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$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), and sulphide electrolytes, such as Li$_2$S-P$_2$S$_5$ (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,
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 (∼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$_3$OCl. Activation energies of 0.3–0.4 eV are predicted by density functional theory (DFT) studies [17–20], yet activation energies as high as ∼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
resistance to Li-ion motion, resulting in low total conductivities. As presented in figure 1(a), this work predicts that the polycrystalline Li$_3$OCl 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$_3$PO$_4$ and Na$_3$PS$_4$) 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$_3$OCl), a thiophosphate (Li$_3$PS$_4$), and a halide (Li$_3$InCl$_6$) [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\(_2\)S-P\(_2\)S\(_5\), the electronic conductivity is of the order 10\(^{-9}\)–10\(^{-7}\) Scm\(^{-1}\) [35–37]. This was used to explain why lithium
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 modulii 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-circuits, 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
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 Li₆PS₅Cl 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 ($K_t$) 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
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 angle 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.

| Pellet | Phase purity | Microstructural properties | Mechanical properties | Electrochemical properties |
|--------|--------------|-----------------------------|-----------------------|---------------------------|
|        |              | Relative density (%) | $d_{ave}$ (µm) | Misorientation angle (°) | H (GPa) | $K_{IC}$ (MPa m$^{-1/2}$) | $\sigma_{total}$ (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 \( \text{Li}_{6.19}\text{Al}_{0.27}\text{La}_3\text{Zr}_2\text{O}_{12} \) (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 \( \text{Li}_3\text{PO}_4 \) target in a nitrogen-based atmosphere to produce a material with a \( \text{Li}_x\text{PO}_4-\text{N}_y \) 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$_7$P$_3$S$_{11}$ 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$_2$S-30P$_2$S$_5$ 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$_2$OHX, 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$_2$OCl [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.
Critical research fronts necessary to gain a complete understanding of the role of grain boundaries in solid-state electrolytes, and reduce their detrimental effects.

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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