Electrochemical Compatibility of Solid-State Electrolytes with Cathodes and Anodes for All-Solid-State Lithium Batteries: A Review

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All-solid-state lithium-metal batteries (ASSLMBs) are considered promising next-generation energy-storage devices for their high safety, high energy density, and long cycle life, where solid-state electrolytes (SSEs) play an essential role in adapting a lithium metal anode to a high-capacity cathode. However, there are still many obstacles to overcome for SSEs, including the narrow electrochemical window with an oxide cathode and a Li anode, low ionic conductivity, and poor interfacial mechanical property. Herein, the critical issues of electrochemical compatibility between some key SSEs and their adaptive electrode materials are focused on. The adaptation of different SSEs to electrode materials is summarized, recent methods for improving the electrochemical compatibility of SSE/electrode interfaces are highlighted, and the perspective for future development of SSEs is discussed.

1. Introduction

Lithium-metal batteries (LMBs) are considered the most promising energy-storage devices for both macroscale electric vehicles and microscale integrated electronic devices in the next decades. Compared with intercalation-type anodes (e.g., graphite) for lithium-ion batteries (LIBs), lithium-metal anodes possess a higher theoretical specific capacity (3860 mAh g⁻¹), lower density (0.59 g cm⁻³), and lower electrochemical potential (≈3.04 V versus the standard hydrogen electrode). Lithium-metal anodes are also irrereplaceable for Li-air and Li–S batteries, both of which can deliver specific energies comparable to traditional fossil fuel. However, since the first rechargeable Li/TiS₂ battery was invented by Whittingham in the 1970s, the commercialization of rechargeable LMBs using organic liquid electrolytes has been hindered by their safety issue and poor cyclability. As shown in Figure 1, to meet the ever-growing demands for high-safety and high-energy-density batteries, ambitious plans have been made by various organizations, such as the New Energy and Industrial Technology Development Organization (NEDO) of Japan, Department of Energy’s (DOE) Office of the United States, and Chinese Academy of Sciences (CAS), to increase the cell energy density to 300–500 Wh kg⁻¹ in the next decade. Generally, the future development routines of lithium batteries with a high energy density can be realized in two steps: replacing the graphite anode by silicon-based anodes along with high-capacity cathodes (e.g., Li-rich cathodes) and combining the lithium-metal anode with solid-state electrolytes (SSEs) to make rechargeable all-solid-state lithium-metal batteries (ASSLMBs). It is believed that nonflammable SSEs with enhanced mechanical strength can better dispel safety concerns, extend the cycle life, and simplify the battery packaging process.

As shown in Table 1, in the most recent years, considerable efforts have been made by companies, such as Bollore, Toyota, Weilam New Energy, and Solid Power, to promote the applications of some promising SSEs, namely, oxide electrolytes (LiₓLaₓ(Zr₂O₁₂ (LLZO), Liₓ₁₋ₓAlₓTi₂₋₅₋ₓPO₄ (LATP), etc.), sulfide electrolytes, and solid polymer electrolytes (SPEs). The critical issues of these SSEs have been discussed in a few reviews. Xiao et al. (2019), Wang et al. (2020), Wang et al. (2020), and Kim et al. (2020) have published reviews on oxide electrolytes. Zhang et al. (2020), Wu et al. (2020), and Park et al. (2018) have reviewed the sulfide electrolytes. SPEs were also reviewed by Zhou et al. (2019) and Lopez et al. (2019). Wan et al. (2018), Dirican et al. (2018), Li et al. (2020), and Zheng et al. (2020) gave detailed reviews of organic/inorganic composite electrolytes. Reddy et al. (2020) published a comprehensive review of sulfide and oxide electrolytes with valuable opinions in these areas.

In this review, we focus mainly on the key issues of electrochemical compatibility between promising SSEs and their suitable electrodes: First, the adaptation of different SSEs to electrode materials is summarized; second, frontier approaches for promoting the electrochemical compatibility of these SSEs are highlighted; finally, our perspectives on the future development of SSEs are proposed.
2. Fundamental Understanding of Electrochemical Stability

The structure of an ASSLMB can be divided into four parts: current collectors, lithium metal anode, SSE, and cathode. During discharge, lithium metal is stripped from the Li anode to become Li ions, which are transferred to the cathode through the SSE, and electrons are also transferred from the anode to the cathode through an external circuit, driving devices to work. The maximum driving voltage \( V_{oc} \) for ions at open circuit can be described by the following equation

\[
V_{oc} = \frac{\mu_a - \mu_c}{\epsilon}
\]

where \( \mu_a \) and \( \mu_c \) stand for the chemical potential of the anode and cathode, respectively, and \( \epsilon \) stands for the magnitude of electron charge.

Ideally, to maintain a low interfacial impedance over multiple cycles, an SSE should be thermodynamically stable against both the anode and the cathode, as shown in Figure 2a. This requires the potential range of electrodes (from \( \mu_a \) to \( \mu_c \)) to be within the electrochemical window of the SSE, which is defined as the energy gap \( E_g \) between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO); otherwise, the SSE would be reduced by the anode (when \( \mu_a > \text{LUMO} \)) or oxidized by the cathode (when \( \mu_c < \text{HOMO} \)).

The electrochemical windows of SSEs are usually measured by cycling voltammetry (CV), where a linear polarization is applied...
to the Li/SSE/inert-metal semiblocking electrode. However, the poor contact between the SSE and current collector would overestimate the range of electrochemical windows. The error can be corrected by increasing the interfacial contact area, such as replacing the inert metal with a cold-pressed SSE/carbon electrode.[24] Figure 2b summarizes the electrochemical windows of various SSEs. It is obvious that most SSE/electrode interfaces are thermodynamically unstable, resulting in the following consequences. 1) Formation of a solid electrolyte interphase (SEI) at the anode side and a cathode electrolyte interphase (CEI) at the cathode side.[25] Although these interfaces help to extend the electrochemical windows, they often hinder the ion transportation by being poor ionic conductive and mixed electronic–ionic conductive, which thus cannot stop the further reactions between the electrode and the SSE, leading to serious self-discharge and polarization. Furthermore, the worse interfacial wettability of SSEs compared to liquid electrolytes can result in excessive current density in the local areas, which induces lithium dendrites to penetrate the interphase layer and expose to fresh SSEs. 2) Formation of a space charge layer at SSE/cathode interface. Huge chemical potential difference would drive Li\(^+\) to transport from the SSE to the cathode, forming a Li\(^+\) concentration gradient. In a mixed conducting cathode, the concentration gradient can be eliminated by electrons, and this gradient redistribution can induce more Li\(^+\) to transport from the SSE to the cathode, eventually leading to a Li\(^+\)-depleted layer on the SSE side with huge impedance.[26]

Because the deterioration at the electrolyte/electrode interface is actually inevitable, other methods for characterizing the interfacial region are needed. Electrochemical impedance spectroscopy (EIS) is the most frequently used nondestructive method to determine the electrochemical properties.[27] However, because of the inhomogeneity of the interfacial structure and composition, methods like cross-sectional transmission electron microscopy,[28] energy-dispersive spectrometer line scanning and X-ray photoelectron spectroscopy (XPS) depth profiling,[29] electron energy loss spectroscopy,[30] and atomic force microscopy are needed to determine and explain the difference of the interfacial structure in local areas.[31] On the other hand, as the formation of the SEI and CEI are time-dependent, in situ characterizing methods such as in situ optical observation,[32] in situ XPS,[33] in situ Raman spectroscopy, and in situ transmission electron microscopy can be useful to observe dynamic changes of the interfacial regions directly during electrochemical cycling.[30,34] More advanced technologies using synchrotron X-ray, solid-state nuclear magnetic resonance, and neutron scattering are also needed to capture subtle and complex changes in the interfacial region.[35]

3. LLZO Solid Electrolyte

Since the discovery of the first Li-stuffed garnet Li\(_5\)La\(_3\)M\(_2\)O\(_{12}\) (M = Nb, Ta) in 2003,[36] the garnet-type electrolyte has been considered as one of the most promising SSEs for ASSMBs. By replacing M with Zr, LLZO was found to possess high room-temperature ionic conductivity (10\(^{-3}\)–10\(^{-4}\) S cm\(^{-1}\) for the doped cubic phase) and high mechanical strength to suppress lithium dendrites physically. However, as shown in Figure 3, the electrochemical window of LLZO ranges from 0.05 to 2.9 V, which indicates that it is thermodynamically unstable against lithium metal or high-voltage cathode materials such as NCM and LCO.[24] Furthermore, due to the excessive hardness of LLZO and formation of Li\(_2\)CO\(_3\) on the LLZO surface, a high local current density can be generated, which amplifies the electrochemical instability factors.[37–40]

3.1. Interface Between LLZO and Anode

First-principles calculations prove the reduction tendency of LLZO into equilibrium phases such as Zr\(_2\)O, La\(_2\)O\(_3\), and Li\(_2\)O...
at the LLZO/Li interface with an onset reduction voltage of 0.05 V, which is the lowest among various SSEs.\cite{24,41}

Although Ma et al. observed a tetragonal-phase LLZO layer form at the interface, which suppresses further decomposition,\cite{30} the electrochemical stability of the LLZO/Li interface still remains uncertain for practical uses. First of all, the electrochemical stability of the interface layer is dependent on the type of doping elements, which is necessary for promoting the ionic conductivity of LLZO by stabilizing the room-temperature cubic phase and introducing point defects. Based on density functional theory calculations, Gao et al. proposed that the reactions prefer to happen between lithium metal and undercoordinated Zr sites on the surface of LLZO, and the doping elements Nb and Ga have a greater tendency to be reduced than Al and Ta.\cite{42} This result is consistent with experimental observation by Zhu et al., who reported that Al helps to form a more intensive oxygen-deficient interphase, which maintains a low and stable interfacial resistance, whereas surface Nb segregation and reduction can destabilize the interface (Figure 4a).\cite{43} Pesci et al. found the segregation of Ga and Al at grain boundaries using the time-of-flight secondary ion mass spectrometry method, which induced uneven current distribution.\cite{44} Till now, the best comprehensive electrochemical performance has been achieved in Ta-doped LLZO (LLZTO) in the aspects of interface stability and ionic conductivity.

Second, it is clear that the SEI layer is mechanically or electrochemically unstable to suppress lithium dendrite growth, especially at a high current density for practical utility. According to the US Advanced Battery Consortium, the charge rate of ASSLMBs in 2023 should reach 3.2 C to fulfill the need of fast-charging EVs;\cite{45,46} however, the penetration of lithium dendrites has been found through grain boundaries or pores in LLZO at current densities of only hundreds of microamperes.

Figure 3. Voltage-phase equilibria profile of LLZO based on first-principles calculations. Reproduced with permission.\cite{24} Copyright 2016, Wiley-VCH.

Figure 4. Illustration of factors for electrochemical instability at the LLZO/Li interface. a) Reduction of doping elements. Reproduced with permission.\cite{43} Copyright 2019, Wiley-VCH. b) Lithium dendrite growth. Reproduced with permission.\cite{49} Copyright 2017, American Chemical Society. Different methods to enhance electrochemical compatibility at the LLZO/Li interface, including c) surface treating and d) applying external pressure. (c) Reproduced with permission.\cite{37} Copyright 2017, American Chemical Society. (d) Reproduced with permission.\cite{53} Copyright 2019, American Chemical Society. e) Creating a mixed ionic–electronic conductive interlayer. Reproduced with permission.\cite{56} Copyright 2020, American Chemical Society. f) Creating a single-ionic conductive interlayer. Reproduced with permission.\cite{62} Copyright 2018, American Chemical Society.
per centimeter square, leading to both electrochemical and mechanical failure.\textsuperscript{47,48} As shown in Figure 4b, Aguessa et al. summarized three reasons for lithium dendrite growth competing with (b1) normal Li\textsuperscript{+} plating at the LLZO/electrode interface, which are (b2) the local current density, (b3) reduction of Li\textsuperscript{+} by the oxygen backbone of LLZO, and (b4) reduction of Li\textsuperscript{+} by the non-zero electronic conductivity.\textsuperscript{49} The conclusion is supported by other work. Tian et al. reported that LLZO has a much greater bandgap difference between the surface and bulk compared with other SSEs, which traps excess electrons in pores and cracks.\textsuperscript{50,51} Kim et al. explained the propagation of lithium dendrites along the grain boundary of LLZO by a reduced Schottky barrier height (0.5 eV), caused by defect state localization.\textsuperscript{52} While dendrites would further induce the formation or deterioration of defects. According to Krauskopf et al., vacancy diffusion is the controlling step of the stripping process.\textsuperscript{53} When the current density exceeds the limit of vacancy diffusion, the supersaturated vacancies aggregate into pores on the Li surface, resulting in continuous increase in inhomogeneity of the current density with self-accelerated interfacial deterioration.\textsuperscript{49} Moreover, Flatscher et al. found that the current density needed for lithium dendrites to crack a defect-free single grain of LLZO is only \(\approx 300 \mu\text{A cm}^{-2}\), and this value exponentially decreases with increase of the areal specific resistance.\textsuperscript{54} Such a penetrated corrosion of lithium dendrites can lead to increased contact area between lithium metal and LLZO, resulting in continuous electrolyte reduction.

In short, to improve the electrochemical compatibility between lithium metal and LLZO, it is vital to maintain good physical contact and electrochemical stability during long-term cycling. Methods such as chemical polish, heat treatment, and chemical corrosion can effectively eliminate surface impurities, such as LiOH and Li\textsubscript{2}CO\textsubscript{3}, and achieve an intimate contact at the LLZO/Li interface (Figure 4c).\textsuperscript{47} but the stiff surface of LLZO still cannot release the stress caused by the volume change of lithium metal during cycling, resulting in quick deterioration of the surface contact. Applying external pressure, as shown in Figure 4d, is another method for achieving long-lasting contact. Krauskopf et al. reported that a stable and compact contact can be realized by applying external pressure (\(\approx 35 \text{MPa}\)) because of plastic deformation and creep of lithium metal.\textsuperscript{53} But this method is still questionable because the high density (>5.0 g cm\textsuperscript{−3}) suggests that the thickness of the LLZO pellet should be lower than 100 μm for practical use, which makes the electrolyte mechanically vulnerable to crush. Note that the aforementioned methods pay no attention to electrolyte degradation. Using an alternative anode with a higher chemical potential can be effective in inhibiting the reduction of LLZO. Yoshima et al. fabricated a 12 V-class bipolar solid-state battery with an LLZO electrolyte, a Li\textsubscript{17}Ti\textsubscript{3}O\textsubscript{12} (LTO) anode, and a LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4} cathode that can be stably operated at 2 C for 200 cycles.\textsuperscript{29} However, the use of a higher-chemical-potential LTO anode will sacrifice battery energy density.

Surface coating is effective for maintaining both electrochemical stability and physical contact for long-term cycling. There are two major categories of coating materials. The first one is the mixed ionic-electronic conductor, which can be lithiated during electrochemical cycling to form Li alloy. In this case, the high electronic conductivity of the coating layer helps to homogenize the interfacial current density, the high bulk diffusion of Li ions in the alloy suppresses the formation of voids at the Li surface, and the potential upshift of Li in the alloy makes the interfacial layer compatible with LLZO.\textsuperscript{55} Graphite is often chosen as a buffer layer as it can be lithiated to form LiC\textsubscript{6}, which enables good contact to lithium metal and high electronic conductivity for homogenizing the interfacial current. In addition, the low density and low cost of graphite make large-scale interfacial processing possible. As shown in Figure 4e, Zhang et al. coated a candle soot layer on the surface of LLZTO by a facile flame vapor deposition method; the graphitic composition of candle soot formed a mixed electronic-ionic network after lithiation and reduced the original Li\textsubscript{2}CO\textsubscript{3} into a highly lithophilic interlayer.\textsuperscript{56} Sun et al. designed a flake-graphite coating layer by paint-spraying technology and regulated the thickness of the coating layer by spraying distance and time.\textsuperscript{57} Zhang et al. hot pressed LLZTO powder between two graphite foils to densify and modify an LLZTO pellet via a one-step route.\textsuperscript{58} Another example to fabricate a mixed conductive coating layer is to apply the atomic layer deposition (ALD) method to coat a metal (e.g., Ag, Sn) or metal oxides (e.g., Al\textsubscript{2}O\textsubscript{3} or ZnO) on LLZO, followed by infiltrating melting lithium into the coating layer to form a Li alloy. Han et al. used ALD to form a Li–Al alloy, where the high binding energy between Li and the Li–Al alloy greatly reduced the areal specific resistance to 1.0 cm\textsuperscript{−2}.\textsuperscript{37} However, more facile methods should be proposed because the ALD method is rather expensive for mass battery manufacturing.

Zhong et al. fabricated a nanosized interlayer by dropping 10 μL of Zn(NO\textsubscript{3})\textsubscript{2}/isopropanol solution onto the surface of LLZTO, followed by reacting melted lithium metal with Zn(NO\textsubscript{3})\textsubscript{2} to form an interface composed of a Li–Zn alloy, Li\textsubscript{2}O, and Li\textsubscript{3}N, where and the ASSLMB with the modified LLZTO can work at 1 C for 380 cycles.\textsuperscript{59} Sun et al. constructed an Ag/WSe\textsubscript{2} interface by simply buffing a Ag/WSe\textsubscript{2} powder mixture on an LLZTO pellet in air, where the layered lubricant WSe\textsubscript{2} ensured a good LLZTO/Li interfacial contact and Ag reacted with lithium to form an Li–Ag alloy interlayer, bringing a high capacity retention of 90% after 500 cycles for the Li/modifed-LLZTO/LFP battery.\textsuperscript{60}

The second type of coating material is ionic conducting and electronic isolating, thus eliminating the lithium dendrite growth and surface reaction. Li\textsubscript{4}N is considered a promising candidate as it possesses high room-temperature ionic conductivity (10\textsuperscript{−3} S cm\textsuperscript{−1}), is electronically insulating, and has good wettability and electrochemical stability with lithium. Cheng et al. studied the SEI layer at a LiPON/Li interface using cryogenic electron microscopy and a cryogenic focused ion beam. They found that there was a concentration increase of P and N from lithium to LiPON, which is related to the reaction products Li\textsubscript{1}P\textsubscript{2}O\textsubscript{5} and Li\textsubscript{3}N being stable against lithium metal.\textsuperscript{61} Xu et al. used the plasma-enhanced chemical vapor deposition method to fabricate a Li\textsubscript{1}N-coated LLZTO pellet, where the Li/LLZTO/LFP battery showed a long life of more than 300 cycles at 40 °C (Figure 4f).\textsuperscript{62} SPEs were also frequently used for their flexibility and electronic insulation, and excellent thin-film processability can make up for their low conductivity at room temperature. Zhou et al. coated a single-ionic conducting polymer thin layer (\(\approx 3 \mu m\)) on an LLZTO pellet, and the Li/LLZTO/LFP battery showed a...
Coulombic efficiency of nearly 100% during cycling with the crystal structure of LLZTO unchanged.[63]

3.2. Interface Between LLZO and Cathode

Although it was believed that LLZO possesses an electrochemical window of up to 5 V or higher at the LLZO/cathode interface,[64] it may be overestimated by test errors as commented on in the Introduction. By first-principles calculations, it was found that the equilibrium phases of LLZO are Li2O2, La2O3, and La2Zr2O7 at 2.91 V, and O2, La2O3, and La2Zr2O7 above 3.3 V,[65] which are insufficient because the working range of some cathode materials can reach 5.0 V.[66] More recent studies have shown that LLZO can react with common cathode materials such as LFP, LCO, and LiMn2O4 at voltages lower than 4.0 V.[41,66,67] Hansel et al. reported that an ASSLMB composed of Ga-doped LLZO and LiMn1.5Ni0.5O4 cathode cannot be cycled as a voltage drop happens at ∼3.8 V during the first charge process with continuous irreversible reactions at the interface.[68]

On the other hand, a huge interfacial resistance between the cathode and LLZO resulted in poor electrochemical stability, which can be attributed mainly to two reasons: 1) poor initial contact due to the rigidity of the LLZO surface and 2) accumulated volume changes of the cathode materials during repeated cycling, that is, ∼3% for LCO, ∼6.6% for LFP, ∼6.5% for LiMn2O4, and ∼2–6% for NCM depending on the Ni content.[69] Although the pulsed laser deposition, chemical vapor deposition, and radio-frequency magnetron sputtering methods can create compact interfaces for thin-film ASSLMBs, bulk-type ASSLMBs with high loading should adopt a more cost-effective method.

The methods to improve the interfacial compatibility vary with the battery assembly process. For an LLZO-based ASSLMB assembled by the cosintering method, a slurry-containing cathode active material and binder is first coated on the LLZO pellet, followed by sintering to remove the solvent and binder to form a dense solid structure. Adding a proper sintering additive is the most common method to enhance the electrochemical stability at the LLZO/cathode interface. Interfacial engineering is particularly necessary during this process as high sintering temperature (>500 °C) can induce element diffusion at the LLZO/cathode interface, forming unstable phases with huge interfacial resistance. As shown in Figure 5a, Zhang et al. reported that LLZO is unstable against NCM at 873 K as Li in LLZO would exchange with Ni in NCM, forming a Li-depletion layer.[70] By combining thermodynamic simulation and experiment, Il'ina et al. revealed a high reactivity between LLZO and a cathode (LCO, LiMn2O4, and LFP) between 400 and 800 K.[71] To achieve high cathode loading for practical utility, LLZO particles are usually mixed with cathode active materials in slurry to enhance the overall ionic conductivity, where the particle size of the cathode material needs to be reduced to obtain more rapid Li+ diffusion and smaller volume change,[72] but these processes can further facilitate the electrochemical degradation of LLZO. For creating a buffer layer at the LLZO/cathode interface, Li3BO3 is the mostly used additive, which possesses acceptable ionic conductivity (2 × 10−6 S cm−1 at room temperature) and a low melting point (700 °C), and is effective in increasing the interfacial contact and suppressing reactions between LLZO and the cathode.[72,73] To further eliminate the negative effect of Li2CO3, Han et al. fabricated a Li2.3Ca0.7B0.3O3 powder by heating a Li2CO3 and Li3BO3 mixture, and a slurry containing Li2.3Ca0.7B0.3O3, Li2CO3-coated

Figure 5. a) Elemental diffusion at the LLZO/cathode interface fabricated by cosintering. Reproduced with permission.[70] Copyright 2018, American Chemical Society. b) Effect of sintering additives on improving electrochemical stability. Reproduced with permission.[74] Copyright 2018, Cell Press. c) Crack formation due to volume change of cathode particles during cycling. Reproduced with permission.[72] Copyright 2019, American Chemical Society. d) Poor contact at the LLZO/cathode interface. And interface improvement by a flexible solid framework. Reproduced with permission.[80] Copyright 2018, Elsevier. e) Interface improvement by a quasi-solid interlayer. Reproduced with permission.[81] Copyright 2017, American Chemical Society. f) Interface improvement by a liquid interlayer. Reproduced with permission.[84] Copyright 2017, American Chemical Society. “LiTFSI” stands for lithium bis[( trifluoromethyl) sulfonyl] azanide and “SCN” stands for succinonitrile.
LCO, and LLZO powders was cosintered on the LLZO pellet. As shown in Figure 5b, the spontaneous reaction between Li$_{2}$$_{3}$+Ca$_{2}$+B$_{2}$O$_{3}$ and Li$_{2}$CO$_{3}$ created a highly conductive Li$_{2}$$_{3}$+Ca$_{2}$+B$_{2}$O$_{3}$ interface.[74] Liu et al. used both Li$_{3}$BO$_{3}$ and high-electronic-conductive In$_{2}$SnO$_{3}$ as sintering additives, and the NCM/Li$_{3}$BO$_{3}$/In$_{2}$SnO$_{3}$ composite cathode without LLZTO achieved a capacity of 101 mAh g$^{-1}$ at a relatively high loading.[75] Liu et al. coated NCM particles with LTO, and a Li[Ti$_{0.1}$Mn$_{0.9}$]O$_{2}$ interface formed at the particle surface of the active material, during the co-sintering of NCM, Li$_{3}$BO$_{3}$, and In$_{2}$$_{3}$+Sn$_{2}$O$_{3}$, which enhanced the electrochemical performance of the Li/LLZTO/NCM battery.[76] Precoating rigid oxide layers with a wide electrochemical window on the surface of LLZO was also frequently applied. Alexander et al. deposited amorphous LiNbO$_{3}$ on both sides of LLZTO, which decreased the interfacial resistance from 1078 to 91 Ω cm$^{-2}$.[77] Sastre et al. fabricated a Nb$_{2}$O$_{3}$ interlayer by the ALD method, and during cosintering at 700 °C, the in situ formed Li–Nb–O layer successfully inhibited the formation of LaCoO$_{3}$ at the LLZO/LCO interface.[78] However, during high-rate cycling, the aforementioned rigid interface is fragile due to rapid volume changes of the cathode particles, resulting in crack formation and poor cycling behavior (Figure 5c).

The traditional slurry-casting method, in which the slurry containing the active material, binder, and conductive carbon is directly coated on the LLZO surface or current collector, is more facile compared to cosintering. However, the method cannot be directly used in bulk-type ASSLMB systems due to the insufficient interfacial contact,[79] which can be explained by massive interspaces formed at the LLZO/cathode interface during solvent evaporation. During this process, the assistance of a soft antioxidant interlayer is needed to guarantee both good contact and electrochemical stability, and the flexibility makes the interlayer more effective in dealing with accumulated volume changes of the active material particles during repeated cycling. Plastic crystals are promising candidates as they possess high ionic conductivity, a wide electrochemical window, and excellent flexibility. However, previous studies showed that LLZO is not chemically stable against carbonate-based liquid electrolytes, where Li$^{+}$/H$^{+}$ ion exchange and continuous formation of impurities such as Li$_{2}$CO$_{3}$ at the LLZO surface can occur during cycling.[82,83] On the other hand, the decomposition products of a liquid electrolyte, such as LiF, Li$_{2}$CO$_{3}$, and CH$_{3}$OH, possess low ionic conductivity, which would result in capacity decay during cycling. Xu et al. added the superfine n-BuLi into a liquid electrolyte interlayer between LLZO and a cathode, where the Lewis basic additive suppressed the decomposition of the liquid electrolyte and Li$^{+}$/H$^{+}$ ion exchange, forming a liithiated LLZO/liquid electrolyte interface to improve the interfacial ionic conductivity (Figure 5f).[84] An ionic liquid (IL) with much improved thermal stability, extremely low flammability, and a wide potential window might be a better candidate, and components based on piperidinium, tetraalkylammonium, or pyrrolidinium cations are stable against lithium metal.[85] Pervuz et al. employed N-methyl-N-n-propylpyrrolidinium bis[(fluorosulfonyl)imide] (Pyr$_{14}$FSI) as the interlayer and the assembled bipolar battery (Li/LLZO/LFP) can operate stably at room temperature under 20 mA g$^{-1}$ at a voltage of 6.8 V and deliver a specific capacity of 145 mAh g$^{-1}$.[86] It is worth mentioning that sulfur with low plateau voltage (<2.5 V) and high theoretical capacity (1675 mAh g$^{-1}$) might be more electrochemically stable with LLZO, but the chemical potential difference between the oxide and sulfide can lead to the formation of a space charge layer with huge interfacial resistance. Hitz et al. designed a novel tri-layer Ga-doped LLZO (LIZGO) structure and the assembled Li/LLZO/S battery exhibited a low total areal specific resistance of 7 Ω cm$^{-2}$ by using a 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonil)imide IL.[87]

4. LATP Solid Electrolyte

Since Hagman and Kierkegaard reported the crystal structure of NASICON (Li$_{3}$[PO$_{4}$]), M = Ge, Ti, Zr) in 1968, the properties of different chemically substituted NASICON-type electrolytes have been studied.[88] Among those, LATP shows good comprehensive properties, including high ionic conductivity (10$^{-4}$ S cm$^{-1}$ at room temperature), lower raw material cost compared with LLZO, lower density (2.9 g cm$^{-3}$), and good chemical stability against moisture. Although another NASICON electrolyte, Li$_{1.1}$Al$_{0.9}$Ge$_{2.5}$PO$_{4}$ (LAGP) possesses similar properties and a relatively higher ionic conductivity (up to 10$^{-3}$ S cm$^{-1}$ at room temperature), large-scale production of LAGP is inhibited by the much higher price of germanium compounds.[12]

It is widely accepted that the LATP/cathode interface is electrochemically stable. According to Zhu et al., LATP possesses not only the highest oxidation onset voltage of 4.31 V, but also the lowest decomposition energy of ~0.06 meV per atom at 5 V (Figure 6a), indicating the best electrochemical stability among the most common SSES.[81] Also, there have been studies using LATP as a surface coating layer for various cathodes to enhance structure stability and to resist electrolyte erosion, and great electrochemical stability has been found even at a high cycling temperature of 150 °C.[89,90] However, due to the rigid nature of oxide electrolytes, the LATP/cathode interface still suffers from poor contact. Yu et al. studied the high-temperature (500–800 °C)
chemical stability between LATP and various cathode materials and found that although a thermodynamically stable phase formed at the LATP/LFP interface at a temperature lower than 500 °C, the interface between LATP and a layered or spinel cathode can degrade at 600–700 °C due to disparity of Li concentrations,[91] which is consistent with the report by Gellert et al. that oxide cathodes are highly reactive to LATP at a sintering temperature as low as 500 °C.[92] Therefore, research on low-cost, effective LATP/cathode interfacial engineering is still needed.

However, real attention should be paid to the LATP/Li interface. As shown in Figure 6b,c, the redox voltage at ≈2.5 V versus Li/Li⁺ indicates that LATP is highly electrochemically incompatible with lithium metal, and the immediate reaction after contact will cause amorphization of the electrolyte and reduction of Ti⁴⁺ to Ti³⁺. The obtained composition is not only a lower ionic conductor, but also has an electronic conductivity three orders of magnitude higher than that of the bulk electrolyte. This can be explained by the much lower bandgap of the Ti³⁺-containing product, thus facilitating insertion of lithium into the electrolyte and causing further deterioration.[93,94] In addition, the lithiation process can lead to an elongation along the c-axis and shrinkage along the a-axis, which can generate a huge stress inside the rigid LATP pellet, forming pores and cracks during cycling, with eventual mechanical failure. As shown in Figure 6d, in situ transmission electron microscopy observation conducted by Zhu et al. shows that the original Li₁₋ₓAl₀₋ₓTiₓ(PO₄)₃ was reduced to Li₁₋ₓAl₀₋ₓTiₓ(PO₄)₃ upon contact with Li, where the stress generated from the crystal structure change was huge enough to bend the LATP nanorod.[95]

Recently, Kou et al. optimized the morphology and ionic conductivity of LATP by adjusting the hydrologic synthesis pH value to 6.0, and the optimized LATP exhibited good electrochemical stability against lithium and the assembled Li/LATP/LCO battery retained 94% of its initial capacity after 300 cycles at current density of up to 2.0 C at room temperature.[96] However, the mechanism for suppressing LATP reduction by this method is unclear. Research on improving electrochemical and physical compatibility at the LATP/Li interface is focused mainly on constructing interfacial layers, where coating metal oxides on either side of the interface is commonly used to block electronic conduction, but this method can also lead to a huge interfacial resistance, and the batteries usually operate at only low current density. Liu et al. used the ALD method to coat a robust Al₂O₃ layer on LATP, but the in situ formed Li–Al–O layer cannot fully suppress the reduction of Ti⁴⁺, resulting in a Ti³⁺ dominant depth of 16 nm and huge interfacial resistance (150 KΩ after 300 cycles).[97] Bai et al. fabricated an Al₂O₃–ZnO composite layer by radio-frequency magnetron sputtering, where the semiconducting nature of ZnO resulted in an increase in areal resistance from 1.04 × 10⁴ to 3.65 × 10⁵ Ω cm² for the Li/LATP/Li symmetric battery.[98] Hao et al. introduced a ZnO interlayer by magnetron sputtering, which reacted with lithium to form an SEI layer composed of electronic conducting Zn and electronically insulating Li₂O, both homogenizing the interfacial current and suppressing the LATP reduction.[99] Nevertheless, the
The aforementioned coating methods are always expensive and time-consuming, and more facile methods should be adopted for practical fabrications. LiF, with a wide electrochemical window and an electronically insulating nature, is effective not only in suppressing side reactions at the SSE/Li interface, but also in inhibiting the penetration of lithium dendrites. Recently, numerous facile methods to fabricate a LiF-rich SEI layer have been proposed, for example, reacting lithium with F2 gas or various kinds of fluorides. As shown in Figure 7a, Yang et al. used a 2 min coating process by dropping a dimethoxy ethane (DME) solution of LiBF4 and Mg(ClO4)2 on Li foil, where the formed coating layer composed of LiF, MgF2, and B2O3 inhibited LATP reduction in a Li/LATP/LFP battery, resulting in a capacity retention of 98% after 500 cycles at 1.5 C. However, the poor ionic conductivity of LiF requires precise thickness control of the Li-rich layer, which is also the case for Li3PO4, a Si material that is chemically stable against both lithium metal and the liquid electrolyte, but suffers from poor ionic conductivity.

As shown in Figure 7b, Liu et al. fabricated a Li3PO4-rich SEI layer by immersing lithium metal in 0.4 wt% poly(phosphoric acid) in a dimethyl sulfoxide solution and using a commercial carbonate-based liquid electrolyte for LATP/Li interfacial wetting. The Li–Li3PO4/LATP/Li–Li3PO4 symmetric battery showed a total resistance ten times higher than that of Li/LATP/Li (≈18 000 Ω), and the existence of the liquid electrolyte not only reduced the total areal specific resistance to 57.82 Ω cm−2, but also formed a stable solid–liquid interfacial layer. Li3PO4 effectively blocked the continuous consumption of the liquid electrolyte by lithium metal, thus enhancing both the electrochemical and physical stability during long-time cycling.

As shown in Figure 7c, SPEs are also commonly used to ensure electronic isolation and good contact. PEO-based SPEs are widely chosen for their low cost and flexibility. However, the high glass transition temperature of PEO limits the operation temperature of the battery, and it is not mechanically tough enough to fully suppress the penetration of lithium dendrites. Yu et al. drop coated the surface of LATP with a mixture of highly ionic conducting poly(bis(2-(2-methoxyethoxy)ethoxy)phosphazene) and mechanically stable PVDF–HFP, and the optimized SPE showed an ionic conductivity of 0.26 mS cm−1 at 50 °C. However, the large interfacial resistance at LATP/SPE led to a 35% increase of the total resistance of SSE, and the battery can only be operated at elevated temperature.

Also, to avoid dendrite penetration during cycling, the total thickness of SPE layers is usually tens or even hundreds of microns, which not only lowers battery energy density, but also increases the total resistance. Therefore, it is important to limit the thickness of the SPE interlayer and add plasticizers to decrease the interfacial resistance. Lin et al. fabricated an ion-conductive gel (ICG) interlayer by drop coating a mixture of Pyr13TFSI, a polymer monomer, a salt, and an initiator on the surface of an electrode followed by in situ thermal polymerization (Figure 7d). The existence of the IL greatly increased the ionic conductivity and wettability of the interlayer, and the decomposition products of TFSI− (LiF, Li3N) provided durable protection for LATP. As a result, the Li/ICG/LATP/ICG/LFP

Figure 7. Interlayers with different components for improving the electrochemical stability at the LATP/Li interface. a) A rigid interlayer. Reproduced with permission. Copyright 2020, Wiley-VCH. b) A rigid–liquid composite interlayer. Reproduced with permission. Copyright 2017, Royal Society of Chemistry. c) A soft interlayer. Reproduced with permission. Copyright 2019, American Chemical Society. d) A soft–liquid composite interlayer. Reproduced with permission. Copyright 2020, American Chemical Society. e) Rigid–soft–liquid composite interlayers. Reproduced with permission. Copyright 2019, Cell Press. “Pyr13TFSI” stands for “N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide” and “BN” stands for “boron nitride”.

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battery achieved a capacity retention of 92% after 200 cycles at 0.5 C.[111] As shown in Figure 7e, Cheng et al. fabricated a composite interlayer composed of a BN and poly(ethylene glycol dimethyl ether)-plasticized PEO–LiTFSI SPE. The chemically stable BN layer with a thickness of 5–10 nm possessed low electronic conductivity (10⁻¹⁰ S cm⁻¹) and a high Young modulus (≈1.0 TPa), which suppressed the LATP reduction and lithium dendrite growth. The Li/PEO/BN/LATP/PEO/LFP battery showed a high capacity retention of 97% at 0.5 C after 500 cycles with 98% of the surface titanium remaining as Ti⁺.¹¹⁴

5. Sulfide Electrolytes

Compared with oxide electrolytes, sulfide electrolytes have several advantages. First of all, they possess higher ionic conductivity (up to 10⁻² S cm⁻¹ at room temperature) as their crystal lattices provide smaller binding energy and larger immigration changes. As shown in Figure 8, the narrow electrochemical windows make them incompatible with conventional electrode materials, which makes strategies to enhance electrochemical stability vital for sulfide-based ASSLMBs.[115]

5.1. Interface Between Sulfide Electrolyte and Anode

At the sulfide/Li interface, as calculated, the decomposition of the sulfide by lithium metal is inevitable as all the sulfides have high reduction potentials above 1.7 V. The equilibria phase against lithium metal can be divided into three categories: 1) ionic and electronic isolated compounds such as lithium halides (LiCl, LiBr, LiI and Li₂S); 2) ionic conducting compounds such as Li₃P; and 3) mixed conductive Li–M alloys (M = Ge, Sn, and Sb).[115] Schwietert et al. provided a reaction pathway of argyrodite LiₓPₓS₂-ₓCl where Li₆PS₅Cl decomposed at 2.24 V into Li₉PS₆, S, and LiCl by forming the unstable Li₁₁PS₅Cl mesophase first, followed by further oxidation of Li₆PS₅ into 2.9 V into P₂S₅⁺. On the other hand, Li₆PS₅Cl can be decomposed around 1.08 V into P, Li₂S, and LiCl by forming unstable Li₆PS₅Cl first, and after that, P is further reduced to Li₂P at 0.63 V.[116] Han et al. designed a novel Li/LGPS/LGPS–C/Pt cell to enhance interfacial contact by mixing LGPS with carbon, revealing that the oxidation of LGPS begins at 2.1 V and the reduction begins at 1.7 V, and pointed out the narrow electrochemical window originates from the oxidation of S and the reduction of P or Ge.[114]

As shown in Figure 9a, the electrochemical stability of the SEI layers varies with the composition, according to the work by the Janek group, who studied the SEI layers of several sulfide electrolytes (LiₓPₓS₂ₓ, LGPS, Li₆PS₅Cl, LiₓPₓSₓX (X = Br, Cl, I)).[117] The SEI sickness is proportional to the square root of time.[117–119] As shown in Figure 9b, Sang et al. designed a novel Au/SSE/Li battery by e-beam deposition of Au on β-Li₂PS₅ or LGPS and revealed that the significant decomposition of both electrolytes happened at ≈0.3 V, and for β-Li₂PS₅, the degradation process of PS⁴⁻ into P₂S₅⁺ was reversible as Li ions were reintroduced into the electrolyte, whereas the degradation of LGPS was irreversible.[115] Tan et al. also found that the Li-In/LiₓPₓS₂ₓCl/LiₓPₓS₂ₓCl–C half-battery can be cycled reversibly, as LiₓPₓS₂ₓCl will be first reduced to LiₓPS₄ before forming Li₂S and LiP (Figure 9c).[116] Due to the insufficient electronic isolation of Li₂S (10⁻⁹ S cm⁻¹ at room temperature) and huge volume change (150%) during reduction,[121,122] the growth of lithium dendrites has been found in different sulfide electrolytes once the current density reaches 1 mA cm⁻² (Figure 9d).[123–125] Han et al. determined the growth of lithium dendrites in LiₓPS₄ during Li plating using in situ neutron depth profiling, and they suggested that the presence of mobile electrons in the electrolyte provided the driving force for Li nucleation.[126]

Although applying pressure is practical in sulfide-based ASSLMBs as the electrolytes are deformable without cracking, as shown in Figure 9e, Li-In/In cells applied with external pressure could be steadily discharged at 2 mA cm⁻².[127] However, this method cannot suppress the decomposition of the electrolytes by lithium metal. There have been methods focusing on enhancing the electrochemical compatibility of the sulfide/Li interface thermodynamically. With a flat voltage plateau of 0.62 V, LiₓIn (0 < x < 0.9) alloy is frequently used to partly suppress the sulfide decomposition, but it will lower the energy density of the battery due to the reduced voltage and higher density (7.3 g cm⁻³) of indium. Replacing a part of the sulfur with oxygen can also enhance the electrochemical stability and moisture resistance of sulfide electrolytes, but the introduction of grain boundary resistance and reduction in lattice volume can lead to lower ionic conductivity.[128] Sun et al. fabricated Liₓ₀GeₓPₓS₁₋ₓOₓ (0.3 ≤ x ≤ 0.6) electrolytes with room-temperature ionic conductivity ranging from 1.03 × 10⁻² to 8.43 × 10⁻³ S cm⁻¹ and wider electrochemical windows, but

Figure 8. Decomposition energy of various sulfide electrolytes as a function of Li chemical potential or applied voltage. Reproduced with permission.[115] Copyright 2015, American Chemical Society.
the enhancement is not sufficient enough to suppress the reduction of electrolytes, resulting in rapid capacity fading of the Li/sulfide electrolyte/LCO batteries in a few cycles. Recently, a few types of oxysulfide-type electrolytes with lower activation energies have been theoretically discovered, but the slightly enhanced electrochemical windows cannot satisfy practical utility yet.

As the aforementioned methods are not effective and the thermodynamic decomposition of sulfides is almost inevitable, strategies for enhancing electrochemical stability should be developed to kinetically suppress the decomposition of sulfides. Recently, Lee et al. replaced Li with a Ag–C nanocomposite, where the Li from Li6PS5Cl and NCM reacted with Ag to form a uniform Li–Ag alloy, which guaranteed that a more uniform Li deposition with C remained at the top of the anode to separate the sulfide electrolyte and the Li–Ag alloy. Lithium halides can also stabilize the sulfide/Li interface as they are thermodynamically stable against lithium metal, among which LiF has a bandgap of 8.70 eV and high interface energy against lithium metal, which is sufficient to suppress lithium dendrites or electrons. As shown in Figure 9f, surface treating of Li by I2 or HFP to form a LiI- or LiF-rich SEI layer could effectively consume the penetrated lithium dendrites for Li2P3S11. The result showed that a much higher energy at the LiF/Li interface, compared to that at the LiI/Li interface, effectively relieved the interfacial stress and promoted a more uniform Li deposition. Thereby, good cycling stability was realized for the LiF–Li/Li2P3S11/LCO battery.

IL and organic liquid electrolytes can be added at sulfide electrolyte/electrode interfaces to in situ form ionically conducting and electronically isolating SEI layers, and the existence of the liquid phase can fill the pores between the solid electrolyte and the electrode, as well as the voids inside the electrolyte, to homogenize the current density. Gao et al. added different liquid electrolytes to form an SEI layer against the reactions between...
lithium and LGPS and revealed the dependence of SEI stability on the types of salts and liquids.\cite{135} The work of Zheng et al. revealed that bare IL Pyr13TFSI could hardly stabilize a Li10SnP2S12/Li interface, while F-containing Li salts played a critical role by forming an optimized amount of LiF (Figure 9g).\cite{136} According to the work of Oh et al., ether groups in the cation of [Li(triglyme)][TFSI] can react with Li3PS4 or LGPS because of the attack by oxygen toward electropositive elements (P and Ge).\cite{137} However, more studies on the stability between liquid additives and sulfide electrolytes should be conducted.

5.2. Interface Between Sulfide Electrolyte and Cathode

To achieve good contact at the sulfide/cathode interface, electrode processing methods, such as pulsed laser deposition or solvent-based routes are explored.\cite{138,139} One of the most facile and economical methods is dry processing, where conductive carbon, an active material, and a sulfide electrolyte are mixed and densified by external pressure. By adding a minimum amount of polytetrafluoroethylene (PTFE) as binder, Hippaud et al. fabricated a flexible and self-standing composite cathode by a scalable mixing and shearing process and compressed it on the electrolyte pellet to achieve a low interfacial resistance.\cite{140} However, typical sulfide electrolytes can be oxidized below 2.5 V, and the oxidation products are mainly sulfur, GeS2, and P2S5.\cite{115} The presence of sulfur is unfavorable because its lithiation can generate a huge volume expansion.\cite{122} Partial delamination has been observed between the electrolyte and cathode because a sulfide electrolyte such as β-Li3PS4 cannot reoccupy the void space caused by volume change of nickel-rich layered oxides.\cite{143} Apart from oxidation, the interdiffusion of transition metal elements in the cathode and P or S in the electrolyte can lead to the formation of highly resistive interfaces. Chen et al. found that severe reactions occurred between sulfides like Li3PS4–90Li10PS4–10LiI, 90LiI3PS4–10LiCl and cathode materials like NCM, LiNi1–x–yCo0.15Al0.85O2 (NCA), especially in the charge process.\cite{142} An interlayer between LCO and Li3S–P2S5 also formed when the battery was charged to 4.2 V because of the high reaction activity of the delithiated cathode.\cite{144} As shown in Figure 10a–c, a combination of volume change, side reactions, and the space-charge effect at the sulfide/oxide interface could lead to severe capacity fading of sulfide-based ASSLMBs.\cite{143,145,146} For Li3PS4Cl, the cathode site contributed more to the interfacial resistance, as revealed by Tan et al.\cite{120} Applying pressure can ensure good contact between the cathode and sulfide electrolyte during cycling. As reported by Ye et al., with mechanical constrictions, sulfides such as LGPS and Li9.54Si1.74P1.44S11.7Cl0.3 can form a stable core–shell structure composed of pristine electrolyte and the decomposed product with further sulfide decomposition suppressed. For LGPS, as the pressure increased, the upper limit of voltage for maintaining thermodynamic stability could be extended from 2.1 to nearly 4 V, and the battery under high pressure could be operated steadily with a Li/graphite anode and LiCo0.5Mn1.5O4.

Figure 10. Illustration of factors for electrochemical instability at the sulfide–electrolyte/cathode interface. a) Oxidation of electrolyte. Reproduced with permission.\cite{143} Copyright 2010, American Chemical Society. b) Contact loss during cycling. Reproduced with permission.\cite{146} Copyright 2017, American Chemical Society. c) Formation of space-charge layer. Methods to enhance the electrochemical stability at the sulfide–electrolyte/cathode interface, including d) applying external pressure, e) altering the composition of the sulfide electrolyte, and f) fabricating an interficial coating layer. (d) Reproduced with permission.\cite{147} Copyright 2020, Wiley-VCH. (e) Reproduced with permission.\cite{156} Copyright 2020, Elsevier. (f) Reproduced with permission.\cite{157} Copyright 2020, Springer Nature. “NCA005” stands for “LiNi0.8Co0.15Al0.05O2,” “NCA015” stands for “LiNi0.7Co0.15Al0.15O2,” and “NCA025” stands for “LiNi0.6Co0.15Al0.25O2.”
cathode at 2.5–5.5 V (Figure 10d).\[147\] Introducing an electronic isolating oxide buffer layer (e.g., Al₂O₃, ZrO₂) is also known to eliminate the space-charge effect and suppress the decomposition of sulfides kinetically.\[148,149\] Among various oxides, LiNbO₃ is the most studied as it has a relatively high room-temperature ionic conductivity of 10⁻⁶ S cm⁻¹ and enables effective suppressing of elemental interdiffusion.\[140,150\] Other candidates such as Li₂SiO₃, LTO, LiTaO₃, and Li₁₃PO₄ were also used for surface coating by various methods.\[143,151–153\]

Altering the composition of sulfide electrolytes or cathode materials can also be effective in improving electrochemical stability. Eom et al. found that the presence of Li₃BO₃ could enhance the ionic conductivity of Li₂S–P₂S₅, and the Li–In/97(0.78Li₂S·0.22P₂S₅)·Li₁₃BO₄/LCO battery exhibited a nearly 100% Coulombic efficiency and a high capacity retention of 96% after 40 cycles at 0.1 C.\[154\] A work by Xu et al. showed that the formation of an Al-rich domain with a low electronic conductivity at the surface of LiAlₓCo₁₋ₓO₂ can act as a passivation layer against an electrolyte.\[155\] Li et al. revealed that heavy Al substitution in LiNi₀.₅ₓ₋₀.₅Co₀.₁₅AlₓO₂ (x = 0.05, 0.15, 0.25) could enhance its interfacial stability with LGPS, as shown in Figure 10e.\[156\] Recently, Lim et al. proposed a cosintering route to in situ fabricate a Li–W–O and Li–Ta–O layer on the surface of NCM to improve its interfacial stability against the sulfide (Figure 10f).\[157\] Deng et al. introduced carbon nanotubes in a cathode to homogenize the current density of the composite cathode, where the decomposition of LGPS caused by NCM or nanotubes was successfully suppressed by polymer coating on both the carbon nanotubes and NCM.\[158\]

6. Solid Polymer Electrolytes

Composed of a polymer matrix as the solvent and lithium salt as the solute, SPEs possess higher flexibility and lower density (1.0–1.5 g cm⁻³) than inorganic SSEs, which enhances the energy density of batteries, and are compatible with tape-casting processing of current LIBs.

Since the first report of a PEO-based SPE by Fenton et al. in 1973,\[159\] different kinds of polymers have been investigated to fabricate SPEs, such as polyethylene, polycarbonate, polyester, polyvinylidene fluoride, polyacrylonitrile, polyvinyl alcohol, and polyaniline. The electrochemical stability of these polymers has been studied by theoretical calculations. Chen et al. calculated the electrochemical windows of ten polymers with different structural complexities (single chain, ordered slabs, and disordered slabs) and claimed that all the polymers showed a wide electrochemical window >4.74 eV, indicating that they are thermodynamically stable against a lithium metal or oxide cathode (except for PEO and poly(propylene oxide)).\[160\] On the other hand, higher electronegativity means stronger absorption of the polymer to Li atoms. A work by Ebadi et al. indicated that PAN is unstable in contact with metallic Li due to the strong electron- withdrawing nitrile groups, and polymers such as poly(ethylene carbonate), PTMC, and poly(e-caprolactone) are also unstable with Li in the presence of the strong polarity of the carbonyl C=O bonds.\[161\] Moreover, the electrochemical stability of polymer is also influenced by their decomposition products. According to Mirsakiev et al., although the –OH groups in polymers such as PEO can react with lithium, as shown in Figure 11a, the as-formed Li₂O layer makes further decomposition unfavorable.\[162\] For PVDF, a stable LiF interface could be generated during cycling, as reported by Zhang et al.\[163\] Other studies showed that apart from the polymer itself, the Li salts used also affect the interfacial stability between SPE and Li (Figure 11b).\[164\]

6.1. Interface Between SPE and Li

Compared with single Li⁺ hopping in inorganic SSEs, ionic conduction in SPEs is achieved by Li⁺ coupling and decoupling with polar groups in polymer chains through segmental motions of polymer chains under an electric field. As shown in Figure 12a, the mobility of anions under this environment can lead to polarization of SPEs, during which a high accumulation of anions at the SPE/Li interface occurs.\[165\] As the Li⁺ transference number of most SPEs is below 0.5, the decomposition products of lithium salt become the key compositions in the SEI layer at the SPE/Li interface (Figure 12b).\[165,166,167\] Moreover, according to the space-charge theory, the depletion of anions can produce a space-charge layer and induce rapid lithium dendrite growth.\[168\]

To overcome electrochemical instability at the SPE/Li interface, it is important to fabricate a stable interlayer before or during cycling. Because the decomposition of lithium salt is almost inevitable, it is necessary to choose a lithium salt with suitable anions to form a stable SEI, where LiClO₄ or LiAsF₆ could provide best Li passivation, but the safety and environmental concerns limit their applications.\[169\] LiPF₆ is the most frequently used lithium salt for current LIBs, but it cannot successfully passivate the lithium metal surface.\[170\] Instead, more attention has been paid to Li salts with imide-based anions such as LiFSI and LiTFSI. As shown in Figure 12c, when LiTFSI was used as Li salt in a PEO-based SPE, the SPE presented a superior interfacial stability against lithium metal with an optimized amount of LiF.\[171\] In a dual-salt system for a poly(ethylene glycol)dimethyl ether based SPE, LiTFSI could elevate the ionic conductivity, and LiFSI enabled the formation of a favorable LiF-rich SEI layer.\[172\] A work by Sheng et al. showed that the addition of Li₂S in a PEO-LiTFSI battery could enable a long cycle life of a Li/PEO–LiTFSI–Li₂S/LFP battery (85% after 1000 cycles at 0.5 C) via accelerating the breaking of C–S and C–F bonds in LiTFSI to form a LiF-rich, uniform SEI layer.\[173\]

From another perspective, reducing the mobility of anions can be effective in eliminating unwanted side reactions during cycling so as to enhance electrochemical stability. Single-ion conducting solid polymer electrolytes (SIC-SPEs) have been found to show much higher Li⁺ transference numbers compared with conventional SPEs, and they better suppress lithium dendrite growth.\[174,175\] However, the ionic conductivity of SIC-SPEs (10⁻⁷–10⁻⁵ S cm⁻¹ at room temperature) is lower than that of conventional SPEs. Adding an organic liquid electrolyte into SIC-SPEs as a plasticizer is a useful method to uplift the ionic conductivity. Liu et al. fabricated a LiBF₄SEI that possessed a high Li⁺ transference number of 0.93 and an ionic conductivity of 2 × 10⁻⁴ S cm⁻¹ at 35 °C (Figure 12d).\[176\] Note that introducing anion receptors with strong Lewis acidity into SPEs can avoid sacrificing ionic conductivity, as Lewis acid–base interactions
between receptors and anions can both immobilize anions and facilitate the dissolution of the lithium salt, among which calixarenes with NH units and boron-based receptors are the most investigated.\cite{177-180} As a member of SSEs, ionic covalent organic frameworks (COF) have drawn much attention for energy storage as their aligned channels can be ion-conductive and skeletons with various functional groups can be useful to improve electrochemical properties. Ionic COFs with trimethyl borate, linked spiroborate, or substituted imidazolate-based skeletons have been reported to possess high $\text{Li}^+$ transference numbers.\cite{181-183}

Xu et al. designed the first solid-state polyelectrolyte COFs, which consisted of phenyl-based skeletons and flexible oligo(ethylene oxide) chains, and possessed much higher ionic conductivity and thermal stability compared to traditional PEO-based SPEs.\cite{184}

Compared with the aforementioned methods, adding an inorganic solid electrolyte into SPEs can be more effective to enhance the overall electrochemical properties of SPEs. An inorganic solid electrolyte can provide fast ion pathways inside the fillers, increase the $\text{Li}^+$ transference number and the organic/inorganic interfacial ionic conductivity, and the high mechanical strength

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**Figure 11.** a) Impact of PEO decomposition on extending electrochemical window of an SPE. Reproduced with permission. Copyright 2019, American Chemical Society. b) The calculated electrochemical windows of various polymers and lithium salts before and after forming SPEs. Reproduced with permission. Copyright 2020, American Chemical Society. “PEI” stands for polyethylenimine, “PVA” stands for poly(vinyl alcohol), “PEC” stands for poly(ethylene carbonate), and “PCL” stands for poly(ε-caprolactone).
is also helpful in blocking lithium dendrites. For such a composite electrolyte system, a larger organic/inorganic surface area is required for better electrochemical property as lithium salt can be dissolved more effectively and more anions can be immobilized. To this end, two methods can be used, that is, reducing the particle size and increasing the filler volume fraction. Zhang et al. fabricated a salt-free LLZTO–PEO composite electrolyte and found that reducing the LLZTO size (C2540 nm) could increase the ionic conductivity and enable long-term (700 h) and dendrite-free cycling of the Li/SSE/Li cell at a high current density (3.0 mA cm\(^2\)).\(^{[110]}\) Designing fillers with different shapes and dimensions, such as nanofibers, nanoflakes, and templates, can enhance the interfacial stability of the composite electrolyte while avoiding agglomeration.\(^{[185–187]}\) Regulating the arrangement of the fillers can also be effective, such as using a single layer of Li\(_{x}\)Al\(_{0.5}\)Ti\(_{0.95}\)Ta\(_{0.05}\)(PO\(_4\))\(_3\) particles bonded by a polymer host,\(^{[188]}\) and vertically aligned and connected LATP particles (Figure 12c).\(^{[189]}\)

6.2. Interface Between SPE and Cathode

At the SPE/cathode interface, oxidation at high voltages mainly happens in polyethylene-based SPEs, although PEO-based SPEs were reported to be antioxidant above 4.2 V.\(^{[196,190]}\) These results, however, may overestimate the upper limit of the electrochemical window of polyethylene-based SPEs as it neglects imperfect contact between the SPE and cathode. Actually, the measured electrochemical windows vary depending on the testing methods.\(^{[191,192]}\) As shown in Figure 13a, for full batteries assembled with PEO-based SPEs, “voltage noises” have been observed when batteries are charged to \(4.1 \text{ V}\), which can be explained by the oxidation of the electrolyte.\(^{[190,192]}\) A work by Yang et al. suggested that the ether chains are stable against high voltage till 4.3 V, whereas the \(-\text{OH}\) terminal group in PEO or poly(ethylene glycol) can be oxidized to \(-\text{COOH}\) with formation of Li\(_2\)O at 4.05–4.3 V (Figure 13b),\(^{[172]}\) which was supported by another report.\(^{[193]}\) On the other hand, as the “voltage noises” only occurred during the charge process, the phenomenon is also partly due to penetration of lithium dendrites during delithiation of the cathode. A recent work by Homann et al. suggested that replacing the linear structure of PEO with a semi-interpenetrating network could enable PEO-based SPEs to resist oxidation up to 4.6 V.\(^{[192]}\)

To enhance the SPE/cathode stability, one of the most facile ways is to fabricate a stable CEI layer, where choosing suitable lithium salts is important.\(^{[194]}\) Boron-based lithium salts such as LiBF\(_4\) and lithium bis(oxalato)borate (LiBOB) can also decompose at the SPE/cathode interface to form passivation layers, but...
the low ionic conductivity (LiBF₄) and low solubility (LiBOB) restrict their applications.\textsuperscript{[170]} Combining the advantages of several salts can be effective in forming a stable CEI layer at the SPE/cathode interface. As reported by Li et al., a PEO-based battery can sustain a long cycle life (85% retention after 200 cycles) when a triple-salt system (0.3 M LiTFSI, 0.2 M LiBOB, 0.025 M LiPF₆) is used, where the LiBOB and LiPF₆ decompose on LAGP-coated LCO to form a stable CEI layer (Figure 13c).\textsuperscript{[195]} A work by Wang et al. indicated that the use of a new Li salt Li(CF₃)₃COBF₃ could enable stable cycling of a PEO-based Li/SPE/NCM battery at 2.5–4.3 V by forming a CEI layer containing boron and lithium fluoride.\textsuperscript{[196]} Zhao et al. found that an effective CEI layer containing LiF formed by using AlF₃, as both additive and initiator for in situ polymerization of 1,3-dioxolane.\textsuperscript{[197]}

The instability of the SPE/cathode interface can also be eliminated by optimizing both sides. Surface coating of inactive materials such as lithiated NaFon, Al₂O₃, and LAGP on cathodes can suppress their catalytic property toward electrolyte decomposition.\textsuperscript{[193,198,199]} Redesigning the composition and structure of the polymer host can enhance the oxidation resistance and mechanical strength of SPEs. As shown in Figure 13d, cross-linking can elevate the mechanical strength of polymers, although it also restricts the movement of polymer chains, sacrifices ionic conductivity, and leads to inferior interfacial contact.\textsuperscript{[192,200,201]} Other methods, for example, fabricating a microphase-separated copolymer, have also been proposed to improve the mechanical and electrochemical properties of SPEs.\textsuperscript{[202–204]} A more convenient and low-cost method is polymer blending, using which enhanced oxidation resistance and better cycling performance could be achieved.\textsuperscript{[205–207]} Moreover, introducing side chains in linear PEO is also a useful method to improve its resistance to oxidation up to 4.73 V.\textsuperscript{[208]}

Constructing a laminated SPE by placing an antioxidant SPE layer at the cathode side and an antireductive SPE layer at the anode side is also promising due to the excellent fabricability of the SPE. Duan et al. used a conventional tape-casting method to fabricate a double-layer SPE (Figure 13e) where the combination of an LAGP-added PAN layer (antioxidant) and a PEGDA layer (antireductive) ensured good electrochemical stability on both electrodes, leading to a relatively high capacity retention of 82% after 200 cycles at 0.5 C at a high cut-off voltage of 4.5 V for the Li/SPE/NCM battery.\textsuperscript{[209]} Similar results were found by Zhou et al. and Wang et al., who obtained good electrochemical properties using a double-layer polymer electrolyte.\textsuperscript{[210,211]}

7. Conclusion

This review summarizes the basic principles of electrochemical stability of SSEs, provides a brief survey of electrochemical compatibility between SSEs and lithium-metal anodes and oxide cathodes, and sums up the recent advances in the understanding and solving of electrochemical instability at SSE/electrode interfaces. On October 9, 2020, Solid Power Inc. officially announced mass production of the first generation of ASSLMBs, which possess a high energy density of 320 Wh kg\textsuperscript{–1}, enable a fast discharge rate at 5 C, and show stability over a wide temperature range.\textsuperscript{[212]} The success of this battery can be attributed to the highly processable and stable solid electrolyte, which highlights the future development route for various SSEs. As summarized in Table 2, on the pathway toward commercialization, each type of SSE has unique challenges to overcome. 1) For oxide electrolytes, the excessive rigidity of ceramics hampers their commercialization as the rigidity makes large-scale processing...
Table 2. Comparison of different types of SSEs.

| Criteria                | Oxide electrolytes | Sulfide electrolytes | SPEs |
|-------------------------|--------------------|----------------------|------|
|                         | LLZO               | LATP                 |      |
| Ionic conductivity      | Medium             | Medium               | Good |
| Interfacial contact     | Poor               | Poor                 | Medium |
| Stability against air   | Medium             | Good                 | Poor |
| Stability against reduction | Medium          | Poor                 | Poor |
| Stability against oxidation | Medium          | Good                 | Medium |

of the electrolytes difficult and rigid electrolyte/electrode interfaces can lead to contact loss during cycling. In addition, uneven distribution of current density can cause electrochemical instability during cycling, especially at the LLZO/cathode and LATP/Li interfaces. Therefore, it is necessary to modify the oxide electrolyte/electrode interface by fabricating soft and electronic isolating interlayers to maintain constant interfacial contact and block the electrochemical decomposition of the electrolyte kinetically. Developing methods to fabricate such soft interlayers, such as in situ copolymerization of SPEs, requires more advanced techniques on regulating the properties of interlayers as well as more studies to understand the interactions between the interlayer, electrolyte, and electrode during electrochemical cycling. 2) For sulfide electrolytes, commercialization is inhibited mainly by the narrow electrochemical window, and the incompatibility with oxide cathode materials. Novel strategies to inhibit electron transportation at the electrolyte/electrode interface, such as surface coating of an electronic isolating material for both electrodes or fabricating in situ or ex situ single-ionic conductive SEI (CEI) layers, are necessary for inhibiting electrochemical decomposition of the sulfide electrolyte, as well as eliminating the formation of the “space-charge layer.” On the other hand, due to the deformability of sulfides, it is also practical and important to apply external pressure for sulfide electrolyte–based batteries to inhibit the mechanical degradation caused by volume changes of the oxide cathode and morphology change of the lithium anode during cycling. 3) For SPEs, the difficulty of commercialization is caused mainly by the low ionic conductivity and insufficient mechanical strength and mismatch of the working voltage range of each kind of polymer–salt system for high-voltage LMBs. As polymers possess good plasticity, it is practical to construct a laminated structure to enhance electrochemical compatibility by using different polymer–salt couples matched with the working voltage of each electrode. On the other hand, adding an ionic–conductive ceramic filler into the SPE is an effective method to enhance both the ionic conductivity and mechanical strength of SPEs. However, more studies are required to clarify the impact of fillers on electrochemical and mechanical properties of SPEs, and practical methods to adjust the filler content, shape, and arrangement in the electrolyte for are also needed for mass production. 4) Finally, in addition to the critical issues for each type of SSE mentioned previously, for practical uses, an ASSLMB should be composed of a thin lithium metal anode (≥50 μm), a high cathode active material loading (5 mAh cm⁻²), and a thin SSE layer (≥30 μm) to avoid sacrificing the overall energy density. In addition, a current density of at least 5 mA cm⁻² should be applied to determine the electrochemical and mechanical stability of SSEs against lithium dendrite formation.[213]

As an essential component in an ASSLMB, the electrochemical stability of the SSE is vital for its practical use, and great efforts have been made by numerous researchers in this area in the past decades. It is hoped that with the joint efforts of the scientific research groups and industrial circles, further development of SSEs can overcome the current obstacles and make important breakthroughs for full practicality of solid-state batteries in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

energy storage, interfacial compatibility, lithium-metal batteries, solid-state electrolytes

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