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Mechanistic understanding and strategies to design interfaces of solid electrolytes: insights gained from transmission electron microscopy

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Abstract

Solid electrolytes (SEs) have garnered increased attention for their promise to enable higher volumetric energy density and enhanced safety required for future battery systems. SEs are not only a key constituent in all-solid-state batteries, but also are important "protectors" of Li-metal anodes in next-generation battery configurations, such as Li-air, Li-S, redox flow batteries, among others. The impedance at interfaces associated with SEs, *e.g.* internal grain/phase boundaries and their interfacial stability with electrodes, represent two key factors limiting the performance of SEs, yet analyzing these interfaces experimentally at the nano/atomic scale is generally challenging. A mechanistic understanding of the possible instability at interfaces and propagation of interfacial resistance will pave the way to the design of high-performance SE-based batteries. In this review, we briefly introduce the fundamentals of SEs and challenges associated with their interfaces. Next, we discuss experimental techniques that allow for atomic-to-microscale understanding of ion transport and stability in SEs and at their interfaces, specifically highlighting the applications of state-of-art and emerging *ex situ* and *in situ* transmission electron microscopy (TEM) and scanning TEM (STEM). Representative examples from current literature that exemplify recent fundamental insights gained from these S/TEM techniques are highlighted. Applicable strategies to improve ion conduction and interfaces in SE-based batteries are also discussed. This review concludes by highlighting opportunities for future research that will significantly promote the fundamental understanding of SEs, specifically further developments in S/TEM techniques that will bring new insights into the design of high-performance interfaces for future electrical energy storage.

Introduction

Ion transport in solids and their associated interfaces forms the basis of various current and next-generation energy storage technologies. In state-of-art conventional Li-ion batteries, the lithium ion transport within solid-state electrode materials and at the interfaces of solid electrodes and liquid electrolyte dictates the battery performance. In batteries involving solid electrolyte (SE) materials, such as all-solid-state batteries where SE is used as a primary component or some future battery configurations (*e.g.* Li-S, Li-air, and redox flow batteries) where SE is the crucial protecting layer for lithium metal anodes, the ion transport within SE and at SE interfaces directly determines the rate capability and energy density for the battery. Three major types of SEs have been intensively studied: polymers, glasses, and crystalline electrolytes.[1,2] Polymer electrolytes offer the advantage of facile processability and flexibility over glassy or crystalline SEs, and thus are useful for flexible alkali batteries. However, their mechanical strength is relatively low and their chemical stability could be an issue at an elevated operation temperatures. In comparison, crystalline SEs are often more stable at high temperatures. They often show a desirable mechanical strength which could potentially prevent the growth of dendrites from high capacity anodes such as metallic Li or Na. This review mainly focuses on the crystalline SEs, while reviews on polymer and glassy materials can be found in earlier literature.[3-6]

Li^+ transport in crystalline solids is primarily based on mobile ions hopping among energetically favorable sites in a surrounding potential. The motion of the surrounding ions provides the activation energy for mobile ions to move through channels in the crystalline framework under an externally applied electrical field. The activation associated with the movement of ions within a crystalline lattice is often higher than that in liquid, and as a result, the ionic conductivity in SEs is generally lower. Owing to the concerted efforts from both experimentalists and theorists, designing superionics from the atomic scale is emerging, as several fast-conducting materials were recently discovered that exhibit ion conductivities comparable to those of organic liquid electrolytes.

Crystalline SEs of current interest can be broadly classified to three major categories: sulfides, oxides, and nitrides, each with different structural families. Sulfide-based SEs in the thio-LISICON (lithium superionic conductor) and argyrodite structural families received much attention in the past decades from the scientific community due to their enhanced room-temperature (RT) ionic conductivity and technologically viable Arrhenius activation energy when compared to other families of solid electrolytes. Generally, the total observed ionic conductivity displays an Arrhenius behavior according to the following relationship: $\sigma = \sigma_o \cdot e^{\frac{-E_a}{kT}}$, where σ_0 denotes the temperature-independent ionic conductivity of the film, k represents the Boltzmann constant, and E_a denotes the activation energy. A low Arrhenius activation energy ensures similar Li-ion diffusion over a wide temperature range. Prime examples of the thio-LISICON and argyrodite ion conductors include β-Li_3PS_4 (0.16 mS/cm at RT, E_a = 0.35 eV),[7-9] $Li_7P_3S_{11}$ (17 mS/cm at RT, E_a = 0.18 eV),[10] $Li_{10}GeP_2S_{12}$ (12 mS/cm at RT, E_a = 0.22-0.25 eV),[11,12] heat-treated Li_2S–P_2S_5 glass-ceramics (17 mS/cm at RT, E_a = 0.18 eV),[13] and Li_6PS_5Br (6.8 mS/cm at RT, E_a = 0.32 eV).[14] Oxide-based SEs, in comparison with sulfides, represent higher mechanical and chemical stability under ambient conditions. Oxide-based SEs fall into three main structural families: garnet, perovskite, and NASICON-like (sodium superionic conductor). Some prime examples of oxide-based ion conductors include tetragonal $Li_7La_3Zr_2O_{12}$ (0.11 mS/cm at RT, E_a = 0.41 eV),[15] $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$ (0.40 mS/cm at RT, E_a = 0.26 eV),[16] $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (0.7 mS/cm at RT, E_a = 0.20 – 0.35 eV),[17] and $Li_{3x}La_{2/3-x}TiO_3$ (10^{-2} – 1.0 mS/cm at RT, E_a = 0.26 – 0.40 eV).[18-20] Amongst the reported lithium nitrides, Li_3N holds the highest ionic conductivity (0.66 mS/cm at RT, E_a = 0.25 eV).[21] In terms of sodium ion conductors, the ionic conductivity of β-alumina ($NaAl_{11}O_{17}$) is amongst the highest (14 mS/cm at RT, E_a = 0.16 eV).[22]

The mass and charge transfer at solid-solid interfaces are complex yet performance-limiting for the electrochemical energy systems involving SEs.[1,23] In comparison to liquid/solid interfaces, ion transport through solid-solid interfaces are inherently different and often dictate the overall battery performance. Not only the structural heterogeneity, the chemical interfusion and the electrochemical stability, but the inherent space-charge layer, the potential discontinuous contact, and interfacial strain induced between the two adjacent materials before and during electrochemical cycling can also significantly influence the ion conduction at solid-solid interfaces. However, our fundamental understanding of mass transport and charge transfer at solid-solid interfaces is limited, hindering rational designs of interfaces with desirable ion conductivity and cycling stability. This limitation is partially due to the small number of *operando* or *in situ* studies of solid-solid interfaces at the atomic scale.[24-26]

Developing a precise understanding of ion transport behavior at solid-solid interfaces is challenging. Since solid-solid interfaces are often spatially confined and embedded, limited characterization techniques can clearly reveal the structural and chemical nature of interfaces at an adequate spatial resolution. Studying ion transport at ionic solid interfaces is equally challenging to theoretical calculations, as practical interfacial structure is often non-centrosymmetric and unpredictable. The strong interaction among charge carriers and between charge carriers and the lattice further complicates theoretical calculations. Nevertheless, recent rapid developments in characterization techniques and computations have brought unprecedented opportunities to investigate interfacial mass and charge transport behavior related to SEs down to the atomic scale. It is our intention in this review to highlight the fundamental understanding of ion transport and stability of SEs and their interfaces, by emphasizing recent atomic-scale insights gained through advanced characterization techniques such as electron microscopy and different spectroscopy-based methods. It should be noted that, in the past few years, several related reviews have emerged that discuss bulk solid-state ion conducting materials in general.[27-31,6,5,32-36,4] This review therefore focuses on the atomic-scale understanding and the design of SEs, especially their interfaces, towards optimized ionic conductivity and electrochemical stability, underlining the knowledge recently developed by the integration of high-resolution microscopy and spectroscopy characterization methods. Different strategies to improve ion conduction and stability in SEs and their interfaces are also discussed based on the atomic-scale insight offered by studies with superb spatial resolution. We conclude this review with future perspectives of interfaces associated with SEs and further developments needed in experimental approaches, which are anticipated to help bridge the gap between the fundamental understanding of different SEs and their performance.

Interfaces of solid electrolytes: critical challenges

Solid electrolytes, also known as solid-state superionic conductors, are characterized by high ionic conductivity and low electronic conductivity. In the last several decades, many fast ion conducting materials have been introduced in the literature, including oxide-based, sulfide-based, fluoride-ion, silver ion conductors, amongst others,[1] which have paved the way towards the development of new and improved technologies, including solid-state batteries,[1,37,38] Li-air batteries,[39] fuel cells,[40] sensors,[41,42] electrochromic devices,[43] and other important applications. More specifically, solid electrolytes are especially of interest for energy storage technologies where enhanced volumetric energy density is requisite, such as mobile electronic devices or electric vehicles.

Though several superionic conductors have been recently discovered, the ionic conductivity in most SEs is still lower than that of organic liquid electrolytes.[30,44] In particular, only a very few compounds show a room temperature ionic conductivity exceeding 10^{-4} S/cm,[30,44] presenting a number of limitations towards their practical applications. Another major concern associated to many current SEs is their ambient chemical stability. So far, sulfide-based lithium SEs have shown the highest Li^+ conductivities amongst solid-state materials at room temperature.[30] However, many of these compounds are extremely unstable under ambient atmospheres and such instability becomes one of the major hurdles for their practical applications. The discovery of new superionic conductors with sufficient ion conduction and desirable chemical stability is therefore crucial.

Perhaps the greatest challenge in the application of solid electrolytes is preserving low interfacial resistance at the electrode/SE and SE/SE interfaces.[25,45] High resistivity is often found at interfaces involving SE materials. Overcoming this challenge requires a clear understanding of complex interfacial phenomena at the atomic to microscopic scale in model SE-based systems as well as a reliable link between the atomic phenomena with macroscopic performance at these local features. Various interfaces are involved in batteries employing SEs, schematically illustrated in Fig. 1. SEs are often processed into membranes that are polycrystalline in nature and contain a high concentration of grain boundaries, where the grain boundary conductivity could significantly influence the overall bulk ionic conductivity. On the other hand, in many cases, a SE could be composed of multiple phases in the format of a composite or a lamellar layered structure in order to enhance the ion conductivity, mechanical stability, or chemical stability with electrodes; the interface between the two heterogeneous SE materials, therefore, becomes vital.[31,46] The most important and challenging interface associated with SE materials are those with electrodes. Due to the large dissimilarity in the structural, chemical, mechanical, electrochemical and electrical properties between SEs and electrodes, multiple interfacial mechanisms can be involved in the charge transport, such as chemical/electrochemical decomposition, elemental interfusion, structural deformation of the crystal lattice, and changes in the mechanical integrity.[45,47-57] These mechanisms can influence each other and may evolve during different stages of charging, complicating the analysis of interfaces with SEs. A fundamental understanding of which mechanisms are at play and how they influence each other is the key to develop descriptors of design for chemically stable and highly conductive SEs and their interfaces at the atomic to microscopic scale. In the following sections, we review and discuss some of the most recent advances in probing different interfaces with SEs at the atomic scale as well as strategies to improve ionic transport, chemical stability, and interfaces within systems involving SEs.

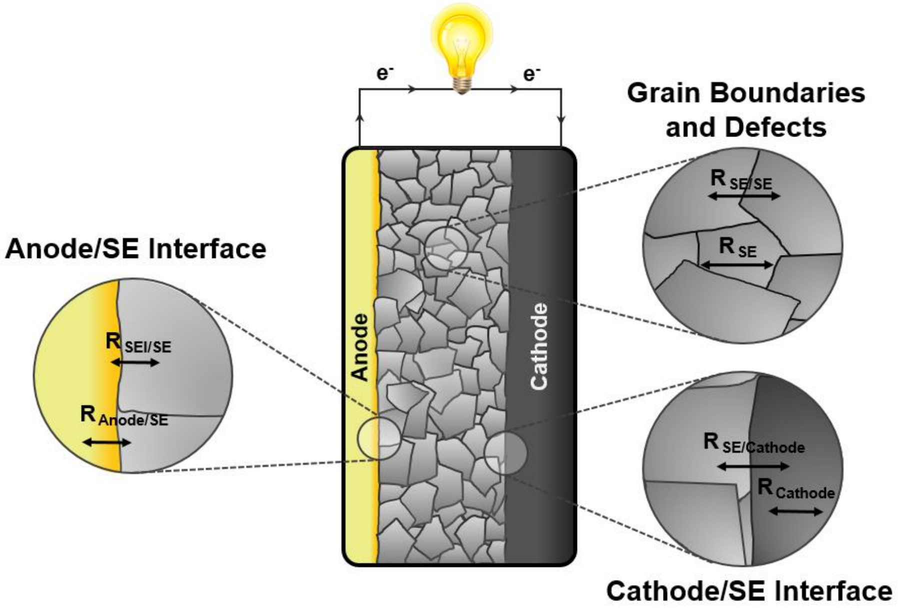

Fig. 1 Schematic configuration of a typical battery employing solid electrolyte (SE), detailing the different interfaces associated with SEs. Different interfaces within such batteries hold altered resistances, which change the overall performance of the battery.

Atomistic understanding of ion transport within solid electrolytes and at their interfaces

Limited characterization techniques exist for probing the atomistic mechanism of ion transport in solids and their interfaces. Conventionally, nuclear magnetic resonance (NMR) spectroscopy,[58-60,19,61] electrochemical impedance spectroscopy (EIS),[62-66] cyclic voltammetry (CV),[11,13,67] and scanning probe microscopy (SPM)[68,62] are broadly used and provide valuable averaged information of ion conduction in SEs, especially for buried solid-solid interfaces. However, directly probing the interfacial phenomena at the atomic scale or at individual interfaces using these methods is challenging, largely due to the scarcity of techniques that can probe these confined interfaces. Here, we mainly focus on the recent insights gained from different characterization techniques that have broadened the overall understanding of conductivity and stability of interfaces with a sufficient spatial resolution. In particular, we discuss knowledge recently gained by state-of-art transmission electron microscopy (TEM). Other techniques, such as X-ray photoelectron spectroscopy (XPS), that has been used to probe interfaces involving solid electrolytes, and provided complementary information to TEM, will also be discussed.

Grain boundaries within solid electrolytes

Grain boundaries in polycrystalline materials represent a critical feature influencing their overall mechanical, thermal, and conducting properties. From the microscopic perspective of SEs, the grain boundary (GB) characterizes structural and chemical discontinuity, which can significantly influence the ion conductivity of the SE. In fact, many current ion conductors show high GB resistivity with a 2-3 orders of magnitude higher than grain interior. The GB resistance is recognized in the literature, yet the exact structural and chemical origins of large GB resistance for a number of classes of SEs are unknown.[20,69-73] Understanding the origin of high GB resistivity in these materials is crucial, but challenging. Many of these GBs are confined to nanoscale lengths, and in some cases, these interfaces consist of only a few unit cells.

A recent microscopy study demonstrates the power of atomic resolution electron microscopy imaging and electron energy loss spectroscopy (EELS) towards a clear understanding of grain boundary resistance at atomic scale.[74] Atomic-scale analysis of $(Li_{3x}La_{2/3-x})TiO_3$ (LLTO) GBs revealed different atomic arrangements for the boundary when compared to the grain interior. Fig. 2a shows a high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of LLTO, displaying the alternative stacking of the La-rich and La-poor A-site layers, a feature exhibited by most LLTO materials.[74-76,18] Fig. 2b displays a representative HAADF-STEM image of a LLTO GB, where two different variations of GB structure: the majority of GBs showing darker contrast in HAADF-STEM images (labeled as Type I), and some of the GBs showing a limited feature with a relatively reduced contrast difference across the GB (labeled as Type II). Type II GBs are often terminated with La-rich atomic layers at the GBs that are deficient in mobile carriers and vacancies, which do not permit fast ion conduction. In Type I GBs, increased chemical deficiencies in both La^{3+} and Li^{+} were observed, resulting in a binary Ti-O layer of 2-3 unit cells at the GB core (Fig. 2c). This feature is not energetically preferred for Li$^+$ transport, which presents higher GB resistivity. Further calculations based on the Nudged Elastic Band method revealed a lower formation energy of such grain boundaries and the traditional vacancy migration mechanism does not work.[77] Such atomic scale microscopy and theoretical studies not only allow for a mechanistic understanding of the GB resistance in SEs, but also point out potential grain boundary modifications that could deliver fast ion conduction.

Here, we would like to emphasize that the origin of high GB resistivity in different types of SEs vary and further characterizations are necessary to develop a general understanding for ion conduction across GBs.[25,78] A universal strategy, equivalent to the criteria of designing fast ion conduction at the unit cell level, must be developed. Although it is a general phenomenon of highly resistive GBs in crystalline ion conductors, garnet structured oxides, *e.g.* $Li_7La_3Zr_2O_{12}$ (LLZO), is an exception. It gives an acceptable GB conductivity which is comparable to that of the grain, while the exact reason is not clear.[79-84] Such conductive GBs deserve special research attention in order to develop strategies towards the design of grain boundaries with high ionic conductivity and cyclability.

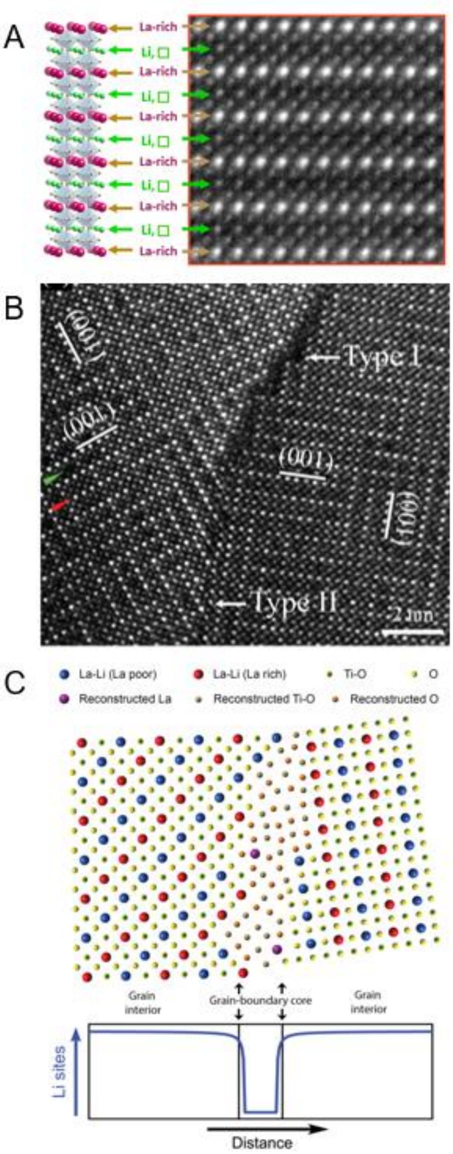

Fig. 2 A) HAADF-STEM image of LLTO, with a schematic showing the La and Li rich layers. B) HAADF-STEM image of an LLTO GB, with green and red arrows displaying the La-rich and La-poor layers, respectively. C) Schematic illustration of the Type I GB based on HAADF-STEM images and EELS analysis, depicting a Li-depleted GB.[74] Reprinted with permission; © 2014 Royal Society of Chemistry.

Ion conduction at the anode/SE interface

The lithium/SE interface represents the most important interface in SE-involving batteries, given the fact that enabling the use of metallic lithium theoretically delivers the highest theoretical capacity (3860 mAh g^{-1}).[85-88] However, as heterogeneous interfaces that are composed of materials with highly dissimilar mobile ion concentrations and chemical potentials, Li/SE interfaces are much more complex than grain boundaries in SEs. In addition to the structural and chemical discontinuity, the space charge, the potential chemical and electrochemical instability, and mechanical integrity all play important roles in determining the ion conduction at Li/SE interfaces.[89-95,50,96,97] High-throughput modeling of interfaces between SEs and the different anode materials is expected to play a critical role in evaluating the thermodynamics of the interfacial electrochemical and chemical stability. To evaluate the interfacial stability, the electrochemical stability of the electrolyte is first evaluated by introducing the Li chemical potentials (μ_{Li}) observed at the anode. The model is then extended to allow for any interfacial reactions to occur. In many of these calculations, the anodic stability window was largely correlated with the related binary system from decomposition products. For example, the anodic stability of $Li_{10}GeP_2S_{12}$ was related with the stability of Li_2S with metallic lithium anode, and since lithium is removed from the electrolyte during the simulation, a Li_nX (n = 1, 2, 3, X = anion) forms as a decomposition product at the interface while the energy of mixing causes other elements to react with the binary.[46] Most of these calculations take into account of the stability of the polyanion matrix, where more energy is required to dissociate stronger polyanion bonds, yet some of these calculations do not match the electrochemical window achieved experimentally for some SEs, such as LiPON, Li_3PS_4, and Li_3PO_4.[37,7,98] From these simulations, passivation layers are expected to form at many SE/Li interfaces. The formation of an ionically conductive while electrically insulating decomposition layer is expected to prevent further interfacial decomposition and therefore create a stable SE/Li interface.

Although the thermodynamics sets the boundary for stability at the Li/SE interfaces, it must be mentioned that other important factors, such as the reaction kinetics, diffusion, and space charge, can also play crucial roles in determining interfacial structure and chemistry. Current theoretical approaches, however, cannot take all these competing interfacial mechanisms simultaneously into consideration and urgently request experimental input and proof. Very recently, several reports have shown the promise of investigating Li/SE interfacial phenomena experimentally with decent spatial resolutions, such as using *in situ* S/TEM or XPS.[99-102]

A recent *in situ* STEM experiment shows that benign phase transformations could happen at SE/Li interfaces, which could bridge the gap of electrochemical windows between lithium metal and SE therefore stabilize the interface. A good example was discovered in cubic $Li_{7-3x}Al_xLa_3Zr_2O_{12}$

(c-LLZO), a promising solid electrolyte material with attractive ion conductivity and a high shear modulus that could potentially prevent the growth of Li dendrites.[99] Cubic LLZO was theoretically predicted to have a reduction potential of 0.05V, indicating the decomposition while being contacted with Li metal. Electrochemical testing, however, often reveals a relatively reasonable interfacial stability, and the reason for this inconsistency was previously unclear.[103-105] Using a unique *in situ* STEM setup, the interfacial mystery was solved. Fig. 3 shows results from the first STEM study of the interfacial phenomena between cubic c-LLZO and metallic lithium anode at the atomic scale.[99] EELS analysis reveals that a localized phase transition occurs at the Li/c-LLZO interface, which was found to be ~5 unit cells thick (Fig. 3c,d). This phase transition was attributed to the simultaneous implantation of lithium ions and electrons, which induced a self-limiting stable interfacial phase transformation from cubic to a tetragonal-like structure. This interphase effectively prevented further interfacial reactions without compromising the ionic conductivity and the structural compatibility, promising greater stability and conductivity across critical interfaces for Li-metal batteries. Such passivation layers are electrochemically preferred when compared to those of chemical decomposition where the multiple reactant phases may potentially introduce inhomogeneous current distributions at the interface upon electrochemical cycling. Therefore, the intrinsic phase transformations in materials may be used as one strategy to enable the formation of stable and conductive interfaces leading to safe and high-performance batteries.

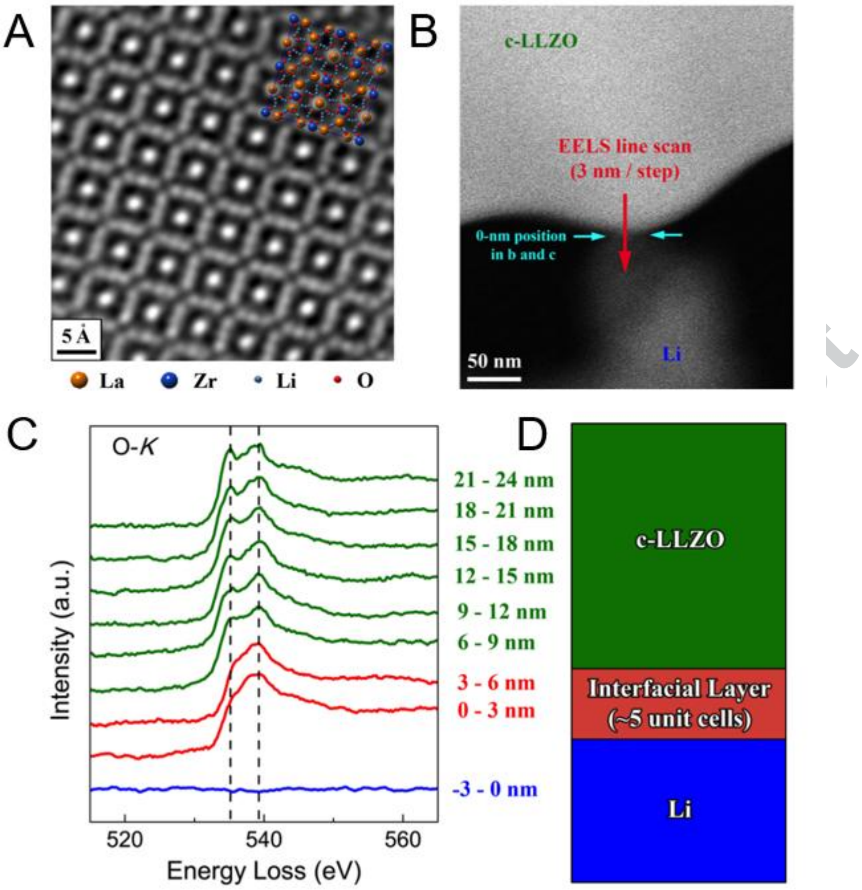

Fig. 3 A) High-resolution HAADF-STEM image of the cubic LLZO specimen. B) HAADF-STEM image of LLZO in contact with a metallic lithium anode. C) O *K*-edges acquired in the EELS scan from (B). D) Schematic of the behavior at the Li/LLZO interface.[106] Reprinted with permission; © 2016 American Chemical Society.

In situ XPS investigations have recently reported possible decomposition reactions at the anode/SE interface.[100,107,108] This technique has a number of advantages, including the surface and elemental sensitivity, the ability to detect light elements such as Li, and the ability to ascertain chemical bonding information. Different ion conductors, such as LiPON,[102] LLTO,[100] NASICON-like,[109,110] and LISICON-like SEs,[107,111] have been explored using XPS to determine the local structures and the possible decomposition product when placed in contact with metallic lithium or sodium anodes. Wenzel *et al.* recently reported the reaction between lithium metal and $Li_{10}GeP_2S_{12}$

(LGPS) with nanometer resolution, highlighting the formation of a clear interphase layer.[107] Using a unique stage for sequential Li deposition and XPS data acquisition,[100] the S2p, Ge3d, and P2p spectra were collected while 31 nm of metallic lithium was deposited on the surface of a LGPS pellet. As the reaction progressed, the XPS displayed a clear change in the oxidation state of Ge and the formation of Li_3P and Li_2S. These results are in good agreement with theoretical studies and also explain the increased interfacial resistance at the Li/LGPS interface over time.[46] Similar XPS approaches were recently applied in the study of Li/LiPON interfaces.[102] These studies found that a chemical reaction also occurs at Li/LIPON interface, leading to the decomposition into smaller units like Li_3PO_4, Li_3P, Li_3N, and Li_2O. Since LiPON has been shown to have good cycling stability with lithium metal anode,[37,38,112] these XPS results suggest that the interface reactions are not continuous, but quickly vanish due to the formation of a suitable passivation layers. However, because of the limited depth resolution and the increased signal from continuous Li deposition on the SE surface, this method cannot determine the exact thickness or morphology of the interphase layers for LiPON. Probing the dynamic evolution of interphase layer upon *in situ* electrochemical cycling is also challenging with XPS. Therefore, high resolution *in situ* techniques, such as S/TEM, are needed to further determine the equilibrium thickness and the cyclability of the interphase layers. Further studies that link *in situ* XPS and S/TEM results are anticipated to provide valuable insights into the chemistry, morphology, and electronic structure of the anode/SE interface.

Ion conduction at the cathode/SE interface

Multiple interfacial phenomena are expected between cathodes and SEs. For example, at the interface between Li_2S-P_2S_5 and $LiCoO_2$ (LCO) cathode, HAADF-STEM imaging with energy-dispersive x-ray spectroscopy (EDS) highlight the interdiffusion and decomposition layers (Fig. 4a)[113]; theory predicts that sulfides tend to decompose to Co_9S_8, Li_2SO_4, and Li_3PO_4, resulting in high interfacial resistance.[114] To overcome this limitation, artificial passivation layers between the SE and cathode are expected to ensure better long-term cycling performance. Artificial passivation layers hold two separate interfaces, one with SE and one with the cathode material, and calculations detailing the decomposition products at these respective interfaces show that only a few nanometers of materials are necessary to protect the cathode and SE from chemical or electrochemical reactions. Applying an interlayer, such as LiPON, Li_3PO_4, $LiSiO_3$, $LiNbO_3$, $Li_4Ti_5O_{12}$, and $LiTaO_3$, between the SE and cathode bridges the electrochemical window at the SE/cathode interface,[115-122] Space-charge effects at the cathode/SE interface were also recently studied by theoretical calculations. By using DFT + U calculations coupled with interface matching, the potential scheme across interfaces of LCO/LPS and LCO/LNO/LPS (Fig. 4) was compared.[123] The LCO/LPS interface forms Li adsorption sites and its atomic structure is rather disordered. When a LNO buffer layer was inserted between the LCO and LPS layers, Li adsorption space and Li inhomogeneity were effectively suppressed leading to an improved interface on the basis of potential variation and structural distortions, leading to enhanced Li transport across the interface. These results provide useful guidance for the design of conductive cathode/SE interfaces at the atomic scale.

Still, experimental investigations probing cathode/SE interfaces using high-resolution imaging and spectroscopy are very limited. STEM, EDS, and nano-electron diffraction were previously utilized to observe the interface between LLZO and a LCO cathode, and an interfacial buffer layer of about 50 nm thick that contained La_2CO_4 was discovered.[90]. Similar studies were also applied to the interface between Li_2S-P_2S_5 and $LiMn_2O_4$.[124] Figure 5 displays recent work detailing the interface between $Li_{10}GeP_2S_{12}$ (LGPS) and c-$LiCoO_2$.[125] The capacity was found to significantly decay as the In/LGPS/c-$LiCoO_2$ cell cycled at 0.1 C. Further investigation by ADF-STEM imaging and EELS shows that significant Co interdiffusion occurs are the interface between LGPS and c- $LiCoO_2$ (Fig. 5C), which agrees with mutual elemental diffusion as predicted by computation.[126] The degradation at the cathode/SE interface is shown schematically in Fig. 5D where three possible situations are expected to occur. In Situation I (the ideal case), LGPS maintains intimate contact with c-$LiCoO_2$ and there is minimal decomposition of LGPS; here, it is important to note that Li^+ can be transferred reversibly between the SE and the cathode material. In Situation II, LGPS loses contact with c-$LiCoO_2$ at high voltages due to volume change and inhomogeneous mixing during the cathode preparation.[127] Such loss in interfacial contact will prohibit Li^+ migration and will lead to capacity fade in the battery performance as well as a non-uniform current distribution at the LGPS/c-$LiCoO_2$ interface. In situation III, LGPS completely decomposes at high voltages and forms a Li^+ depletion zone. This depletion zone will not only contribute to an overall higher internal resistance at the SE/cathode interface, but is also allow for electronic flow across the cathode/SE interface. Such electronic flow will further oxidize the SE and cause more severe capacity fade in the battery. Similiar depletion zone in $LiCoO_2$ was also observed by Nomura *et al* using $Li_{1+x+y}Al_x(Ti, Ge)_{2-x}Si_yP_{3-y}O_{12}$ (LASGTP) as the solid electrolyte.[128] In this study, *in situ* STEM and EELS combined with hyperspectral image analysis of non-negative matrix factorization (NMF) was used to resolve the evolution of Li^+ distribution under an external bias. The $LiCoO_2$ film of about 10-20 nm near the LASGTP/c-$LiCoO_2$ interface was found to be electrochemically inactive, which could be one of the reasons for high interfacial resistance in full batteries.

In addition to the chemistry and structure at interfaces, another important feature that is critical to the understanding of interfacial phenomena is the local electric potential. The local electric potential at electrolyte and electrode interfaces is currently unknown, and measuring it experimentally is extremely challenging. It requests not only a sufficient spatial resolution, a good sensitivity to bulk potential detection, and a reasonable temporal resolution. Electron holography has been demonstrated to map the electric potential at the interface of Pt/LASGTP.[129] This work illustrates the dynamic potential change in solid electrolyte as a function of biasing. However, the cyclability of the nanodevice and the spatial resolution of electron holography, in some cases, are limited to nanometer resolution. As a result, detailed charge distribution, such as that caused by the space charge effect, was not resolved. Further developments related to *in situ*/*operando* electron microscopy techniques are needed to enable to the full resolution of holography or differential phase contrast in order to better reveal charge distribution at interfaces.[130-133] These works provide valuable insights into the origin of unknown high resistivity at the interfaces between cathode and electrolyte, and demonstrated the rich information provided by using *in situ* S/TEM imaging combined with spatially resolved EELS analysis. Collectively, previous studies reveal that elemental inter-diffusion often occurs during the fabrication of SE/cathode interfaces, leading to an increase in charge-transfer resistance. As some form of thermal annealing is necessary to form crystalline phases and dense interfaces, these results pinpoint that lowering crystallization temperatures of Li^+ ion conductors, especially of solid electrolytes, represents the future task in optimizing and designing new fast ion conducting solid electrolytes.

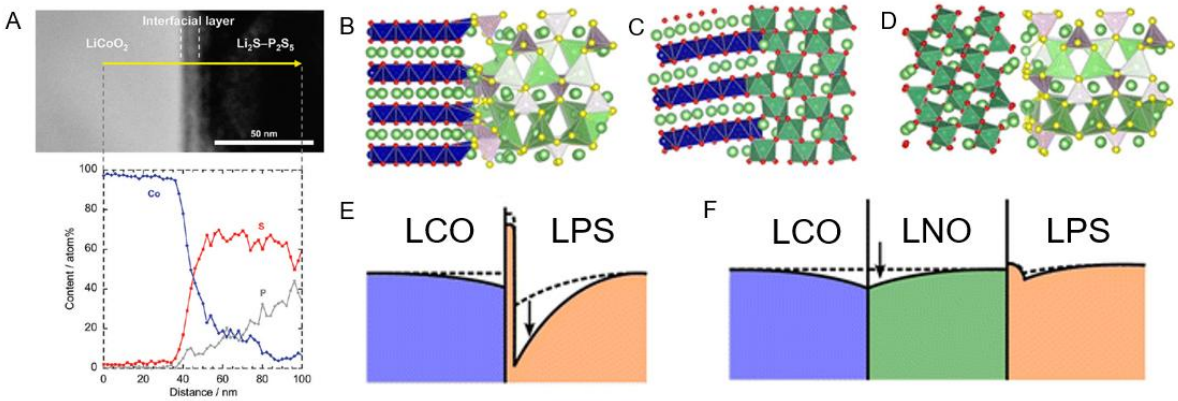

Fig. 4 A) HAADF-STEM image of the $LiCoO_2$-Li_2S-P_2S_5 interface and EDS line profile, highlighting the interdiffusion at the solid-solid interface.[113] Reprinted with permission; © 2009 American Chemical Society. Calculated interface structures between B) LCO(110)/ LPS(010) C) LCO(110)/ LNO(1$\bar{1}$0) D) LNO (1$\bar{1}$0)/LPS(010). Schematics in E) and F) describe the lithium concentration change at the initial stage of charging for the LCO/LPS and LCO/LNO/LPS interfaces, respectively.[123] Reprinted with permission; © 2014 American Chemical Society.

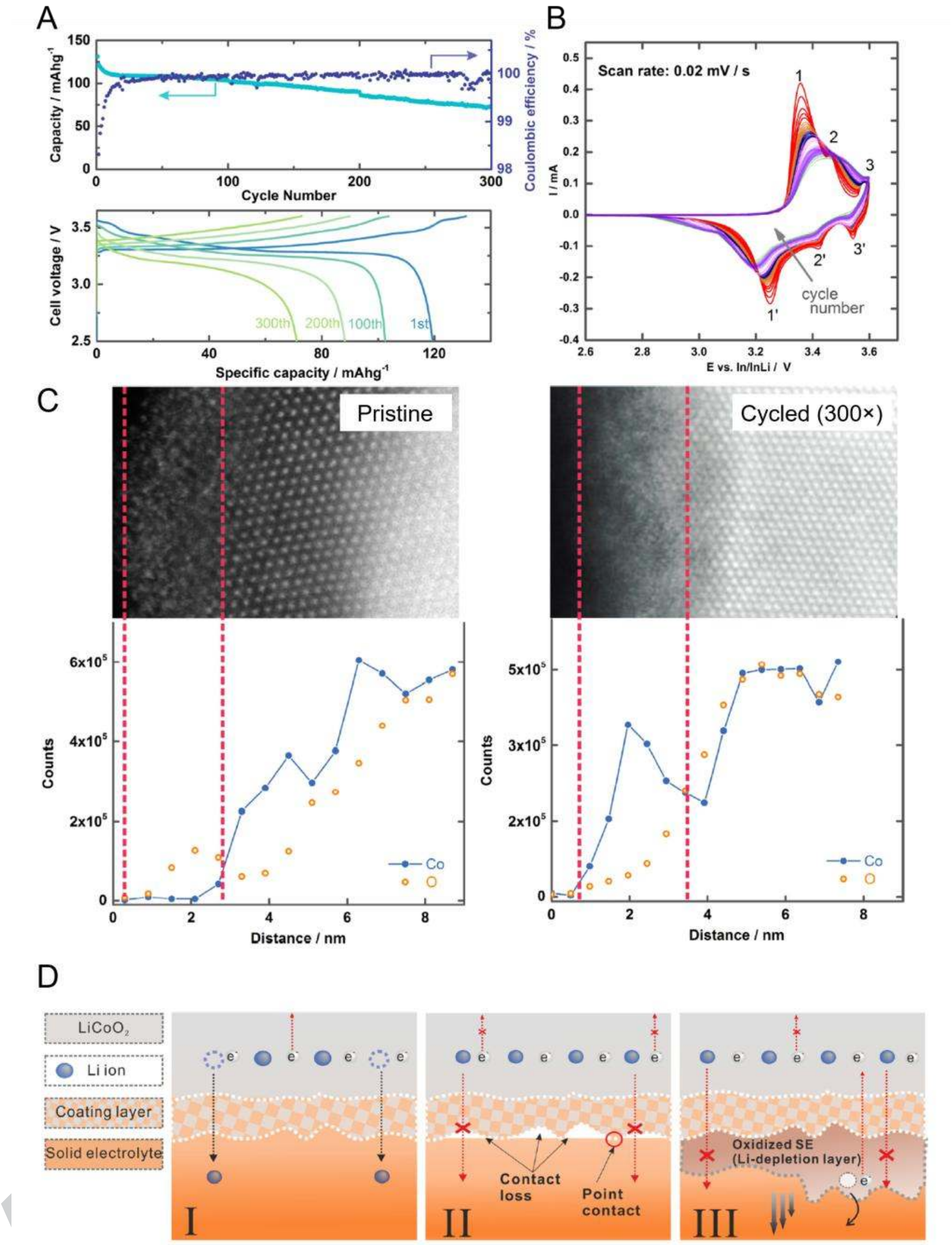

Figure 5. A) Capacity fading and increase in the overpotential of an In/LGPS/c-LiCoO$_2$ cell at 0.1 C. B) Change in the cyclic voltammogram as a function of cycle number. C) High-resolution ADF-STEM images of the pristine and cycled c-LiCoO$_2$ along the [211] zone axis, together with the corresponding EELS line scans. The Co signal at the coating layer was significantly increased after 300 cycles. D) Schematic model for three situations that could potentially occur at the LGPS/c-LiCoO$_2$ interface: I) ideal case where LGPS maintains intimate contact with c-LiCoO$_2$ and there is little-to-no decomposition of LGPS; II) Loss of contact at the LGPS/c-LiCoO$_2$ interface at high

voltages; III) Decomposition of LGPS at high voltage and the formation of a Li^+ depletion zone.[125] Reprinted with permission; © 2018 American Chemical Society.

The above-discussed experimental and theoretical approaches have and will continue to provide invaluable insights of atomistic understanding of the structure, chemistry, and even their evolution at different interfaces associated with SEs. The thickness of the interfacial layers, depending on the nature of the two comprising materials and formation methods, can range from sub-nanometer to hundreds of nanometers or even microns. Characterization techniques that offer moderate spatial resolutions can also play an important role. For example, using newly-developed SPM approaches, such as electrochemical strain microscopy (ESM), allow for the relationship between Li-ion flow and microstructure in Si/LiPON/$LiCoO_2$ thin-film batteries.[63,62] Depth-resolved X-ray absorption spectroscopy **(**XAS) can be used to interrogate interfacial phenomena with a resolution of several nanometers, as demonstrated in a recently published work, where the chemical and electronic structure and the identification of decomposition products at the LATP/LCO interface was performed.[134] *In situ* Raman scattering experiments can also be used to study dynamic interfacial structural evolution where the ionic framework breaks and reforms at the SE/electrode interface during lithium deposition and stripping.[135] Small angle neutron scattering was also used to study the nanostructures formed within SE and at the SE/electrode interfaces, by which the size, morphology, and evolution of the nanostructure can be revealed.[136] [137] Linking these microscopic phenomena to their macroscopic performance will significantly benefit the mechanistic understanding of SEs and their associated interfaces.

Strategies to improve ionic transport and chemical stability of interfaces associated with solid electrolytes

Depending on the nature of the two adjacent materials and the utilized fabrication method to create the interface, the structure and performance of interfaces as well as the ion conduction mechanism across interfaces may vary among material systems. While the exact interfacial phenomena and their influence on ion transport behavior are still not clear, various methods to tune interfaces associated with SEs have been reported, and in some cases, show enhanced interfacial performance. Previous research results can aid in developing a fundamental understanding of interfacial ion and charge transport at SE interfaces. In this section, we review recent reports on strategies used to enhance ion conduction of interfaces and boundaries involving SEs while highlighting insights from S/TEM.

Tuning ion conduction within solid electrolytes by utilizing domain structures

Designing highly conductive superionic solids based on the unit cell level can essentially be achieved in the near future by the rapid developing high-throughput computations. Still, at the microscopic or macroscopic level, attention has been directed at overcoming the high resistivity associated with grain boundaries, interfaces, or impurity phases. In order to design solids with high ionic conductivity, features at different length scales, which could contribute to enhancing the overall ionic conductivity, must all be considered and explored. A recent microscopy study showed that mesoscale features, such as domain structures, could be used to maximize ion percolation pathways, resulting in enhanced ionic conductivity in solid electrolytes. The size of the 45° domains in LLTO was recently found to be tunable through varying post-synthesis annealing conditions, while the size of domains can directly modify the ionic conductivity in bulk LLTO. Fig. 6 shows the mesoscopic domain structure in LLTO that was discovered to highly enhance the ionic conductivity.[138] Such a mesoscopic domain structure (with a domain size of 2-3 unit cells) integrates the advantages of ordered unit cell structures, fast conduction domain boundaries and three-dimensional domain configurations, significantly boosting ion percolation pathways and resulting in enhanced ionic conductivity. Sophisticated molecular dynamics (MD) simulations further demonstrate the advantage of integrating small domains to the ion conduction in this material (Fig. 6e). This work provides insight into the design of fast ion conductors beyond the unit cell scale. It should be noted that the mesoscopic scale is rarely explored for SEs and necessitates future research for such features to be better understood.[139-141]

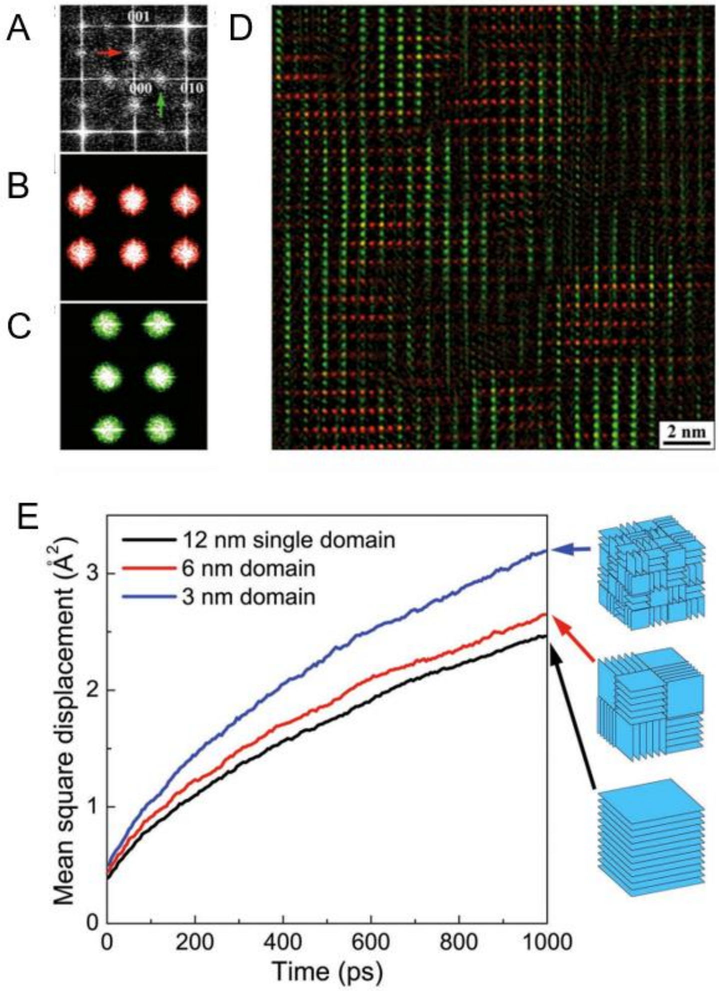

Fig. 6 A) FFT pattern of LLTO with representative 1/2(eeo) and 1/2(eoe) spots donated with red and green arrows, respectively. B) Masked FFT pattern in (A), showing only 1/2(eeo) spots. C) Masked FFT pattern in (A), showing only 1/2(eoe) spots. D) Reconstructed atomic-resolution image by overlapping the inverse FFT in (B) and (C), displaying a clear mesoscopic framework. E) Molecular dynamics simulation of LLTO with different domain sizes, revealing that domain size affects the mobility of the mobile ion.[138] Reprinted with permission; © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Tuning ion conduction within solid electrolytes by forming composites

Beyond individual phases, forming nanocomposites between an ion conductor and an insoluble second phase represents another potential strategy to enhance ion conduction and stability of SEs. This approach takes advantage of the possibility to control the rich interfacial phenomena, such as the formation of fast conducting interfacial phase, possibly enhanced ion conduction along the interfacial core, or improved charge carrier concentration through the design of space-charge layer.[142-151] An enhanced lithium ion conductivity has been experimentally observed in several recently explored SE nanocomposites, such as those between β-Li_3PS_4 and oxide fillers, yet the exact mechanism(s) responsible to each case is not known.[152-155]

The formation of polymer/ceramic nanocomposite electrolytes have recently gained increased attention for their enhanced cyclability and mechanical flexibility.[156,157,3,158-164] Inorganic ceramic SEs provide higher ionic conductivity and can potentially suppress Li dendrite growth.[165,166] However, ceramic SEs are often brittle, therefore the fabrication of ultrathin films of SEs becomes increasingly challenging. Forming composites with polymers has been previously demonstrated to enhance the mechanical flexibility of SE membranes.[160,58,167-169] Enhancing ionic conductivity in such composite materials largely relies on facilitating ion transport across and along the interfaces between ceramic and polymer. However, the overall knowledge with respect to ion transport mechanisms at such interfaces is largely inadequate and require a closer examination, especially at the nanoscale. A recent NMR study demonstrated that lithium ions do not diffuse across or along the interfaces in PEO-LLZO nanocomposites.[58] Instead, the mobile ions were found to prefer conduction pathways through either polymer or ceramics.[58] This work highlights the importance of developing a clear understanding of mass and charge transport behavior at ceramic-polymer interfaces in order to improve the design principles for composites with high ionic conductivity. Advances in electron microscopy will be critical for interrogating the interface between ceramic-based SEs and electron-beam-sensitive polymers at the atomic scale since cryo-TEM-based techniques, widely applied to study structural biology, help to mitigate beam damage[170-172] in both organic materials like proteins, small molecules, and cells and in battery materials.[173-175] These methods, with some modification, are expected to allow for atomic-scale interrogation of hard-soft interfaces in next-generation composite SEs.

Forming conductive and stable electrode/SE interfaces via the consideration of compatibility

In order to enable the use of metallic lithium, a conductive Li/SE interface that is stable before and during electrochemical cycling is requisite. While nearly all existing SEs are predicted to hold instability with lithium anode, some show decent cycling ability, such as in LiPON, β-Li_3PS_4, LLZO, $Li_7P_2S_8I$, amongst others.[37,7,67] This compatibility can be attributed to the formation of a self-forming passivation layer while the SEs are contacted with metallic lithium. These passivation layers must be ionic conductive while electrically insulating. Ideally, the thickness of the layer needs to be small such that the interface remains highly conductive. The thickness of the interphase layer is defined by the nature of the self-forming products, the reduction voltage of SE vs. Li/Li^+, and the processing method used to form the interface. The interphase thickness therefore varies significantly in different SE systems. For example, the passivation layer at the Li/c-LLZO interface is around 6 nm, as elucidated by S/TEM, while it was reported to be ~50 μm at the Li/Li_2OHCl interface, as elucidated by scanning electron microscopy.[99,176] Two major formation mechanisms have been reported. One is the phase transformation as in the case of the Li/c-LLZO interface that was discussed earlier,[99] and the other one is the interfacial reaction between SE and Li induced by electrochemical instability, as in LiPON and Li_2OHCl.[102,176] A self-forming interphase layer of ~50 μm was discovered at the interface of the metallic lithium anode and Li_2OHCl. After cycling in a symmetric cell configuration at 195 °C using a current density of 1.0 mA/cm^2, the SE membrane was able to cycle without a significant increase in the interfacial resistance. Though these self-forming passivation layers have been proposed in multiple SE materials, their exact nature, *e.g.* phase(s), distribution, and thickness, as well as their evolution during electrochemical cycling is not yet been clearly understood.[50,114,177,46] *In situ* electron microscopy and spectroscopy are expected to provide enhanced structural, chemical, elemental, and morphological insight with regards to the formation mechanism of interfacial layers between SEs and electrodes.

Reducing charge-transfer resistance at the electrode/SE interface through interfacial thermal treatments

Ion conduction at interfaces is largely determined by the interfacial chemistry and structure. Surface or interface treatments, such as chemical or thermal treatments, atomic facets or atomic termination selections, are expected to tune ion conduction at the electrode/SE interfaces. Reports detailing interfacial treatment are continuing to rise in the literature, though many conclusions are rather speculative as to how thermal treatments affect the surface of the solid electrolyte. For example, several groups have heated the Li/SE interface and show that this treatment improves the lithium wetting.[178,179] This method necessitates solids with thermal stability past the melting point of lithium metal (>180 °C). Sharafi *et al.* studied the charge transport across the Li/LLZO interface by treating Li/LLZO/Li symmetric cells at 175 °C, just below the melting point of metallic lithium.[180] Fig. 7a shows the Nyquist plots of Li/LLZO/Li symmetric cells at room temperature before and after treating the Li/LLZO interface at 175 °C, where the interfacial resistance across Li/LLZO was found to undergo a > 10-fold decrease due to an improvement in the lithium wetting. Additionally, the performance of thermally-treated Li/LLZO/Li cells showed significant differences in the critical current density (CCD) when cycled at 30 and 160 °C, and the interfacial Li/LLZO charge-transfer resistance was found to decrease with increasing temperature (Fig. 7b), similar to previous reports on sodium-ion conductors.[181,182] This and more recent work[183] have shown that thermal treatment improves the lithium wetting at the Li/SE interface, thereby reducing the charge-transfer resistance. Still, the interface between the SE and the anode needs further interrogation at the atomic scale in order to better understand the nature of lithium wetting at the Li/SE interface.

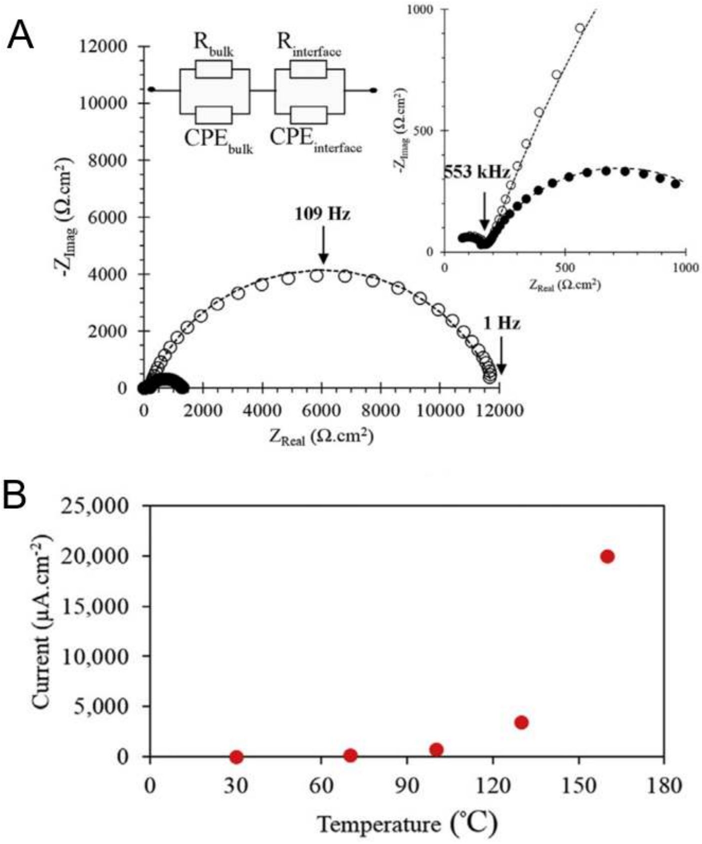

Fig. 7 A) Nyquist plots for a representative Li/LLZO/Li cell at room temperature before (∘) and after (•) conditioning the Li/LLZO interface at 175 °C. B) Critical current density for the Li/LLZO interface when cycling symmetric cells at different temperatures.[180] Reprinted with permission; © 2016 Elsevier.

Insertion of a thin third phase in between the solid electrolyte and electrode

More recently, the improvement of the SE/electrode interfacial ionic conductivity and stability have been intensively investigated by deliberately inserting an ultrathin third phase in between the SE and electrode. The main goal of these passivation layers is to reduce the charge-transfer resistance at the interface, extend the electrochemical window, and improve the wettability between the SE and the electrode material. Based on the nature of the SE/electrode interface, different types of materials, such as oxides, polymers, or even metals, have been studied.[1] The fabrication of ultrathin passivation layers at the interface between SEs and electrodes can be achieved by using different thin film techniques, including radio frequency (RF) magnetron sputtering,[184-186] pulsed laser deposition (PLD),[115,187,188] atomic layer deposition (ALD),[189,121,190,191] chemical vapor deposition (CVD),[192] vacuum evaporation,[193,194] sol-gel methods,[113] and coating polymers or different ceramics using hot pressing or wet chemical methods.[195-197] Though a general principles detailing the selection of effective interphase materials is still missing, several recent reports provide valuable insights of potential strategies, such as adding a passivation or a wetting layer, or a layer which can tune the space-charge scheme across the SE/electrode interfaces.

A recent example of the combination of these ideal properties was shown by Han *et al.*, where a thin Al_2O_3 interlayer was grown by ALD on the garnet-based $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$, enabling enhanced wetting of metallic lithium with the garnet electrolyte surface (Fig. 8).[189] TEM examination with EELS of the Al_2O_3 interlayer confirmed the thickness, morphology, and elemental distribution across the $Al_2O_3/Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ interface, as well as the existence of Al in pores of the SE. The thin Al_2O_3 layer enhanced charge transfer between a lithium anode, as evidenced by both EIS and symmetric cell cycling experiments that tested the lithium stripping and plating at the interface. At a current density of 0.2 mS/cm^2, the materials were able to cycle well when the thin Al_2O_3 interlayer was present, agreeing with reports of sodiated and lithiated Al_2O_3.[198-201] Other recent reports of improving the lithium wetting have also shown the enhancing cycling performance of SEs with metallic lithium anodes.[202,192,190,66,203] It is expected that similar ALD methodology will allow for careful tuning of the interfacial chemistry with different SEs. In addition, other materials, such as LiPON or Ge, have also been used as passivation layers to improve charge-transfer resistance at electrolyte-electrode interfaces.[114,185,115] *In situ* and *ex situ* S/TEM evaluations of interlayers are expected to provide crucial atomistic and morphological insight with regards to the impact of interlayers on battery performance.

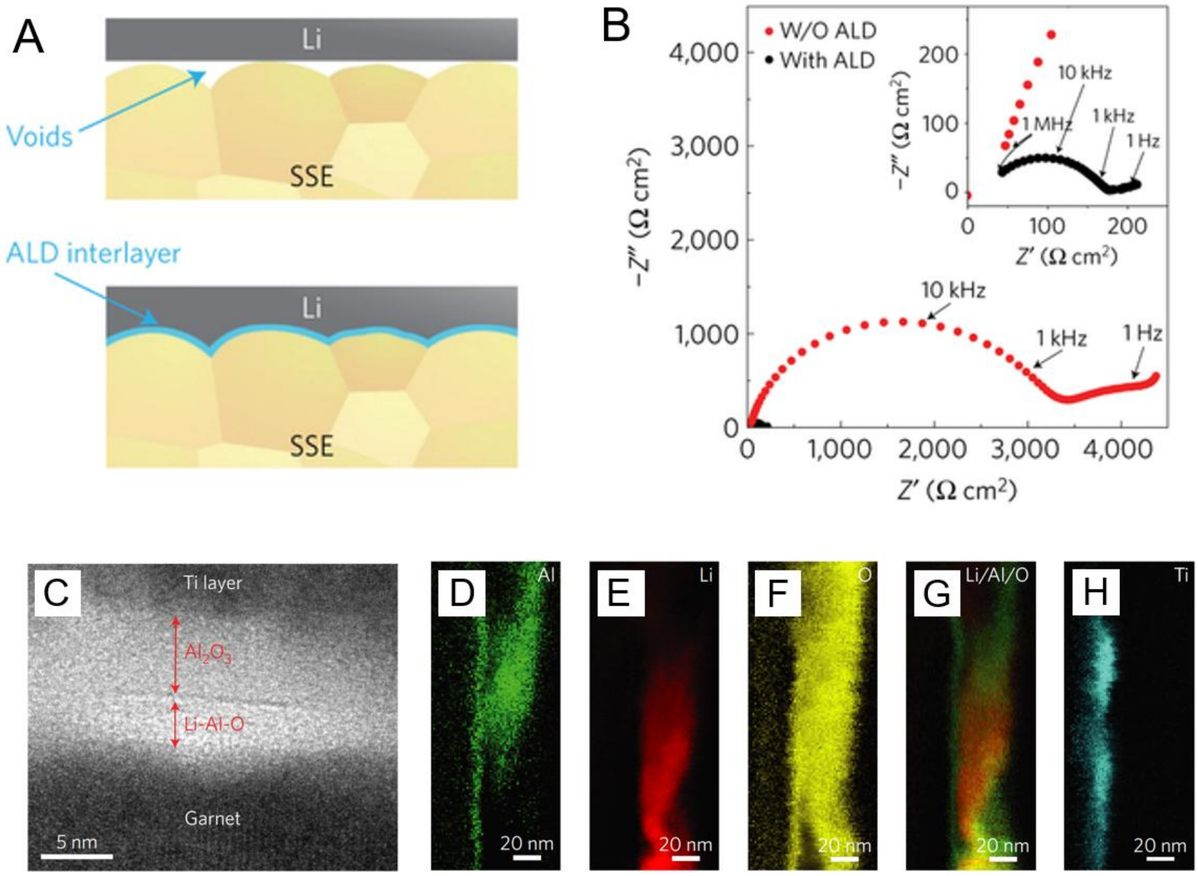

Fig. 8 A) Illustration of the metallic lithium wetting behavior on a garnet-based solid-state electrolyte with and without an Al_2O_3 layer deposited by ALD. B) EIS profiles of symmetric Li non-blocking garnet cells with and without an Al_2O_3 layer deposited by ALD.[189] C) Typical TEM cross section of the Al_2O_3-coated garnet; EELS maps for D) Al, E) Li, F) O, G) Li/Al/O, and H) Ti at the cross section of the Al_2O_3-coated garnet. Reprinted with permission; © 2017 Nature Publishing Group.

Inserting an interphase layer to modify the interfacial potential drop was demonstrated to be effective to enhance charge transfer across interfaces where space-charge effect dominates. As discussed earlier, juxtaposing an LNO layer between LPS/LCO smoothed the interface in both structure and electric potential.[123] This work not only highlights the important of considering the space-charge effect into ion transport at interfaces involving SEs, but also provide potential strategy to lower the high resistivity introduced by the space-charge layer. However, it must be noted that the model used in this work is simplified and other practical interfacial phenomena, such as reaction or diffusion, are not considered.

The aforementioned works have shown that multiple strategies can be taken towards improving interfacial performance by altering the material at the nanoscopic level. However, much is unknown as to the root interfacial phenomena at electrode/SE interfaces and their correlation with chemical, electrochemical, and mechanical stabilities at interfaces upon extended electrochemical cycling. Further advances, especially the design of new high-performance interfaces, have to rely on a mechanistic understanding of potential interfacial phenomena and their interplay both at open circuit and upon electrochemical cycling.

Future perspectives of research

The past few years have witnessed tremendous progress in the area of developing highly conductive SEs and techniques for understanding their interfaces. Thanks to the efforts of many research groups, SEs have found uses in next-generation battery systems. It is clear that electron microscopy-based experimental and characterization techniques, such as TEM and STEM imaging, EELS, EDS and electron holography, have provided significant insight to improve our understanding of SEs. These research activities have guided researchers in designing better ion conductors, improving interfaces within batteries, and clarifying long-standing misconceptions of structure-property relationships within ion conductors.

Further improvements in S/TEM are urgently needed in order to clearly elucidate interfacial phenomena that happens at the interfaces within solid electrolytes and at the electrolyte-electrode interfaces. The most urgent improvements include (1) the development of a new stage that integrates both cryo and low-noise biasing capabilities. Solid electrolyte materials are extremely beam sensitive in a TEM, largely due to the weak bonding of mobile ions and being electronic insulators. Temperature, electron dose, dose rate and electron energy should all been considered in order to make representative TEM measurements. Furthermore, most solid electrolytes are air and/or moisture sensitive. A cryo-transfer specimen stage with *in situ* biasing capability thus is necessary for the studies of interfaces in solid electrolyte; (2) An improved design of a Micro-Electro-Mechanical Systems (MEMS) biasing devices allows robust fabrications of nanobatteries for *in situ* electrochemical cycling in a TEM. One major difficulty in TEM *in situ* biasing studies is the fabrication of a working nanodevice with an electron-transmitted thin area of interest. Two major types of biasing holder currently present: *i)* tip-based and *ii)* MEMS holders.[78] However, the former provides insufficient stability for routine atomic-scale analysis in its current form and would benefit from further improvements; while the fabrication of specimen using the latter configuration is primarily based on the use of focused ion beam milling, which often induces unavoidable ion beam damage and re-depositions. Future improvements will rely on the redesign of the MEMS-based device geometry and the technical improvement of FIB. For example, the recently developed Xeon FIB combined with a cryo-stage should help minimize ion beam damage. And (3) a robust technique that simultaneously allows the mapping of ions, structure, and charge. As mentioned earlier, holography can be used to probe electric potentials with a limited spatial resolution. Holography is performed in TEM mode making simultaneous chemical analysis challenging. Recently developed 4D-STEM based differential phase contrast (DPC) imaging, combined with EDS or EELS analysis, allows atomic-scale analysis of ions, structure and electric field from a single dataset.[204] This technique is expected to yield significant insight into the role of charge redistribution and transfer in ion conduction at solid state interfaces involving solid electrolytes.

There is no doubt that the design of new, high-voltage, safer batteries will be realized if the overall understanding of SEs and their interfaces is improved. Towards this end, several technical issues must be further explored to better understand the interfacial phenomena: (1) atomic-scale characterization techniques have to be spatially correlated in order to elucidate key descriptors of SEs, including charge, ions, structure, chemistry, etc., (2) improvements are necessary to advance *in situ* and *in operando* techniques for atomic-scale understanding of electrode/SE interfaces, such as TEM and XPS techniques, (3) theoretical modeling and simulations should provide insight as to the interfacial changes between the different interfaces associated with SEs and be directly compared with experiment, where possible, (4) correlative technique developments, which can precisely correlate atomic-scale parameters with global performance in practical batteries, are important for the future developments of SE-based energy storage research, and (5) the last but not the least, improved efforts have to be taken to the fundamental understandings of the largely unknown interfacial formation mechanisms in solid-state synthesis and processing methods. It must be emphasized that one technique cannot bridge the gap between the overall mechanistic understanding with the performance of SEs and their interfaces, but rather, theoretical and experimental approaches should be highly corroborated to develop clear descriptors of interfacial phenomena for SEs.

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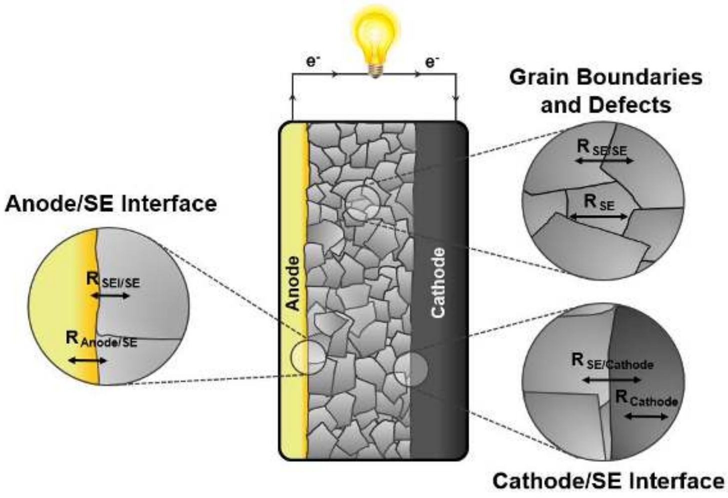
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Grain Boundaries and Defects
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