Unlocking the Failure Mechanism of Solid State Lithium Metal Batteries

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Solid-state lithium metal batteries are regarded to be the ultimate choice for future energy storage systems due to their high theoretical energy density and safety. However, the practical applications of solid-state batteries are hindered by severe interfacial issues, such as high interfacial resistance, inferior electro-/chemical compatibility, as well as poor stability. Moreover, lithium dendrite growth and mechanical degradation caused by interfacial stress during repeated cycling induce the failure of a working solid-state battery. Therefore, understanding the failure mechanism of a solid-state lithium battery is imperative and significant to construct a better interface for a safe solidstate lithium battery. In this review, the current fundamental understanding of the impact of the lithium/solid-state electrolyte interface on the solid-state ionics and interfacial chemistry are introduced first. The failure mechanisms underlying electrical, chemical, electrochemical, and mechanical aspects of solid-state lithium batteries are summarized. The emerging perspectives regarding future research directions are also included. This sheds fresh light on the rational construction of high-efficiency solid-state lithium batteries.

1. Introduction

Rechargeable lithium-ion batteries have innovated the energy-consuming structure. The batteries have been widely employed in portable electronic and electric vehicles. Current commercial lithium-ion batteries with graphite anode, however, have begun to approach their theoretical energy density limit that cannot satisfy the burgeoning demand of high-end

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storage applications.^[1] Lithium (Li) metal, as the "holy grail" anode, exhibits the ultra-high theoretical specific capacity $(3860 \text{ mA h g}^{-1})$ and the lowest electrode potential (-3.04 V vs standard hydrogen electrode), which can effectively widen the battery working voltage and reduce active material amounts, contributing to an enhanced battery energy density.^[2] Nevertheless, lithium metal batteries (LMBs) are normally paired with inflammable organic liquid electrolytes, and thus suffer from the risk of explosion when short circuiting occurs, attributing from uncontrolled dendrite growth during repeated cycling.^[3] Meanwhile, the organic electrolytes are featured with narrow electrochemical window and cannot put high-energydensity advantages of LMBs to work.

Replacing liquid electrolyte with nonflammable solid electrolyte has strongly been considered as a promising strategy to

achieve high energy density and safety of LMBs.^[4] On one hand, the solid-state electrolyte (SSE) can not only effectively avoid the safety hazards caused by leakage, flame, and explosion of organic liquid electrolyte, but also is expected to prevent Li dendrite propagation considering its high mechanical modulus, essentially improving the safety performance of batteries.^[5] On the other hand, the superiority of wide electrochemical window renders SSE easily matched with high-voltage cathode materials and thus broadens the battery working window, showing the ability to attain high-energy-density LMBs.^[4b,6] Preferably, ideal SSEs for practical applications in solid-state LMBs (SSLMBs) should feature some characteristics: i) high ionic conductive properties for fast electrochemical kinetics during cycling; ii) good chemical and electrochemical stability for improved interfacial dynamics and reduced interface resistances, and iii) sufficient mechanical strength for resisting volume changes and Li dendrite propagation. Since 1960s, many promising solid materials have constantly emerged and can be categorized into two distinct families: solid polymer electrolytes (SPEs) and solid inorganic electrolytes (SIEs).^[7] The SIEs generally possess superior mechanical modulus, wide electrochemical window, good ionic conductivity, but inferior chemical stability and poor interface compatibility, while the SPEs are opposite. Unfortunately, neither of them is omnipotent.

Facilitated by advanced interface science and nanotechnology, numerous attributes have been committed to improving



the physicochemical properties of SSEs mentioned above, such as interfacial wetting, lithiophilic engineering, alloying, and artificial interphase modification, etc.^[8] However, the SSLMBs based on these SSEs still exhibit much lower electrochemical performance compared to their liquid counterparts, largely limiting their practically industrial applications.^[9] Therefore, deeply understanding on the failure behavior of SSEs is critically importantly to realize highly efficient SSLMBs. It is prevailing that the failure of SSLMBs is mainly ascribed from large interfacial resistance, severe dendrite growth, unfavourable interface reaction, inferior interfacial evolution, and mechanical deformation,^[10] yet the in-depth analysis and comprehensive summarization on the failure mechanisms of SSEs matched with LMBs are still lacking.

In this contribution, we begin by the fundamental understandings of the solid-state ionics and interfacial chemistry at Li/SSEs interface. We summarize the failure mechanisms of SSLMBs with an emphasis on the analysis of electric failure (electric contact loss and short circuiting), chemical failure, electrochemical failure, and mechanical failure. The summary and perspective regarding the future research direction are also included. Focusing on these failure behavior analyses, we hope our work sheds a fresh light on the rational construction of high-energy-density SSLMBs.

2. Understandings of Solid-State Electrolytes and the Interfacial Chemistry

2.1. Solid-State Ionics in SSEs

The SSLMBs work through the SSEs that can transport Li ions towards electrode surface for electroreduction, and therefore fast ion transportation kinetic in SSEs represents a critical factor in high electrochemical performance.^[11] **Figure 1** compares the ionic conductivities of typical SSE groups, which vary with the structure and physicochemical properties of SSEs.^[7f] The SPEs generally exhibit ionic conductivities below 10⁻⁴ S cm^{-1,[12]} In contrast, highly crystalline SIEs, such as perovskite-type, garnet-type, LISICON-like, and argyrodite



Figure 1. The ionic conductivity of solid-state electrolytes at room temperature. Reproduced with permission.^[77] Copyright 2015, American Chemical Society.

electrolytes, have much higher bulk ionic conductivities in the range of 10^{-4} – 10^{-3} S cm⁻¹ at room temperature. More importantly, among all the SSEs, the sulfide-based superionic conductors (thio-LISICONs), especially Li₁₀GeP₂S₁₂ (LGPS) and Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, have currently been reported to reach a remarkable conductivity of 10^{-2} S cm⁻¹, comparable to that of their liquid counterparts, offering a great promise for next-generation solid-state LMBs.^[13]

For crystalline ceramic electrolytes, the ionic conductivity is strongly correlated with the content and distribution of point defects, such as Schottky defects (vacancies) and Frenkel defects (interstices), which directly dictate the concentration of carriers (**Figure 2**a).^[14] Thus, increasing the proportion of vacancies and interconnected interstitial sites through dopant, substitution, and nonstoichiometry, efficiently aids the high ionic conductivity of a given SSE.^[11b,15]

Besides charge carriers, the ion transport pathways related to the ion mobility within solid lattice also contribute to the ion migration behaviors. Wang et al. revealed the topology of anion arrangement is critical in determining intrinsic ionic mobility.^[16] The particular body-centred cubic (bcc) anion framework enables the lowest diffusion activation barrier compared to the face-centred cubic and hexagonal close-packed lattices, allowing Li ion directly hopping between adjacent tetrahedral sites and thus achieving a fast ion movement (Figure 2b). This bcc anion packing exists in many fast Li ion conductors, such as superionic conductors LGPS and Li₇P₃S₁₁, anti-perovskite Li₃OCl, and Li₃OBr. Unfortunately, the aforementioned principle of bcc anion structure framework may not be applicable to all SIEs. For example, the garnet-type Li₇La₃Zr₂O₁₂ (LLZO) and NASICON-like Li1.3Al0.3Ti1.7(PO4)3 (LATP) electrolytes do not have bcc anion arrangement, yet they still render high ionic conductivity at room temperature.^[17] By employing ab initio molecular dynamics simulations, Mo and coworkers investigated various fast Li⁺ conductors with distinctive structural frameworks, and proposed that the fast ion diffusion occurred by concerted migrations of multiple ions, which featured low energy barriers attributed from unique mobile ion configuration and strong ion-ion interactions, rather than through isolated ion hopping as the classical diffusion model recognized (Figure 2c).^[18] Furthermore, Zeier and coworkers elucidated the lithium diffusion pathways in LGPS using neutron powder diffraction. The LGPS exhibited quasi-isotropic 3D diffusion processes that combined the 1D diffusion channels crossing two diffusion planes (Figure 2d).^[19] The demonstration of anisotropic Li-ion transport in LGPS has further been well validated by multiple solid-state NMR methods, in which the 1D tunnel together with 2D in-plane paths ensures the fast ion migration and high ion conductivity.^[20] Generally, the anisotropic 3D ion diffusion in fast Li ion conductors is already prevalent, such as Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, garnet-type conductors, and NASICONlike electrolytes.^[17,21]

The SPEs are composed of polymers and lithium salts, in which the polymers serve as hosts for dissolution of lithium salts. The commonly used polymers include polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) composites, and among them PEO is the most attractive.^[8c,22] Various works have

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Figure 2. a) Schematic representation of the point defects in crystalline ceramic electrolytes. b) The Li ion migration path and calculated energy path in bcc lattices. Reproduced with permission.^[16] Copyright 2015, Nature. c) Schematic illustration of multiion concerted migration. Reproduced with permission.^[18] Copyright 2016, Nature. d) 3D Li distribution nuclear density maps for different sections within the unit cell. Reproduced with permission.^[19] Copyright 2016, American Chemical Society. e) In transport mechanism of in PEO electrolyte. Reproduced with permission.^[24a] Copyright 2015, Royal Society of Chemistry.

currently been conducted to explore the ion conduction mechanism of SPEs.^[23] The prevailing opinion is that Li ion conduction occurs through segmental relaxation in amorphous region. Li ions are coordinated with polar groups (such as -O- in PEO and $-C\equiv$ N in PAN) on segmental polymer chains similar to the ion solvation in liquid electrolytes (Figure 2e).^[24] Under an electrical field, the Li ions migrate from one coordination site to another through intrachain or interchain hopping within polymer chains, along with continuous segmental rearrangement, the long-range ion transportation can be therefore realized. Reducing crystallinity can efficiently increase ionic conductivity of SPEs.

2.2. Solid Interfacial Chemistry

2.2.1. Solid Electrolyte Interphase

High interface stability between electrode and SSEs is essential for effective cell operations.^[25] However, owing to the lowest electrochemical potential and high reaction reactivity of metallic Li anode, the Li/SSEs interface is chemically unstable. Most SSEs can be spontaneously reduced when they encounter with Li anode and form a passivating interphase layer at the interface, which highly influences the Li ion transportation kinetics and battery performance.^[26] An in-depth understanding on the interfacial chemistry, especially its formation mechanisms and interface effects, benefits in high-efficiency SSLMBs.

For solid-state batteries, the interphase formation can be qualitatively described by the potential window of SSEs, which is defined as the energy gap between the bottom of conduction band (CB) and the top of valence band (VB) of electrolyte materials (**Figure 3a**).^[27] Ideally, if the chemical potential of electrodes lies in the potential window of SSEs, the electrode/ electrolyte interface is kinetically stable and can guarantee the

long lifespan during cycling. However, in the scenario of Limetal anode, its chemical potential is generally above that of CB of most SSEs, and the interphase formation will thus occur because of the decomposition of electrolytes.

According to the characteristics of interphase layer, three main types of Li-SSE interface can be included.^[28] i) Thermodynamically stable interface with no interfacial reaction phases formed (Figure 3b). Such an interface is highly desirable for SSLMBs, which can not only allows uniform Li ion transfer but also avoids interfacial side reactions during cell cycling. Unfortunately, this is not the case in the practical SSEs, ii) Thermodynamically unstable interface with a mixed ionic-electronic conducting (MIEC) interphase (Figure 3c). This MIEC interphase allows continuous electrochemical reduction of SSE and eventually leads to cell failure. The SSEs, such as LAGP, NASICON-type, and perovskite-type LLTO, preferentially produce such type of interphase layers.^[29] iii) Thermodynamically unstable interface with ionically conductive but electronically insulating interphase (Figure 3d). This interphase layer, also called as "stable SEI," can suppress electrons transfer across SSEs, and therefore maintain a stable interface during chargedischarge cycling, which is usually found in typical SSEs including LLZO, LiPON, and Li₇P₃S₁₁.^[26a,30]

2.2.2. Space Charge Layer Theory

In LMBs, the electrode-electrolyte interfaces at which the electrochemical reactions occurred are decisive for Li ion plating/ stripping behaviors and thereby dictate the reversibility of batteries.^[31] However, because of the interface between electrodes and SSEs is always heterogeneous, there is a chemical potential gradient between them when they come into contact, providing a driving force for Li ion redistribution and spontaneously generating a space charge layer at the electrode/SSE





Figure 3. a) The energy gap between its lowest unoccupied and highest occupied molecular orbitals for stable solid electrolytes. Reproduced with permission.^[27] Copyright 2013, American Chemical Society. Schematic illustration of interphase between Li metal and SSEs. b) Thermodynamically stable interface; c) Thermodynamically unstable interface with a mixed ionic-electronic conducting interphase formed; d) Thermodynamically unstable interface with ionically conductive but electronically insulating interphase formed. Reproduced with permission.^[28] Copyright 2015, Elsevier.

interface.^[32] The space charge region is generally high-resistance and worsens the Li ion transfer through interface, giving rise to a high interfacial impedance and poor cycling capability.^[33] Takada et al. investigated the interfacial phenomena in sulfide-based solid-state Li battery, and suggested the space charge layer was the primary contributor to high resistances.^[34] As the oxide was more attractive to Li ions than sulfide, Li ions easily migrated from the sulfide SSE to the $Li_{1-x}CoO_2$ cathode, eventually leading to the increase of Li ion concentration on the cathode side and decrease on the electrolyte side. However, because of the electron conducting properties of Li_{1-x}CoO₂ cathode, the electrons can balance the Li ion concentration gradient, which further promotes the movement of Li ion and generation of space charge layer until the interface reaches equilibrium, ultimately developing Li-ion depletion zone on sulfide SSEs side with high resistance. Further, Haruyama et al. theoretically examined the space charge layer effect on the interface between LiCoO₂ cathode and β -Li₃PS₄ SSE,^[33a] revealing the subsurface Li in β -Li₃PS₄ side began to transfer at undervoltage condition and leaded to the growth of space charge layer at initial stage of charging, bringing in high interfacial resistance. More fatally, the presence of space charge layers can also contribute to gradual Li ions depletion from the electrode and accumulation in the electrolyte during cell cycling, exacerbating the charge segregation and eventually reducing reversible capacity.^[35] The incorporation of functional buffer layers, such as LiNbO₃, Li₂ZrO₃, and Li₂O-SiO₂ glassy film, effectively mitigates the low Li chemical potential from cathode material applied on the SSE materials, preventing the space charge layer effect at the cathode/SSE interface and hence promoting the interfacial stability.^[33a,36] However, these achievements mainly focus on the interfaces between high-voltage cathode and SSEs, and the information on the space charge layer at Li anode-SSE interface is lacking.

Indeed, if considering the highly reactive of Li metal to SSEs, the space charge layer at Li anode/SSEs interface might be more sophisticated than that of cathode/SSEs interface, due to the heterogeneous interphase on Li anode featured with different chemical potential for Li ion. Unfortunately, it is still unverifiable up to now. Future research efforts to identify the space charge layer between Li metal anode and SSEs as well as its effect on the electrochemical performance of SSLMBs are extremely urgent Overall, suppressing the space charge layer favors fast interfacial kinetics and reduced interfacial impedance, benefiting to the excellent cell performance.

3. Failure Mechanism of Solid-State Lithium Metal Batteries

An ideal electrochemical battery system should guarantee the reversible charge storage and release, that is, the controllable electron and Li ion transportation. Based on the key failure processes associated with charge transfer behaviors at Li/SSEs interface, four types of failure mechanism in SSLMBs, such as electric failure, chemical failure, electrochemical failure, and mechanical failure, are systematically discussed in this section.





Figure 4. a) Voltage profile of a Li/PEP/Li symmetric cell upon polarization at 0.50 mA cm⁻² showing the short-circuit accident. b) The cross-section SEM image of symmetric cell after short circuiting. a,b) Reproduced with permission.^[38] Copyright 2002, The Electrochemical Society. c) The schematic showing the mechanism for the nucleation and growth of Li globules and voids. Reproduced with permission.^[42a] Copyright 2015, The Electrochemical Society. d) 3D rendering images and e) phase map describe the effect of current density on the nature of nonplanar Li deposition. d,e) Reproduced with permission.^[43] Copyright 2018, American Chemical Society.

3.1. Electric Failure

Unlike prevailing views that Li dendrite growth can be restricted by SSEs with a sufficiently high shear modulus, it actually occurs more easily in SSE systems even at a small current density.^[26b,37] Especially in the soft SPEs, the critical current density for PEO-based SPEs had been reported to be small as 50 µA cm⁻², much lower than their liquid counterparts (3 mA cm^{-2}) .^[38] In fact, the dendrites can easily penetrate most of the SPEs due to their relatively low elastic modulus that is unable to withstand the dendrite growth, consequently bringing about cell failure.^[37c,39] Dollé et al. in situ observed Li dendrites growth in solid polymer batteries upon cycling through scanning electron microscope.^[38] The dendrites continuously grew in both length and thickness with the increasing polarization, and eventually passed through the polymer electrolyte, causing a cell short circuit (Figure 4a,b). Further by in situ OM characterization, Shi et al. elucidated that the dendrite formation mechanisms in gel polymer cell. At low current density, spherical Li deposits are uniformly distributed on the electrode surface. However, with the gradually increasing current densities, the dominant topographies are evolving from spherical deposits to moss-like Li dendrites and then to branch-shaped ones.^[40] More importantly, it is found that a hollow-structured solid electrolyte interphase shell formed on the Li dendrite surface with "dead Li" particles has remained after Li stripping, which can further result in low Li ion transport capacity and capacity fading of working batteries.^[40–41]

In addition, local surface inhomogeneities pre-existing at the Li/SPE interface, such as impurity particles or defects, are

considered as critical spots for dendric Li deposition in polymer batteries (Figure 4c).^[42] The electronically insulated impurity particles prevent the direct reduction of Li metal on the top of them. Instead, the nucleation and growth of Li can be preferentially concentrated at the edge of these impurities due to the increased local conductivity or electric field concentration. giving a globular or dendritic structure. In the other aspect, the irregular Li deposition can also generate voids on the top of the impurities. During cycling, the Li/SPE interface in the vicinity of impurity moves upward, leaving the impurity particle at its original location. Because of the side reactions occurred at the top of impurity, the SPE is degraded and thus separates itself from the surface of the impurity, forming a void. Therefore, the protrusions deposited near the impurities exhibit three types: globule, dendrite, and void, and the current density is believed as the key variable in determining the nature of Li deposition (Figure 4d).^[39a,43] A phase map was experimentally obtained by Maslyn et al. to quantify the effect of current density on nonplanar electrodeposition in a symmetrical solid polymer cells (Figure 4e).^[43] Stable Li deposition without dendritic protrusions can be obtained at very low current densities (orange area). At intermediate current densities, protrusion nucleation and growth can be partial suppressed, leading to the observation Li globular (green area). At high current densities, both globular and nonglobular dendrites were observed accompanied by extremely short cell lifetimes, and the density of dendrite was monotonically increased with the increasing current (blue area). Increasing the elastic modulus of SPEs has been proved to produce high compressive stress around the dendritic protrusion and thus results in decreased exchange





Figure 5. a) Illustration of Li metal plating through LLZO SSE in transgranular or intergranular ways. Reproduced with permission.^[46a] Copyright 2016, Elsevier. b) The internal morphology of LiBH₄ SSE pellets upon cycling that are etched by focused ion beam, in which the inserted white cylinders stand for SSEs, and their dashed area stands for the area for observation. c) Li dendrite formation in LiBH₄ SSE. b,c) Reproduced with permission.^[49] Copyright 2019, Wiley-VCH. d) Proposed mechanism for the mechanical failure of SSE with inhomogeneous interface. Reproduced with permission.^[52] Copyright 2018, Elsevier. e) The electron affinity of c-LLZO indicated by the energy difference between CBM and the vacuum level. f) Phase-field simulation results on the impacts of surface-trapped electrons on the morphologies after Li electrodeposition. d,e) Reproduced with permission.^[53] Copyright 2019, American Chemical Society. g) Schematic of the effect of mechanical properties of Li metal and stack pressure on the shorting failure of SSLMBs. Reproduced with permission.^[55] Copyright 2019, Wiley-VCH.

current density at the protrusion peak compared to that at the valley, efficiently preventing dendritic growth at higher current conditions. $^{[44]}$

As for SIEs, the case is more controversial. Generally, the dendrite penetration is rather prominent in garnet-type or some sulfide electrolytes. The microstructure features of these SIEs, such as grain boundaries (GBs), voids, pores, cracks, and protuberance all contribute to this dendrite-induced shorting behaviors.^[37b,45] GBs are widely thought to be preferential sites for Li dendrite propagation in SSEs. The Li metal is initially nucleated at the Li anode/SSEs interface during cycling, and then intergranular propagation along the GBs considering their softening elastic properties and low ionic conductivities, which eventually leads to cell death (Figure 5a).^[46] However, this gradually dendrite propagating mechanism cannot offer a perfect explanation on the existence of low critical current density.^[47] Recently, various works found that the GBs exhibit relatively high electronic conductivity, which is helpful to promote the reduction of Li ions within the SSEs.^[48] This feature thus induces direct Li dendrite growth inside in the SSEs (Figure 5b,c).^[49] Actually, it has been recently demonstrated the high electronic conductivity of SSEs, which can be induced by the impurities, dopants, GBs, or electrochemical reductions, is the origin of dendrite nucleate and growth within the SSEs.^[50]

The surface chemistry including pre-existed/pregenerated defects, voids, pores, cracks, and protrusions) is also suspicious spots to aggravate Li dendrite growth. These nonintimate sites at the interface can easily generate a locally amplified electric field and thus leads to Li ion initially depositing above them,

inducing inhomogeneous Li dendrite formation.^[26b,51] Further plating of Li into these sites will give rise to locally concentrated pressure and drive irreversibly transgranular cracks of SSEs, exacerbating the propagation of dendrites and finally degradation of cell systems (Figure 5d).^[52] From the other aspect, through Density Functional Theory (DFT) calculations, it has also discovered the insufficient surfaces in SSEs (pores and cracks) show a smaller band gap compared to the bulk, which can easily capture excess electrons and allow isolated Li nucleation, sharply increasing dendrite penetration depth and thereby accelerating Li dendrite growth (Figure 5e,f).^[53]

In addition to the instinct properties of SIEs, soft Li metal as a double-edged sword also plays an important role in regulating dendrite propagation of SSLMBs.^[37a,54] On one hand, rigid interface contact between solid Li anode and solid SSEs can be ameliorated through the plastic deformation of soft metallic Li. On the other hand, however, the violent deformation of Li, also called creep, induces the Li filament propagation along with the voids, defects, cracks, and GBs within SSEs and finally battery short circuit. Meng and coworkers examined the effect of mechanical properties of Li metal and stack pressure on shorting behaviors.^[55] A low stack pressure can provide a good interface contact between Li anode and SSEs by preventing the apparition of voids. However, due to the excellent ductility of Li metal, it can creep through the pre-existing pores in SSEs at a much higher pressure. Such a phenomenon reduced the distance between two electrodes and became preferential sites for Li deposition, leading to dendrite growth and cell shorting after successive cycling (Figure 5g).

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Figure 6. a) Typical discharge curves of Li/LiI(Al_2O_3)/Pbl_2, Pb, cells at different current densities. Reproduced with permission.^[58a] Copyright 1983, The Electrochemical Society. b) The time courses of the W.E. potential and charge transfer resistance at the Li (W.E.)/LLZ interface during dissolution and deposition at 50 μ A cm⁻² in a three-electrode cell. Reproduced with permission.^[59] Copyright 2017, Elsevier. c) Morphology of the Li anode side facing the SSE after long-time stripping. d,e) Schematic of the different mechanisms that illustrate the formation mechanics of voids. c–e) Reproduced with permission.^[60] Copyright 2019, American Chemical Society.

Besides dendrite-induced short-circuiting failure behaviors, the increasing interfacial resistance caused by deterioration of electric contact interface between Li anode and SSEs is also a vital factor accounting for the performance decay of SSLMBs.^[56] Generally, the void formation is believed to be the mechanistic origin of this interface deterioration.^[57] During discharging, metallic Li is oxidized into Li+ and migrates across the SSEs to cathode, leaving vacant sites at anode interface. When the discharge rate is much higher than the diffusion rate of Li atoms to fill vacancies, the voids are eventually formed. These voids result in the loss of interface contact between Li and SSEs, leading to a sharply decreased cell potential at the end of discharge (Figure 6a).^[58] To further separate the dynamic change during cycling, Koshikawa et al. conducted impedance analyses at the Li/LLZO SSE interface with a three-electrode technique (Figure 6b).^[59] The interfacial resistances increased and decreased, respectively, during Li dissolution and deposition. Yet they cannot return back to the initial value after one cycling, suggesting that the voids formation during Li dissolution rather than deposition played a pivotal influence on the interfacial resistance. The morphological change was also used to demonstrate the void formation, which showed the initially flat surface of Li foil exhibited deep etching structures after long-term stripping (Figure 6c).^[60]

Kinetic models are proposed to illustrate the formation mechanism of voids at the Li/SSEs interface.^[60–61] When the applied local current density does not exceed the vacancy diffusion limit in Li metal, stable interface is established and no contact loss will be observed (Figure $6d_{1,e_1}$). But when the local current density exceeds the diffusion limit, the vacancies are supersaturated and thus accumulated to form pores in the Li anode near the interface. The pores will be coalesced and grew, thus contributing to increasing contact loss (Figure $6d_2$,

 d_3,e_2).^[60] Similar mechanisms have also been demonstrated by Mo and co-workers, which further explicated that the interfacial void formation is a result of limited Li diffusion.^[62] Based on these computations, the strategies that can promote Li diffusion during electrochemical cycling, such as increasing working temperature, applied external pressure, and interfacial coating, help to sustain interfacial stability and avoid interface failure. Noteworthily, such as-generated voids with deteriorated interfacial contact also correspondingly elevate the local plating current density at the interface, in turn aggravating dendrite formation and ultimately cell death.^[63]

Overall, the electric failure mechanism in SSLMBs is strongly related to the plating/stripping behaviors of Li ions, which follows distinct pathways in different SSE systems and various operation conditions. This requires further profound investigation. For instance, how do physicochemical properties and interfacial chemistry of SSEs affect the ion migration kinetics and deposition/dissolution behaviors? How to realize uniform electrodeposition by rational protective strategies? These questions still remain to be well-considered towards developing effective strategies for relieving electric failure of SSE batteries.

3.2. Chemical Failure

The stability of SSEs against degradation reactions with Li anode is an important restriction for the practicability of SSE in SSLMBs systems. However, due to the high reactivity of Li metal anode, it can readily react with most of SSEs and spontaneously forms an interphase layer on Li anode surface. The properties of interphase directly dictate the overall performance of SSLMBs.





Figure 7. a) Degradation of the Li/Li_6PS_5Cl interface from NVT AIMD simulations. The blue balls represent the Li metal anode. b) Simulated decomposition products of Li/Li_6PS_5Cl interface after reaction. a,b) Reproduced with permission.^[65] Copyright 2017, American Chemical Society. c) Impedance spectrum of the Li/LGPS/Li symmetrical cell before and after stored 48 h at room temperature. Reproduced with permission.^[67] Copyright 2017, Royal Society of Chemistry. d) Schematic of the interphase formation at the Li/LGPS interface. Reproduced with permission.^[67] Copyright 2016, American Chemical Society.

An ideal interphase layer should endow both good electronic insulation and high ionic conductivity to impede persistent decomposition of SSEs uncompromising battery efficiency. However, it is unrealistic to be achieved due to the strong thermodynamic driving force for Li metal to reduce the SSEs. Based on the thermodynamic calculations, Zhu et al. indicated the chemical stabilities of Li anode and SSEs interface are intrinsically limited.^[64] For those spontaneously formed interphases that are electronic insulated but with poor ionic conduction properties, the ionic transport kinetics of the whole cell system will be weakened, dramatically depressing the cyclic capability. Such a phenomenon has been demonstrated in the interface between Li anode and sulfide SSEs (such as Li2S-P₂S₅, Li₇P₃S₁₁, Li₆PS₅Cl, etc.). Ab initio molecular dynamics simulation on the chemical reactions between Li₆PS₅Cl and Li metal indicated the significant interface decomposition can be quickly observed, which was intrinsically ascribed from the weak bonding between P and S (Figure 7a).^[65] The decomposition products were predicted to be Li₃P, Li₂S, LiCl, and possibly LiP (Figure 7b), which had lower ionic conductivity than that of Li₆PS₅Cl SSE, causing insufficient interfacial transport properties and thus decreasing cell performance.

Additionally, the SSEs containing high-valence metal ions with high ionic conductivities, such as NASICON-like LAGP, LATTP and LATP, fast ionic conductors LGPS, and perovskite-type LLTO, etc., prefer to form MIEC interphase when they are in contact with Li anode.^[29a,64] The mixed-conducting properties of interphase will accelerate electrons transfer across the interface, resulting in rapid electrolyte deterioration and final cell failure. Chen and co-workers investigate the interfacial resistance and stability in Li/LGPS/Li symmetrical cell.^[66] The as-fabricated

cell exhibited significantly enlarged interfacial polarization resistance from 140 to 2000 Ω cm² after stored 48 h at room temperature, verifying the interface instability between Li anode and LGPS SSE (Figure 7c). Further Wenzel et al. identified the interfacial reaction processes at Li/LGPS interface by in situ X-ray photoelectron spectroscopy (XPS) and timeresolved electrochemical measurements.^[67] The decomposition products of LGPS led to the formation of Li₃P, Li₂S, and Li-Ge alloy/Ge metal, in which the presence of Ge or Li-Ge phases locally increased the electronic conductivity and led to continuously degraded LGPS surface, thus increasing cell resistance and lowering cell cyclability (Figure 7d). More importantly, the high electron conductivity of interphase further induce Li dendrite growth to pass through the interphase, in turn intensifying the chemical degradation of the SSEs.[68] Actually, the multivalent cations that contained in SSEs, such as Ti and Ge, potentially generate electron-conducting species layers after reacting with Li and facilitates the formation of MIEC interphase. Therefore, the avoidance of these cations or the integration of anions should be effective strategy in designing advanced SSEs with high compatibility. In addition, the creation of protective layers that prevent the continues interfacial reaction, such as Li₃N and polymers, is believed as a feasible path for controlling interphase evolution.^[69]

The chemical failure is controlled by the thermodynamically interfacial reactions between Li anode and SSEs. If the asformed interphase features with both uniform composition and high ionic conductivity, the adverse interphase evolution will be largely alleviated during cycling. Rationally designing of structure and constitution of SSEs is intrinsically effective to regulate physicochemical properties of interphase.





Figure 8. a) Electrochemical window of solid electrolyte and other materials. Reproduced with permission.^[36b] Copyright 2015, American Chemical Society. b) Schematic of interfacial ion transport between LPS and active materials at different electrochemical windows. c) Polarization voltage curves of Li/LPS/LTO cells at different electrochemical windows. b,c) Reproduced with permission.^[74] Copyright 2020, Elsevier. d) 2D cross sections taken from 3D ⁷Li MRI images of before and after cycled LGPS electrolytes in a Li/LGPS/Li symmetric cell. Reproduced with permission.^[77] Copyright 2018, American Chemical Society.

3.3. Electrochemical Failure

High electrochemical stability of SSEs can render an excellent cycling efficiency and energy density of battery system by matching Li metal anode and high-voltage cathode. It has been previously claimed that some of the SSEs exhibit wide electrochemical windows up to 5 V. Yet contradicting such understanding, recent theoretical and experimental studies indicate the intrinsic stability windows of various SSEs, including most sulfides and garnets, are very narrow (Figure 8a).^[36b,70] For example, the voltage window of LGPS is restricted from 1.71 to only 2.41 V.^[71] Once exceeding the stability windows of SSEs, new interphases will be formed due to the undesirable redox behaviors between the electrodes and electrolyte, indisputably influencing the cell performances.^[72] Considering the cathode and SSEs interface have been widely discussed, this section mainly emphasizes on the dynamic reactions and evolutions of Li/SSEs interphases during charging/discharging.

Liu et. al experimentally studied the formation and evolution of the Li/Li₂S–P₂S₅ SSE interphase.^[73] The interphase consisting Li₃PS₄, Li₄P₂S₆, and S was formed at Li/Li₇P₃S₁₁ interface. During successive platting, the S migrated from the underneath layer to the surface and further reacted with Li to generate a stable Li₂S layer. As the increasing intensity of Li₂S, the Li₂S–P₂S₅ SSE suffered from aging and led to the degradation of battery systems. Zhang and co-workers further investigated the decomposition behaviors of Li₇P₃S₁₁ (LPS) under different voltage windows.^[74] It was revealed a severe redox reaction of LPS occurred at a wide electrochemical window (Figure 8b), and the amounts of decomposition products (Li₂S and S) were

increased with the redox reaction depth. More importantly, the redox reaction of electrolyte was a continuous deterioration process, which caused consecutive generation and accumulation of side products during cycling. Such a result enlarged the interfacial polarization and increased cell resistance, finally rendering the fast capacity degradation (Figure 8c). Similar observations were also widely detected in other SSEs, such as Li₆PS₅Cl,^[75] Ga-doped LLZO,^[76] and LGPS.^[68] Besides, the increased heterogeneity of Li distribution upon electrochemical cycling is also compromised to electrochemical performance. A severe Li depletion at Li/LGPS interface after cycling was depicted by the 3D ⁷Li magnetic resonance imaging study (Figure 8d).^[77] The Li-deficiency zone exacerbated Li concentration polarization in LGPS electrolyte and increased interfacial resistance, resulting in capacity decay. Furthermore, this local uneven Li distribution have also implications for the propagation of Li dendrites, further aggravating efficiency loss and cell failure.^[78]

There are many achievements on unravelling electrochemical failure mechanism of SSBs. However, the evolution of the interphase upon cycling and its effect on the electrochemical dynamic behaviors, such as Li ion diffusion and transportation, interfacial morphology and chemistry evolution, as well as potential change, etc., still need an in-depth investigation. More importantly, different from the interface in liquid electrolyte systems, the solid-solid Li/SSEs interface is embedded inside and difficult to be in situ/operando characterized by frequently applied tools. Advanced characterization techniques are required to be developed for obtaining more detailed information on the interfacial behaviors in the working SSLMBs.





Figure 9. a) Pressure change monitored during galvanostatic cycling of In/LGPS/LiCoO₂ SSBs. Reproduced with permission.^[83] Copyright 2017, The Royal Society of Chemistry. b) Stress accumulates at the tip of the Li filament. Reproduced with permission.^[85a] Copyright 2019, The Electrochemical Society. c) Simplified schematic of a Li filament in a solid electrolyte matrix. d) Inverse square root dependence of Li plating overpotential and crack-extension stress on defect size in LLZTO and glassy LPS electrolyte. c,d) Reproduced with permission.^[86] Copyright 2017, Wiley-VCH.

3.4. Mechanical Failure

The mechanical stability of Li/SSEs interfaces is also instructive in determining cell performance. During Li plating/stripping, the huge volume expansion of hostless anode severely fluctuates the Li/SSEs interfaces due to the rigid properties of solid electrode and solid electrolytes. Such interface fluctuations can lead to contact loss or even delamination at electrode-electrolyte interface.^[79] As a matter of fact, the interface mechanistic voids or disconnection induced by the volume changes during battery cycling had been directly visualized using in situ and in operando synchrotron X-ray tomography by Sun et al.^[80] After fourth cycles, the interface between InLi anode and SSE displayed tremendous morphological changes, of which the cavity/void was clearly observed after discharge, providing a compelling evidence of interfacial degradation. This deterioration of interface accumulated upon cycling brought a barrier for Li transport, drastically increasing the interfacial resistance and eventually aggravating the decay of rate performance in SSLMBs.^[81]

Furthermore, unlike the case in conventional liquid electrolytes, the volumetric changes of interface due to Li deposition/dissolution cannot be cushioned or adsorbed by SSEs and they are instead spatially constrained by the interfacial contact between the anode and the SSEs. Therefore, this naturally generates a significant amount of stress that can mechanically damage the interface.^[58b,82] Zhang et al. quantitatively revealed pressure and height changes during galvanostatic cycling in SSBs, which depicted the pressure increased during charging and decreased during discharging, first demonstrating the generation of macroscopic strain during cycling (**Figure 9**a).^[83] Then, a significant interface bending or microcracking after repetitive cycling arising from the internal mechanical strain at

the interface was clearly observed, which accounted for a loss of grain contact and detrimental effects on electrical connectivity, thus giving rise to the capacity losses. More fatally, these as-generated or pre-existing surface defects can serve, in turn, as preferential sites for Li dendrite infiltration. By integrating atomic force microscope with an environmental transmission electron microscope, Huang and coworkers found that a high growth stress of Li dendrite up to 130 MPa can be built up, much higher than the stresses of bulk Li, and the measured yield strength of Li whiskers can even reach as high as 244 MPa.^[84] Such localized strain accumulated throughout cycling and thus produced, especially, a high stress concentration at the tip of Li filament (Figure 9b), further driving proliferated crack propagation and leading to accelerated Li filaments permeation, which eventually caused the failure of the battery.^[45d,85]

Recently, a chemo-mechanical model to evaluate the generated stresses in a sharp flaw during electrodeposition of Li metal has been developed by Porz et al., and it depicted an inverse square root dependence of Li plating overpotential and crack-extension stress on the crack length (Figure 9c,d).^[86] Once above the Li plating overpotentials and corresponding mechanical stresses, the surface defects or cracks would be extended. Comparatively speaking, SSEs with a relatively high fracture toughness can significantly increase the overpotential and fracture stress required to extend a crack of like size, decreasing the risk of attenuation. The enhancement of the fracture toughness of SSEs would help to resist the crack extension and mitigate the mechanical failure of batteries.^[87]

On the other hand, considering the high reactivity of Li anode towards SSEs, the interphase formation and evolution also have undisputable influence on the mechanical





Figure 10. a) Mechanical degradation of LAGP within a Li/LAGP/Li cell during cycling. Reproduced with permission.^[88] Copyright 2019, American Chemical Society. b) Cross-sectional SEM images of LAGP cycled until failure at a higher current density of 0.5 mA cm⁻². The darker regions are the reacted interphase that has grown into the bulk of LAGP SSE. c) Schematic showing possible reduction pathways in relation to the growth of the mixed-conducting interphase. b,c) Reproduced with permission.^[89] Copyright 2019, American Chemical Society. d) Impedance curves of Li/LAGP/Li symmetric cell after 50 days. The inset image shows the surface of Li anode after testing. e) Schematic of the fracture mechanism during electrochemical reactions. d,e) Reproduced with permission.^[91] Copyright 2017, American Chemical Society.

degradation of SSLMBs. Li insertion and interfacial transformation during interphase growth induces volumetric expansion within SSEs and produces great internal stress, which can mechanically destruct the bulk SSEs and cause high resistance.^[68] Mechanical damage of Li_{1+x}Al_xGe_{2-x}(PO4)₃ (LAGP) SSE caused by continuous interphase growth was revealed by in situ X-ray micro-CT technique.^[88] The fracture initiated at the edges of the Li/LAGP contact sites and propagated with further cycling, which was found to be strongly correlated with increased impedance, revealing that the fracture of SSE during cycling was the primary reason for increased cell impedance, rather than the ionic and/or electronic transport characteristics of the interphase itself (Figure 10a). Further analysis on the stress evolution within the LAGP SSE was conducted for pinpointing the origin of fracture. Two different stress components, circumferential stress and radial stress, were detected as the interphase evolved. The radial stress can cause circumferential cracks and circumferential stress caused radial cracks. At early stages during the reaction process, the circumferential stress was concentrated around the edge of reacted interphase, and its magnitude progressively enhanced throughout the LAGP along with the increased thickness of interphase, resulting in the radial cracks growing even to the extreme edge of the SSE pellet and thus enhancing interphase resistance.

The propensity of interphase evolution is highly dependent on the applied current density. McDowell and co-workers compared the effect of applied current on chemo-mechanical degradation in Li/LAGP/Li symmetric cells and found a higher current density can cause more nonuniform interphase growth and penetrated deep into the SSE pellet (Figure 10b).^[89] In fact, the interphase generated by the chemical reaction of Li and LAGP exhibited mixed-conducting properties and benefited the reduction of LAGP at the LAGP/interphase boundary instead of Li anode surface, allowing for the continuous decrease of Li ion transport length and lowering the ion conduction resistance (Figure 10c). At high current densities, this promotion of short ion transport pathways can be amplified because of the high overall overpotential, thereby contributing to severe nonuniformities. These inhomogeneous growth of the interphase occurred within the bulk of LAGP SSE can create highly localized stress concentrations, which derived fracture in SSE more readily and significantly increased the cell impedance, thus causing accelerated the chemo-mechanical failure.

Intrinsic properties of the (electro)chemically formed interphase can also affect the mechanical integrity. Those SSEs that can chemically react with Li metal to form MIEC interphase are inclined to be mechanically degraded, and then disable the batteries during repeated charge/discharge processes.[90] Chung et al. experimentally unravelled the effects of interphase formed by reaction between Li metal and Li1.5Al0.5Ge1.5(PO4)3 (LAGP) on cell failures.^[91] A gradually and continuously increased electrical resistance of symmetric Li/LAGP/Li cell accompanied with the LAGP pellet completely pulverized was observed for 50 days, indicating the interfacial reaction between Li and LAGP triggered the pulverization of LAGP SSEs (Figure 10d). The fracture mechanism can be understood based on the different conductivities of charge carriers among Li anode, LAGP SSE, and the formed interphase. In detail, the as-formed interphase between Li and LAGP is mixed ionic and electronic conducting with the electronic conductivity dominating, while the LAGP has only ion conductivity and Li anode has both. Upon introducing an electrical current to the anode, most of Li ions can be reduced at the interface between LAGP and the interphase rather than the interface of Li metal | interphase, which



leads to the formation of extra Li oxide-related compounds and increases local volume at the interphase. Such volumetric expansion drives cracks or fractures in the LAGP SSE, eventually mechanically damaging the SSE and resulting in cell failure (Figure 10e). Building stable or soft artificial interphase through engineering the properties of SSEs could prevent the stress accumulation and alleviate cell mechanical failure.^[92]

Actually, stress-induced mechanical degradation is always entangled with chemical or electrochemical reactions. Improving the mechanical modulus of SSEs merely cannot satisfy the mechanically robust interface of SSLMBs. Comprehensively protective strategies, including 3D porous architectures, soft interlayers, and perfect SSEs without surface defects, to realize stress relaxation is essential for mechanical stability. Moreover, dynamic information on the stress distribution and concertation, mechanical strength, ionic transport, and interface evolution behaviors can also help in guiding the design of advanced SSLMBs in the future.

4. Strategies to Construct a Stable Interface

There are strategies have been implemented to sustain a stable interface and prohibit the cell failure for high-energy density SSLMBs. For SPEs, the strategies mainly focus on improving the mechanical rigidity of the electrolyte to suppress dendrite formation. The widely developed tactics includes the addition of inorganic fillers, cross-linked electrolyte, block copolymer electrolyte, and other advanced polymer electrolytes, etc.^[22e,93] For the SIEs, the interfacial challenges are complicated, involving dendrite propagation, unstable interphase, and mechanical fracture or pulverization, thus versatile strategies are emphasized herein.

4.1. Materials and Architecture Design

In fact, the intrinsically unstable interface resulted from the material properties of SSEs is more likely to encourage the deformation or destruction of interface structure, and thus the morphology evolution and stress accumulation upon cycling, resulting in poor electrochemical performance. Current studies have shown that the strategy of composite electrolyte provides a promising approach to enhance the interfacial stability. The composite electrolytes combine the superiorities of their inorganic and organic components, which can not only possess good adhesion for intimate interface and flexibility to accommodate interface fluctuation, but also provide high conductivity for fast ion transportation and robust mechanical strength against dendrite growth. Some effective composite electrolytes, such as PVDF-HFP-LLZO,^[94] PEO-Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂,^[95] Li₇P₃S₁₁-PEO-LiClO₄,^[97] PEO-Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃,^[96] PVDF-Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂,^[98] perfluoropolyether-Li₃PS₄,^[99] have been reported. Besides, the material design of advanced SSEs, such as fluorinated electrolyte, metal-organic-frameworkbased electrolyte, and electrolytes with double-layer or 3D geometry, also demonstrates benefits in the high ionic conductivity for facilitated electrochemical kinetics and mechanical reinforcement for long cyclic lifespan.^[100]

Although the cycling performance can be improved by manipulating the material properties, the intrinsic "hostless" Li anode still endures the issue of large volume change during repetitive cycling, inevitably bringing severe interface degradation or even fracture. Lithiation alloys (Li-Mg, Li-Al, and Li-In, etc.) with rapid Li diffusion capacity and high reduction potential have been demonstrated as ideal alternatives to bare Li metal for stabilizing the Li/SSE interface.^[101] Recently, Li-Mg alloy anode had been investigated on a garnet-type SSE, which allowed Li stripping/plating within the alloy framework to generate Li-deficient or Li-rich alloys that can serve as ion/electron dual-conductive host during cycling, preventing interface deterioration or volume collapse and thereby realizing a long cycle lifespan.^[102] In addition to the nano-scale alloy framework, transforming 2D Li foil to 3D Li metal anode (such as $Li-C_3N_4$) is a frequently-used approach to eliminate dendrite growth and sustain interface stability in solid-state batteries.^[103] Furthermore, the construction of stable porous anode framework for accommodating volume expansion is also an effective solution for highly safe SSLMBs. Recently, Hu and coworkers developed a 3D garnettype Li₇La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O₁₂ framework consisting of a dense layer sandwiched by two porous layers as the Li anode host.^[104] During cycling, Li metal deposited within the preserved pores of the host, effectively relieving the volume change issues. Meanwhile the dense layer blocked Li dendrite penetration, preventing the risk of short circuit (Figure 11a). Besides porous ceramic framework, carbonaceous materials can also be implemented in the SSLMBs to buffer volume change and ensure homogenous Li deposition. Fan and coworkers employed a hierarchical host of carbonized metalorganic framework nanorod arrays with carbon cloth (NRA-CC) for Li anode. This 3D interconnected structure provided sufficient Li nucleation sites for decreasing local current density to avoid Li dendrite growth, and broadened internal space for restricting volume change during Li plating/stripping, synergistically affording stable cycling in SSLMBs.^[105]

4.2. Interfacial Chemistry Manipulation

Interfacial chemistry is of paramount importance for the composition and structure of the interface layer, and hence for the deposition morphology and cycling performance of batteries. Enlightened by the interfacial engineering strategy in liquid systems, various reactive solution and organic electrolytes, such as H₃PO₄ solutions, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in dioxolane (DOL)/1,2-dimethoxyethane (DME), lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/ethyl methyl carbonate (EMC), LiTFSI/N-propyl-N-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₃TFSI) ionic liquid, are used to in-situ regulate the interfacial composition and structure for preventing inferior side reactions and render stable Li/SSEs interface.^[106] For example, Wang and coworkers added liquid electrolyte (1 M LiTFSI in DOL/DME) to form a stable interface for preventing LGPS corrosion.^[106b] The liquid electrolyte was in situ reacted with Li anode upon cycling and can be decomposed to generate nanocomposite interphase on Li. This interphase consisted of organic elastomeric salts







Figure 11. The strategies to construct a stable Li/SSE interface. a) 3D garnet-type porous framework for mitigating volume change and dendrite growth. Reproduced with permission.^[104] Copyright 2018, National Academy of Sciences. b) Schematic of the organic–inorganic nanocomposite as interfacial protective layer for stabilizing Li/LGPS interface. Reproduced with permission.^[106b] Copyright 2018, Wiley-VCH. c) The schematic of mixed conductive interlayer for protecting Li/LLZTO interface. Reproduced with permission.^[108] Copyright 2020, The Royal Society of Chemistry.

(LiO-(CH₂O)_n-Li) and inorganic nanoparticle salts (LiF,-NSO₂-Li, Li₂O), which had excellent chemical and electrochemical stability, thus restricting LGPS reduction (Figure 11b). A more than 3000 h stable Li electrodeposition and a 200-cycle life for a solid-state Li/LGPS/TiS₂ full cell were achieved.

Functional additives can also help reinforce the interphase components and properties.[107] Inorganic Li compounds (LiI, Li₃N) are the most promising candidates. Recently, anti-perovskite Li3OCl was introduced into the Ta-doped Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ (LLZTO) electrolyte to improve the interfacial performance between the garnet-type electrolyte and Li metal.^[108] The amorphous Li₃OCl worked as a binder, filler, and bridge to promote continuous ionic conductive network among LLZTO particles. Moreover, the Li₃OCl also exhibited excellent affinity to Li metal and in-situ formed a stable and dense interfacial layer (Li₂O, LiCl) on anode resulted from the favored reaction between Li₃OCl and Li metal, greatly decreasing the interfacial resistance and suppressing the dendrite growth. Attributed form these advantages, the symmetrical cell based on LLZTO-Li₃OCl composite electrolyte rendered a stable cycle of 1000 h without short circuit.

4.3. Artificial Protective Strategy

An artificial protective layer between Li anode and SSEs provides multiple advantages in alleviating interface instabilities and preventing cell failure. "Lithiophilic" inorganic coatings (such as metal or metallic oxides) driven by the alloy/lithiated reaction between inorganic layer and molten Li significantly improve the interface wettability, which not only provide intimate interface contact for decreased resistance but also reduce local current density for homogenous Li deposition. For example, Hu and coworkers reported an ultrathin Al₂O₃ coating by atomic layer deposition on Li₇La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O₁₂ electrolyte, which dramatically improves the wetting and stability of SSE and thus results in an ultralow interfacial impedance 1 Ω cm².^[109] Coatings of Si,^[110] Au,^[111] Ge,^[112] Ag,^[113] and ZnO^[114] all produced similar effects to that of Al₂O₃ protective layer.

The introduction of functional interlayer is also designed to enhance the interface stability. Such interlayers reported so far can be divided into two categories: ionic- conducted but electronic-insulated layers and mixed ionic/electronic conductive layer. Generally, the highly ion-conducted interlayer promise



to be chemically inert yet mechanically robust to prevent direct interfacial reaction and mitigate volume change during cycling, rendering high cyclability and capacity performance. Examples of Li₃N layer,^[115] and boron nitride (BN) nano-film^[116] are both assigned to this protective layers. On the other hand, the mixed conductive layer can possess synergistic effect of external ionic conductivity and internal electronic conductivity, which alleviates local electric-field distribution to suppress Li dendrite growth and provides fast Li ion kinetics to reduce interfacial impedance.^[117] Recently, Sun and co-workers designed an in situ formed Li₃N/Cu MCL interlayer through a conversion reaction between Cu₃N thin film and molten Li for protecting Li/LLZTO interface.^[118] The Li₃N possessed high ionic conductivity and benefited rapid Li ion transport; while the uniformly dispersed Cu nanoparticles with electronic conducting properties not only guided uniform electronic distribution to avoid dendrite growth but also acted as supported matrix to accommodate volume fluctuation, synergistically exhibiting long-term cycling stability of over 1000 h at 0.1 mA cm⁻² (Figure 11c). Actually, recent computation results had been revealed many nitride materials that are electronic insulators have better stability against Li anode compared to oxides, sulfides, and halides, which can be used as promising protective buffer layers for passivating Li anode interface.^[119] The Li-containing nitrides (e.g., Li₃AlN₂, LiPON, Li₁₈P₆N₁₆ nitridophosphate), high-dose nitrogen doping in interlayers, and mixing nitrogen-containing compounds are potential directions for functional interlayers in SSLMBs.

Besides inorganic coatings, soft polymers are well-known candidates for resolving interfacial contact issue.^[120] Goodenough and coworkers introduced a cross-linked polymer layer between the ceramic electrolyte and Li anode, which effectively wetted the interface and induced homogeneous Li ion flux across interface, suppressing dendrite propagation and delivering stable cycling performance.^[121] In addition, the flexibility of polymer layer is also instrumental in buffering interfacial stress during cycling. Recently, Duan et al. proposed a novel design of ultrathin polymer modified rigid LLZO ceramic layer towards Li anode for dendrite-suppression.^[122] The Li/polymer interface can provide gentle tension against

Li dendrite growth and thus render a flat stripping/plating voltage profile.

Actually, the strategy of improving interfacial stability in solid-state batteries is still in shortage, and advanced regulating strategy is urgently demands prompt development. Moreover, the detailed elucidation about the dynamic evolution of the materials and interfacial chemistry during charge/discharge process remains largely unclear. Deeply understanding on the interface evolution behaviors is strongly required for the construction of a reliable interface in the future.

5. Summary and Perspective

The application of SSEs have received great research interests in rendering high energy density and safety of LMBs due to their superior features of nonflammability, nonleakage, wide electrochemical window and high mechanical strength. Unfortunately, the SSLMBs are suffered from less satisfying electrochemical performances because of high interfacial resistance, severe dendrite growth, undesirable interfacial reaction and evolution, and mechanical deformation, which hinders their practical applications. Numerous contributions have been recently conducted to design advanced strategies for enhancing cell performances, yet limited efficiency is achieved. Understanding the fundamental failure mechanism provides important scientific basis towards the construction of highly efficient SSLMBs.

The failure of SSLMBs is particularly associated with the properties of Li/SSEs interface (**Figure 12**). On one hand, problems involving electric failure and mechanical failure can be attributed from the unstable interface structure during repeated cycling. Specifically, the electric contact loss caused by formation of voids at the interface upon Li stripping generally accounts for sluggish electron transfer and high interfacial resistance; while the dendrite growth related to uneven Li deposition is the main reason for electric short-circuiting failure. As for the mechanical failure behavior, the interface fluctuations caused by Li plating/stripping or the interphase evolution produce great internal stress and have critical consequences for the pulverization and cracking of SSEs, leading to poor lifespan.



Figure 12. The failure behaviors at Li/SSE interface of SSLMBs.



On the other hand, the challenges relating to chemical and electrochemical failure refer to the evolution of interface composition. Most of SSEs are (electro)chemical incompatible with Li anode, which brings about notorious side reactions with the formation of undesirable interphase at the interface, significantly decreasing the interfacial stability and deteriorating battery capacity. The rational construction of a stable and compatible Li/SSEs interface by materials design, interfacial chemistry regulation, and artificial protective strategy can help retain high safe and efficiency SSLMBs.

Despite these achievements, the investigation of failure mechanism in SSLMBs is still in their infancy. Greater efforts are strongly encouraged for practical application of SSLMBs, and some suggested directions are shown as follows herein:

- 1) Comprehensive understanding of the failure mechanism. Generally, the cell failure related to interfacial kinetic behaviors involves interface migration, Li ion/electron transportation, (electro)chemical reactions, as well as stress evolution, which is a complex and dynamic process. The Li deposition and (electro)chemical reactions cause the change in charge transportation and surface stress, and meanwhile the local stress accumulation turns back to affect the interfacial mechanical stability and further Li deposition behavior. Moreover, the Li propagation within SSE exacerbates the irreversible (electro)chemical reactions between Li anode and electrolyte. Dynamic analysis regarding each kind of failure behaviors still requires in-depth investigation. In addition, the evolution and degradation of interface structure is actually a coupled result of the electric, chemical, electrochemical and mechanical processes, but not just one of them. Therefore, a comprehensive understanding of the failure behaviors in an integrated SSLMB system is urgent.
- 2) Facile characterization techniques. The interfacial evolution information have important ramifications for the failure behaviors of SSMBs, yet it is difficult to be tracked because of the buried solid-solid interfaces. Most of characterization techniques currently applied is the ex-situ electron microscopy, X-ray photoelectron spectroscopy, etc., and thus it cannot provide in-depth dynamic information on interfacial evolution. Moreover, these tools are unable to maintain the interface integrity. Therefore, some nondestructive and facile techniques that can in situ/operando characterize the interface dynamic evolution on working SSLMBs, such as neutron diffraction, X-ray computed tomography can be regarded as the promising method in the future.
- 3) Advanced energy materials and chemistries. The robust Li/ SSEs interface is an inevitable request for the practical application of SSLMBs. Although there are some effective contributions have been developed, advanced materials and chemistries must be further explored to speed up the research progress of ASSLBs. Rationally designing or theoretically predicting the material properties of SSEs matched with Li anode, as well as interface stability modification, favor the stable Li/SSEs interface. In addition, most of the recently reported protective strategies are always trial and error which is insufficient and time-consuming. Therefore, artificial intelligence based on the as-proposed failure mechanism must be incorporated for the design of the avaliable protective strategies in the future.

The SSLMBs will be one of the ultimate solutions for highsafety and high-energy-density battery systems. To primarily and systemically understand the failure behaviors is important, not only for the rational design of advanced protective strategies towards high-energy-density SSLMBs, but also the optimization the battery systems for under practical environments. Therefore, we hope our review can give fresh inspirations on the indepth understanding of failure mechanisms in SSE systems, and helps the efficient construction of high-energy-density and highly stable SSLMBs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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