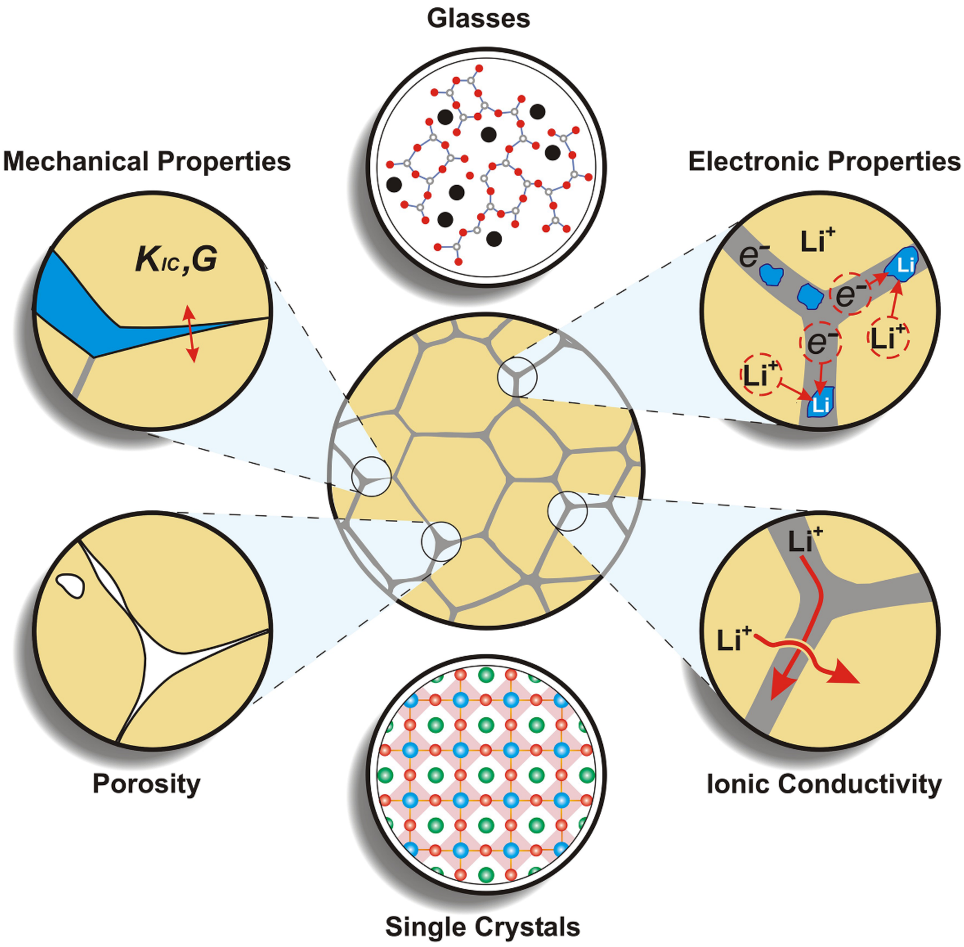

Figure 5. Critical research fronts necessary to gain a complete understanding of the role of grain boundaries in solid-state electrolytes, and reduce their detrimental effects.

doped with lithium ions [81]. Successful materials must have good ionic conductivity and wide electrochemical stability windows. Additionally, in a bid to replicate the lithium-filament resistance of LiPON, it might be beneficial to pursue materials demonstrating high fracture toughness and low electronic conductivity.

5.6. Single crystals

Another solution to removing grain boundaries is to make single crystal electrolytes. For these to be practically useful, a scalable and reproducible method of making single crystals with smooth surfaces is required. Although LLZO single crystals free from voids and grain boundaries have been demonstrated, defects introduced by mechanical polishing are visible in SEM images [62, 82]. Lithium filament growth was observed, however this was proposed to be a result of nucleation from pre-existing flaws at the interface [62]. As well as yielding the benefits of grain boundary removal, having access to atomically-smooth, bulk single crystals will enable other factors impacting the CCD, such as surface roughness, to be investigated without the influence of grain boundaries.

6. Conclusions

In this perspective, the current understanding of the role of grain boundaries on solid-state electrolytes has been approached from both a computational and experimental viewpoint with respect to ionic conduction and lithium filament growth. The most uncertainty surrounding this area relates to the mechanisms underpinning lithium filament deposition along grain boundaries, and the impact of grain size on CCD. Closely linked to these questions are the role of porosity and other microstructural defects in solid-state electrolytes. The challenges which arise when trying to study and control grain boundaries have been presented, as well as suggestions as to how their effects may be minimised and considerations for future studies.

Although it appears that grain boundaries may not always be detrimental to ionic conduction, reports of band gap narrowing, and in turn increased electronic conduction, will be undesirable. As a result, possible strategies to eliminate grain boundaries have been proposed, namely glasses and single crystals. Synthesis of these electrolytes may be essential into gaining further insight into understanding grain boundaries.

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References

[1] Cheng E J, Sharafi A and Sakamoto J 2017 Intergranular Li metal propagation through polycrystalline $Li_{6.25}Al_{0.2}5La_3Zr_2O_{12}$ ceramic electrolyte *Electrochim. Acta* **223** 85–91

[2] Ohring M 2002 Interdiffusion, reactions and transformations in thin films *Materials Science of Thin Films* (New York: Academic) ch 11

[3] Mishin Y and Herzig C 1999 Grain boundary diffusion: recent progress and future research *Mater. Sci. Eng.* **260** 55–71

[4] Dawson J A, Canepa P, Famprikis T, Masquelier C and Islam M S 2018 Atomic-scale influence of grain boundaries on Li-ion conduction in solid electrolytes for all-solid-state batteries *J. Am. Chem. Soc.* **140** 362–8

[5] Lü X, Howard J W, Chen A, Zhu J, Li S, Wu G, Dowden P, Xu H, Zhao Y and Jia Q 2016 Antiperovskite Li_3OCl superionic conductor films for solid-state Li-ion batteries *Adv. Sci.* **3** 3

[6] Lü X, Wu G, Howard J W, Chen A, Zhao Y, Daemen L L and Jia Q 2014 Li-rich anti-perovskite Li_3OCl films with enhanced ionic conductivity *Chem. Commun.* **50** 11520–2

[7] Zhu J, Li S, Zhang Y, Howard J W, Lü X, Li Y, Wang Y, Kumar R S, Wang L and Zhao Y 2016 Enhanced ionic conductivity with $Li_7O_2Br_3$ phase in Li_3OBr anti-perovskite solid electrolyte *Appl. Phys. Lett.* **109** 9

[8] Ma C, Chen K, Liang C, Nan C W, Ishikawa R, More K and Chi M 2014 Atomic-scale origin of the large grain-boundary resistance in perovskite Li-ion-conducting solid electrolytes *Energy Environ. Sci.* **7** 1638–42

[9] Wu J F and Guo X 2017 Origin of the low grain boundary conductivity in lithium ion conducting perovskites: $Li_{3x}La_{0.67-x}TiO_3$ *Phys. Chem. Chem. Phys.* **19** 5880–7

[10] Tiku S K and Kroger F A 1980 Effects of space charge, grain-boundary segregation and mobility differences between grain boundary and bulk on the conductivity of polycrystalline Al_2O3 *J. Am. Ceram. Soc.* **63** 183–9

[11] Tschope A 2001 Grain size-dependent electrical conductivity of polycrystalline cerium oxide II: space charge model *Solid State Ion.* **139** 267–80

[12] Guo X and Ding Y 2004 Grain boundary space charge effect in zirconia *J. Electrochem. Soc.* **151** J1

[13] Durá O J, López De La Torre M A, Vázquez L, Chaboy J, Boada R, Rivera-Calzada A, Santamaria J and Leon C 2010 Ionic conductivity of nanocrystalline yttria-stabilized zirconia: Grain boundary and size effects *Phys. Rev.* B **81** 5

[14] Kjølseth C, Fjeld H, Prytz Ø, Dahl P I, Estournès C, Haugsrud R and Norby T 2010 Space-charge theory applied to the grain boundary impedance of proton conducting $BaZr_0.9Y_0.1O_3$ - δ *Solid State Ion.* **181** 268–75

[15] Yu S and Siegel D J 2017 Grain boundary contributions to Li-ion transport in the solid electrolyte $Li_7La_3Zr_2O_12$ (LLZO) *Chem. Mater.* **29** 9639–47

[16] Dawson J A, Canepa P, Clarke M J, Famprikis T, Ghosh D and Islam M S 7 2019 Toward understanding the different influences of grain boundaries on ion transport in sulfide and oxide solid electrolytes *Chem. Mater.* **31** 5296–304

[17] Lu Z, Chen C, Baiyee Z M, Chen X, Niu C and Ciucci F 2015 Defect chemistry and lithium transport in Li_3OCl anti-perovskite superionic conductors *Phys. Chem. Chem. Phys.* **17** 32547–55

[18] Deng Z, Radhakrishnan B and Ong S P 2015 Rational composition optimization of the lithium-rich $Li_3OCl_{1-x}Br_x$ anti-perovskite superionic conductors *Chem. Mater.* **27** 3749–55

[19] Emly A, Kioupakis E and Van Der Ven A 2013 Phase stability and transport mechanisms in antiperovskite Li_3OCl and Li_3OBr superionic conductors *Chem. Mater.* **25** 4663–70

[20] Mouta R, Melo M A B, Diniz E M and Paschoal C W A 2014 Concentration of charge carriers, migration and stability in Li_3OCl solid electrolytes *Chem. Mater.* **26** 7137–44

[21] Quirk J A and Dawson J A 2022 Design principles for grain boundaries in solid-state lithium-ion conductors *ChemRxiv Preprint* (https://doi.org/10.26434/chemrxiv-2022-0jghq)

[22] Kuhn A, Duppel V and Lotsch B V 2013 Tetragonal $Li_{10}GeP_2S_{12}$ and Li_7GePS_8 – exploring the Li ion dynamics in LGPS Li electrolytes *Energy Environ. Sci.* **6** 3548–52

[23] Bron P, Dehnen S and Roling B 2016 $Li_{10}Si_{0.3}Sn_{0.7}P_2S_{12}$ – a low-cost and low-grain-boundary-resistance lithium superionic conductor *J. Power Sources* **329** 530–5

[24] Duchardt M, Ruschewitz U, Adams S, Dehnen S and Roling B 2018 Vacancy-controlled Na^+ superion conduction in $Na_{11}Sn_2PS_{12}$ *Angew. Chem., Int. Ed.* **57** 1351–5

[25] Krauskopf T, Culver S P and Zeier W G 2018 Local tetragonal structure of the cubic superionic conductor Na_3PS_4 *Inorg. Chem.* **57** 4739–44

[26] Monroe C and Newman J 2005 The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces *J. Electrochem. Soc.* **152** 396

[27] Albertus P, Babinec S, Litzelman S and Newman A 2018 Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries *Nat. Energy* **3** 16–21

[28] Famprikis T, Canepa P, Dawson J A, Islam M S and Masquelier C 2019 Fundamentals of inorganic solid-state electrolytes for batteries *Nat. Mater.* **18** 1278–91

[29] Hao S, Bailey J J, Iacoviello F, Bu J, Grant P S, Brett D J L and Shearing P R 2021 3D imaging of lithium protrusions in solid-state lithium batteries using x-ray computed tomography *Adv. Funct. Mater.* **31** 2007564

[30] Fu K *et al* 2017 Toward garnet electrolyte-based Li metal batteries: an ultrathin, highly effective artificial solid-state electrolyte/metallic Li interface *Sci. Adv.* **3** e1601659

[31] Thangadurai V, Narayanan S and Pinzaru D 7 2014 Garnet-type solid-state fast Li ion conductors for Li batteries: critical review *Chem. Soc. Rev.* **43** 4714–27

[32] Yu S and Siegel D J 2018 Grain boundary softening: a potential mechanism for lithium metal penetration through stiff solid electrolytes *ACS Appl. Mater. Interfaces* **10** 38151–8

[33] Liu X *et al* 2021 Local electronic structure variation resulting in Li ‘filament’ formation within solid electrolytes *Nat. Mater.* **20** 1485–90

[34] Han F, Westover A S, Yue J, Fan X, Wang F, Chi M, Leonard D N, Dudney N J, Wang H and Wang C 2019 High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes *Nat. Energy* **4** 187–96

[35] Chen Y T, Jena A, Pang W K, Peterson V K, Sheu H S, Chang H and Liu R S 2017 Voltammetric enhancement of Li-ion conduction in al-doped $Li_{7-x}La_3Zr_2O_{12}$ solid electrolyte *J. Phys. Chem* C **121** 15565–73

[36] Minami K, Mizuno F, Hayashi A and Tatsumisago M 2007 Lithium ion conductivity of the Li_2S-P_2S_5 glass-based electrolytes prepared by the melt quenching method *Solid State Ion.* **178** 837–41

[37] Rangasamy E, Wolfenstine J and Sakamoto J 2012 The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition $Li_7La_3Zr_2O_{12}$ *Solid State Ion.* **206** 28–32

[38] Li G and Monroe C W 2019 Dendrite nucleation in lithium-conductive ceramics *Phys. Chem. Chem. Phys.* **21** 20354–9

[39] Cheng L *et al* 2015 Interrelationships among grain size, surface composition, air stability and interfacial resistance of al-substituted $Li_7La_3Zr_2O_{12}$ solid electrolytes *ACS Appl. Mater. Interfaces* **7** 17649–55

[40] Cheng L, Chen W, Kunz M, Persson K, Tamura N, Chen G and Doeff M 2015 Effect of surface microstructure on electrochemical performance of garnet solid electrolytes *ACS Appl. Mater. Interfaces* **7** 2073–81

[41] Singh D K, Henss A, Mogwitz B, Gautam A, Horn J, Krauskopf T, Burkhardt S, Sann J, Richter F H and Janek J 2022 Li_6PS_5Cl microstructure and influence on dendrite growth in solid-state batteries with lithium metal anode *Cell Rep. Phys. Sci.* **3** 101043

[42] Tsai C L, Roddatis V, Chandran C V, Ma Q, Uhlenbruck S, Bram M, Heitjans P and Guillon O 2016 $Li_7La_3Zr_2O_{12}$ interface modification for Li dendrite prevention *ACS Appl. Mater. Interfaces* **8** 10617–26

[43] Wu B, Wang S, Lochala J, Desrochers D, Liu B, Zhang W, Yang J and Xiao J 2018 The role of the solid electrolyte interphase layer in preventing Li dendrite growth in solid-state batteries *Energy Environ. Sci.* **11** 1803–10

[44] Sharafi A, Haslam C G, Kerns R D, Wolfenstine J and Sakamoto J 2017 Controlling and correlating the effect of grain size with the mechanical and electrochemical properties of $Li_7La_3Zr_2O_{12}$ solid-state electrolyte *J. Mater. Chem.* A **5** 21491–504

[45] Lee H J, Darminto B, Narayanan S, Diaz-Lopez M, Xiao A W, Chart Y, Lee J H, Dawson J A and Pasta M 2022 Li-ion conductivity in $Li_2OHCl_{(1-x)}Br_x$ solid electrolytes: grains, grain boundaries and interfaces *J. Mater. Chem.* A **10** 11574

[46] Huang Z, Chen L, Huang B, Xu B, Shao G, Wang H, Li Y and Wang C A 2020 Enhanced performance of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ solid electrolyte by the regulation of grain and grain boundary phases *ACS Appl. Mater. Interfaces* **12** 56118–25

[47] Kim Y, Jo H, Allen J L, Choe H, Wolfenstine J, Sakamoto J and Pharr G 2016 The effect of relative density on the mechanical properties of hot-pressed cubic $Li_7La_3Zr_2O_{12}$ *J. Am. Ceram. Soc.* **99** 1367–74

[48] Abdelouas A *et al* 2019 *Springer Handbook of Glass* 1st edn (Cham: Springer)

[49] Viallet V, Seznec V, Hayashi A, Tatsumisago M and Pradel A 2019 Glasses and glass-ceramics for solid-state battery applications *Springer Handbook of Glass* (Cham: Springer)

[50] Grady Z A, Wilkinson C J, Randall C A and Mauro J C 2020 Emerging role of non-crystalline electrolytes in solid-state battery research *Front. Energy Res.* **8** 1–23

[51] Das A, Sahu S, Mohapatra M, Verma S, Bhattacharyya A J and Basu S 2022 Lithium-ion conductive glass-ceramic electrolytes enable safe and practical Li batteries *Mater. Today Energy* **29** 101118

[52] Hamon Y, Douard A, Sabary F, Marcel C, Vinatier P, Pecquenard B and Levasseur A 2006 Influence of sputtering conditions on ionic conductivity of lipon thin films *Solid State Ion.* **177** 257–61

[53] Bates J B, Dudney N J, Gruzalski G R, Zuhr R A, Choudhury A, Luck C F and Robertson J D 1993 Fabrication and characterization of amorphous lithium electrolyte thin films and rechargeable thin-film batteries *J. Power Sources* **43** 103

[54] Wang Z, Santhanagopalan D, Zhang W, Wang F, Xin H L, He K, Li J, Dudney N and Meng Y S 2016 In situ stem-eels observation of nanoscale interfacial phenomena in all-solid-state batteries *Nano Lett.* **16** 3760–7

[55] Westover A S, Dudney N J, Sacci R L and Kalnaus S 2019 Deposition and confinement of Li metal along an artificial Lipon-Lipon interface *ACS Energy Lett.* **4** 651–5

[56] Bates J B, Dudney N J, Neudecker B, Ueda A and Evans C D 2000 Thin-film lithium and lithium-ion batteries *Solid State Ion.* **135** 33–45

[57] Neudecker B J, Dudney N J and Bates J B 2000 "Lithium-free" thin-film battery with in situ plated Li anode *J. Electrochem. Soc.* **147** 517–23

[58] Kalnaus S, Westover A S, Kornbluth M, Herbert E and Dudney N J 2021 Resistance to fracture in the glassy solid electrolyte LiPON *J. Mater. Res.* **36** 787–96

[59] Jackman S D and Cutler R A 2012 Effect of microcracking on ionic conductivity in LATP *J. Power Sources* **218** 65–72

[60] Wolfenstine J, Allen J L, Sakamoto J, Siegel D J and Choe H 2018 Mechanical behavior of Li-ion-conducting crystalline oxide-based solid electrolytes: a brief review *Ionics* **24** 1271–6

[61] Nonemacher J F, Naqash S, Tietz F and Malzbender J 2019 Micromechanical assessment of AL/Y-substituted nasicon solid electrolytes *Ceram. Int.* **45** 21308–14

[62] Porz L, Swamy T, Sheldon B W, Rettenwander D, Frömling T, Thaman H L, Berendts S, Uecker R, Carter W C and Chiang Y M 2017 Mechanism of lithium metal penetration through inorganic solid electrolytes *Adv. Energy Mater.* **7** 1701003

[63] Cheng D *et al* 2022 Freestanding LiPON: from fundamental study to uniformly dense Li metal deposition under zero external pressure (arXiv:2208.04402)

[64] Su J, Pasta M, Ning Z, Gao X, Bruce P G and Grovenor C R M 2022 Interfacial modification between argyrodite-type solid-state electrolytes and Li metal anodes using LiPON interlayers *Energy Environ. Sci.* **15** 3805

[65] Mercier R, Malugani J, Fahys B and Robert G 1981 Superionic conduction in Li_2S - P_2S_5 - LiI - glasses *Solid State Ion.* **5** 663–6

[66] Menetrier M, Levasseur V, Delmas C, Audebert J and Hagenmuller P 1984 New secondary batteries for room temperature applications using a vitreous electrolyte *Solid State Ion.* **14** 257–61

[67] Kennedy J H and Yang Y 1987 Glass-forming region and structure in SiS_2-$Li-2S$-LiX ($X =$ Br, I) *J. Solid State Chem.* **257** 252–7

[68] Kondo S, Takada K and Yamamura Y 1992 New lithium ion conductors based on Li_2S-SiS_2 system *Solid State Ion.* **56** 1183–6

[69] Pradel A and Ribes M 1986 Electrical properties of lithium conductive silicon sulfide glasses prepared by twin roller quenching *Solid State Ion.* **19** 351–5

[70] Aotani N, Iwamoto K, Takada K and Kondo S 1994 Synthesis and electrochemical properties of lithium ion conductive glass, Li_3PO_4–Li_2S–SiS_2 *Solid State Ion.* **68** 35–39

[71] Hayashi A, Tatsumisago M and Minami T 1999 Electrochemical properties for the lithium ion conductive (100-x) ($0.6Li_2\ S \cdot 0.4SiS_2$) · xLi4SiO4 oxysulfide glasses *J. Electrochem. Soc.* **146** 3472

[72] Tatsumisago M, Yamashita H, Hayashi A, Morimoto H and Minami T 2000 Preparation and structure of amorphous solid electrolytes based on lithium sulfide *J. Non-Cryst. Solids* **274** 30–38

[73] Hayashi A, Hama S, Morimoto H, Tatsumisago M and Minami T 2001 Preparation of Li_2S-P_2S_5 amorphous solid electrolytes by mechanical milling *J. Am. Ceram. Soc.* **84** 477–9

[74] Ujiie S, Hayashi A and Tatsumisago M 2013 Preparation and ionic conductivity of $(100 - x)(0.8Li_2S{\cdot}0.2P_2S_5){\cdot}x$LiI glass-ceramic electrolytes *J. Solid State Electrochem.* **17** 675–80

[75] Seino Y, Ota T, Takada K, Hayashi A and Tatsumisago M 2014 A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries *Energy Environ. Sci.* **7** 627–31

[76] Mizuno F, Hayashi A, Tadanaga K and Tatsumisago M 2005 New lithium-ion conducting crystal obtained by crystallization of the Li_2S-P_2S_5 glasses *Electrochem. Solid-State Lett.* **8** A603

[77] Wang S *et al* 2021 Influence of crystallinity of lithium thiophosphate solid electrolytes on the performance of solid-state batteries *Adv. Energy Mater.* **11** 1–11

[78] Biesuz M and Sglavo V M 2019 Flash sintering of ceramics *J. Eur. Ceram. Soc.* **39** 115–43

[79] Campos J V, Lavagnini I R, Zallocco V M, Ferreira E B, Pallone M J A, and Rodrigues A C M Flash sintering with concurrent crystallization of $Li_1.5Al_0.5Ge_1.5(PO_4)_3$ glass *Preprint* https://doi.org/10.2139/ssrn.4130828 (posted online 8 Jun 2022)

[80] Ning Z *et al* 2021 Visualizing plating-induced cracking in lithium-anode solid-electrolyte cells *Nat. Mater.* **20** 1121–9

[81] Lee C H, Joo K H, Kim J H, Woo S G, Sohn H J, Kang T, Park Y and Oh J Y 2002 Characterizations of a new lithium ion conducting Li_2O-SeO_2-$B2O_3$ glass electrolyte *Solid State Ion.* **149** 59–65

[82] Kataoka K, Nagata H and Akimoto J 2018 Lithium-ion conducting oxide single crystal as solid electrolyte for advanced lithium battery application *Sci. Rep.* **8** 9965