Review

Recent progress of sulfide electrolytes for all-solid-state lithium batteries

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Abstract

Solid electrolytes are recognized as being pivotal to next-generation energy storage technologies. Sulfide electrolytes with high ionic conductivity represent some of the most promising materials to realize high-energy-density all-solid-state lithium batteries. Due to their soft nature, sulfides possess good wettability against Li metal and their preparation process is relatively effortless. High cell-level sulfide-based all-solid-state lithium batteries have gradually been realized in recent years. However, there are still several disadvantages that sulfide electrolytes need to overcome, including their sensitivity to humid air and instability to electrodes. Herein, the recent progress for sulfide electrolytes, with particular attention given to electrolyte synthesis mechanisms, electrochemical and chemical stability, interphase stabilization and all-solid-state lithium batteries with high cell-level energy density, is presented.

Keywords: Sulfide electrolytes, electrochemical stability, interphase stabilization, all-solid-state lithium batteries

INTRODUCTION

The increasing demand for renewable energy has inevitably resulted in higher requirements for energy storage devices. Rechargeable lithium-ion batteries (LIBs) has played a significant role in large-scale energy storage on account of their high energy density[1,2]. However, due to the use of liquid organic electrolytes,

combustion, leakage and other safety issues have aroused great concerns[3,4]. All-solid-state lithium batteries (ASSLBs) employing inorganic solid electrolytes instead of liquid electrolytes can effectively solve this dilemma and as a result have received significant attention[5].

Inorganic solid electrolytes are essential for ASSLBs[6,7] and can generally be divided into oxide, sulfide and nitride electrolytes. Among these electrolytes, sulfide electrolytes are considered as some of the most promising candidates because of their high ionic conductivity and suitable mechanical properties[8,9]. In particular, sulfide-based solid electrolytes that possess higher ionic conductivity than that of liquid electrolytes, such as $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (2.5 × 10^{-2} S cm^{-1}), $Li_{6.6}Si_{0.6}Sb_{0.4}S_5I$ (2.4 × 10^{-2} S cm^{-1}) and $Li_{6.7}PS_5ClBr_{0.7}$ (2.4 × 10^{-2} S cm^{-1}), have been developed[10-12]. Though remarkable progress has been made in recent decades, there are still some challenges for the commercial application of sulfide electrolytes. For instance, they have a narrow electrochemical window, which leads to poor electrochemical compatibility with electrodes[13,14]. Moreover, sulfide electrolytes have inferior chemical stability to humid air, which results in the generation of toxic H_2S gas, as well as degradation of the electrolytes[15].

In this review, the recent progress of sulfide electrolytes for ASSLBs is summarized. At first, the synthesis approaches of sulfide electrolytes are discussed systematically. The relationships between the ionic conductivity and crystal structure of sulfide electrolytes are then analyzed, accompanied by a discussion of numerous strategies for improving their ionic conductivity. Moreover, the stability (in terms of electrochemical window and humid air) of sulfide electrolytes is also explored. In particular, the interfacial compatibility between sulfide electrolytes and electrodes (Li metal anodes and oxide cathodes) is described and the corresponding solutions are discussed in detail. The fabrication of thin sulfide electrolyte films for ASSLBs with high cell-lever energy density is also emphasized. Ultimately, we summarize the prospects and consider possible future developments of sulfide electrolytes for ASSLBs.

SYNTHESIS APPROACHES
To date, the synthesis methods of sulfide electrolytes mainly consist of melt-quenching, liquid-phase and mechanical ball-milling approaches.

Melt-quenching approach
Melt quenching is one of the most traditional approaches for the preparation of sulfide glasses. The preparation process involves heating the raw materials at a high temperature and quenching the molten samples in ice water, which is harsh and can easily generate impurities. Minami *et al.*[16] fabricated $70Li_2S·30P_2S_5$ glasses by a melt-quenching technique at different heating temperatures and investigated their local structure. In addition, $70Li_2S·30P_2S_5$ glass ceramics were obtained by crystallization of the glasses[17]. The results showed that the generation of crystalline $Li_7P_3S_{11}$ improved the ionic conductivity of the glass ceramics. However, with increasing heating temperature and holding time, the metastable $Li_7P_3S_{11}$ crystal phase transforms into a thermodynamically stable phase with low ionic conductivity, which decreased the ionic conductivity of the $70Li_2S·30P_2S_5$ glass ceramics. Furthermore, by combining the melt-quenching and hot pressing processes, the grain boundaries and pores of the sulfide electrolytes were eliminated, as shown in Figure 1A-C[18]. As a result, the $Li_2S-P_2S_5$ glass-ceramic conductor delivered an enhanced high ionic conductivity of 1.7 × 10^{-2} S cm^{-1}.

Liquid-phase approach
The developed liquid-phase approach displays large-scale industrial prospects because of its advantages in terms of high efficiency and energy conservation. The raw materials can proceed with a sufficient reaction in solutions and produce homogenous precursors[19]. Furthermore, liquid-phase approaches have been
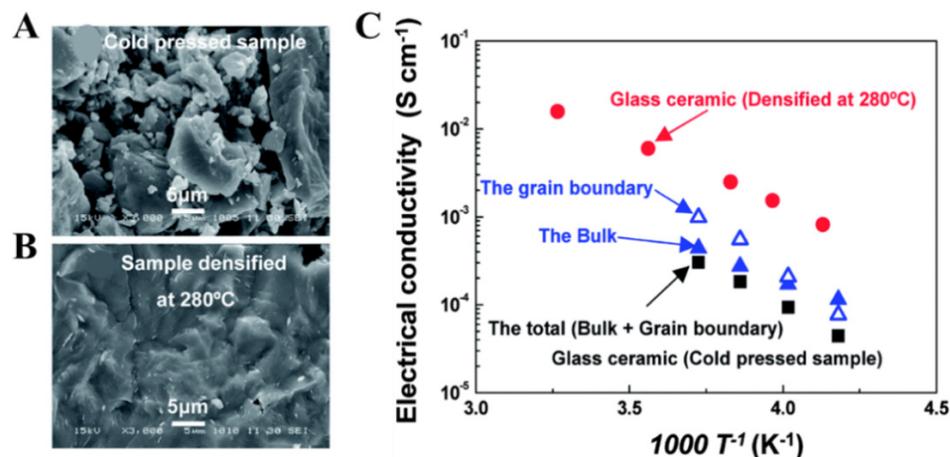
Figure 1. Scanning electron microscopy (SEM) images of $Li_7P_3S_{11}$ glass ceramic from (A) cold-pressed and (B) heat-treated samples. (C) Temperature dependency of the resistances of the glass-ceramic material at different conditions. Reproduced with permission[18] (Copyright 2014, Royal Society of Chemistry).

employed to enhance the electrode/electrolyte interfacial contact for improving the performance of the batteries[20]. Nevertheless, residual organic solvents and impurity phases in the samples are inevitable and hinder the transport of Li^+, resulting in a decrease in the ionic conductivity of the electrolytes and an increase in activation energy[21]. Li_3PS_4 is the most stable phase in the Li_2S-P_2S_5 system. Liu *et al.*[22] employed tetrahydrofuran (THF) as a dispersion medium to synthesize Li_3PS_4. After removing the THF solvent, the obtained β-Li_3PS_4 with a nanoporous structure displayed an ionic conductivity of 1.6×10^{-4} S cm^{-1} and excellent stability against Li metal[22]. Ito *et al.*[21] prepared crystalline $Li_7P_3S_{11}$ by a liquid-phase reaction in a 1,2-dimethoxyethane (DME) organic solvent and its ionic conductivity was 2.7×10^{-4} S cm^{-1}.

Xu *et al.*[19] applied different organic solvents to synthesize a $Li_7P_3S_{11}$ glass-ceramic electrolyte. THF, acetonitrile (ACN) and THF/ACN mixed solvents were used to prepare a $Li_7P_3S_{11}$ glass ceramic and the corresponding scanning electron microscopy (SEM) images and electrochemical impedance spectroscopy (EIS) analysis of the electrolyte are displayed in Figure 2A-C. It was found that the $Li_7P_3S_{11}$ electrolyte prepared with ACN possessed the highest ionic conductivity (9.7×10^{-4} S cm^{-1}) and the lowest activation energy (31.2 kJ mol^{-1}) among all the candidates[19]. In addition, it was reported by Yubuchi *et al.*[23] that argyrodite-type Li_6PS_5X (X = Cl, Br or I) could also be synthesized with the liquid-phase technique. The Li_6PS_5Cl electrolyte prepared via ethanol displayed an ionic conductivity of 1.4×10^{-5} S cm^{-1} at room temperature (RT). Li_6PS_5Br with a high ionic conductivity of 3.1×10^{-3} S cm^{-1} was also synthesized by adopting homogeneous a THF- and ethanol-based solution. Furthermore, solution-processable iodine-based Li-argyrodites with formulas of Li_6P_5SI, $Li_{6.5}P_{0.5}Ge_{0.5}S_5I$ and $Li_{6.25}Sn_{0.25}P_{0.75}S_5I$ were developed by Song *et al.*[24] in anhydrous ethanol. Among them, the $Li_{6.5}P_{0.5}Ge_{0.5}S_5I$ electrolyte showed the highest Li^+ conductivity of 5.4×10^{-4} S cm^{-1} at RT.

MECHANICAL BALL-MILLING APPROACH

Mechanical ball-milling is a popular approach for synthesizing sulfide electrolytes due to its simple operation. Raw materials undergo mixing, glassification and crystallization during the process of high-energy milling[25]. Surprisingly, some undiscovered glass materials can be obtained via the ball-milling method[4]. A 75Li_2S-25P_2S_5 (mol%) glass prepared by mechanical milling showed an ionic conductivity of 3.7×10^{-4} S cm^{-1}[26]. Boulineau *et al.*[27] prepared Li-argyrodite Li_6PS_5X (X = Cl, Br or I) by mechanical ball-milling and the ionic conductivity of the synthesized electrolytes could reach a high level of 2-7 $\times 10^{-4}$ S cm^{-1}.
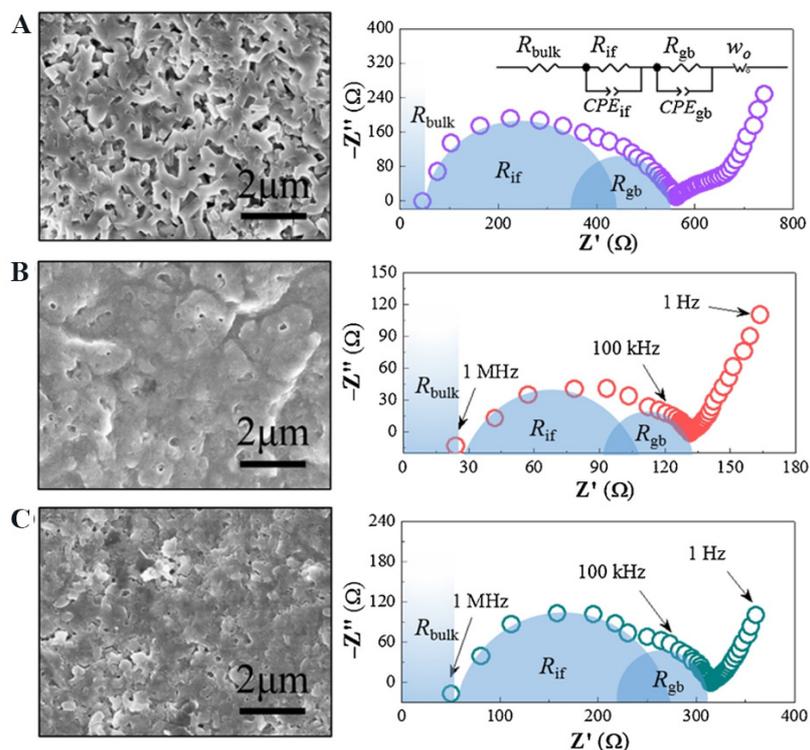
Figure 2. SEM images of $Li_7P_3S_{11}$ pellets prepared by (A) THF, (B) ACN and (C) THF + ACN, and the matching impedance figures at RT. The equivalent circuit is inserted in the impedance spectrum. Reproduced with permission[19] (Copyright 2016, Elsevier). SEM: Scanning electron microscopy; THF: tetrahydrofuran; ACN: acetonitrile; RT: room temperature.

As described in Figure 3A and B, a Li_6PS_5I[28] phase with optimization of the milling time could exhibit a high ionic conductivity of 1.82×10^{-3} S cm^{-1}. To further improve the ionic conductivity of a sulfide electrolyte, the resulting ball-milled materials were annealed. A series of sulfide electrolytes has been developed via mechanical milling plus annealing, including $70Li_2S-30P_2S_5$ (mol%, 3.2×10^{-3} S cm^{-1})[29], $75Li_2S-25P_2S_5$ (mol%, 5×10^{-4} S cm^{-1})[30], $80Li_2S-20P_2S_5$ (mol%, 7.2×10^{-4} cm^{-1})[31], $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (2.5×10^{-2} S cm^{-1})[10], $Li_{10}SnP_2S_{12}$ (3.8×10^{-3} S cm^{-1})[32] and $Li_{5.5}PS_{4.5}Cl_{1.5}$ (1.2×10^{-2} S cm^{-1})[33]. Recently, Liu *et al.*[34] synthesized a $Li_{5.6}PS_{4.6}I_{1.4}$ glass-ceramic electrolyte using an ultimate-energy mechanical alloying method. As a consequence, S^{2-}/I^- disorder was successfully introduced into the system. The glass-ceramic electrolyte possessed a high ionic conductivity of 2.0×10^{-3} cm^{-1}. However, the ball-milling process is usually tedious and time-consuming, resulting in an increase in production costs. Moreover, the stoichiometric compositions are only uniform over small areas and are inhomogeneous on large scales because the raw materials tend to stick together during the milling process, which may generate impurities[35].

The selection of preparation methods is a key factor for determining the properties of sulfide electrolytes. The melt-quenching method requires high operating temperatures and is prone to the generation of impurities. In addition, it is difficult to control the crystallinity of the material obtained by the melt-quenching method. However, the melt-quenching method is easy to operate and is well suited to the preparation of glassy sulfide electrolytes. The liquid-phase approach is suitable for large-scale production. Nonetheless, sulfide electrolytes prepared by the liquid-phase method display inferior ionic conductivities, mainly resulting from the existence of residual organic molecules during the preparation process. Mechanical ball-milling approach enables the reaction precursor to be well mixed. Moreover, some glassy sulfides or glass-ceramic sulfides can be obtained by this method. With the post-annealing treatment, the
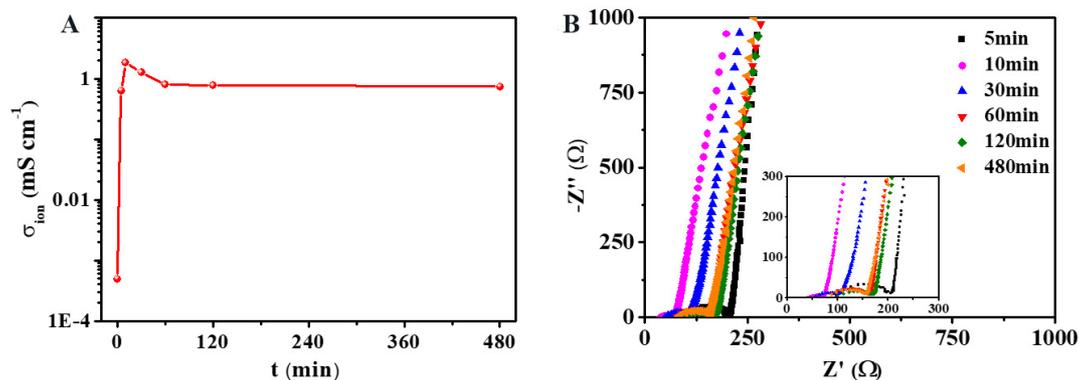
Figure 3. (A) Ionic conductivity (σ) of Li_6PS_5I electrolytes *vs.* milling time. (B) Nyquist plots of Li_6PS_5I electrolytes for different milling times. Reproduced with permission[28] (Copyright 2021, Wiley-VCH).

ionic conductivity and crystallinity of sulfides prepared by the mechanical ball-milling approach will be improved. However, this method is not practical for realistic production. The ionic conductivities of representative sulfide electrolytes prepared by different methods are displayed in Table 1.

STRUCTURE AND CONDUCTIVITY OF SULFIDE ELECTROLYTES

Research into sulfide-based electrolytes can be traced back to 1981 with the Li_2S-P_2S_5 system[36]. After considerable efforts, the ionic conductivity of sulfide electrolytes can now match or exceed that of liquid organic electrolytes[10,51]. In this section, the relationship between the structure and ionic conductivity of sulfides, including glasses and glass ceramics, thio-LISICONs, $Li_{11-x}M_{2-x}P_{1+x}S_{12}$ (M = Ge, Sn or Si) compounds and Li_6PS_5X (X = Cl, Br or I) argyrodites, is reviewed. A detailed summary of the ionic conductivities and activation energies of sulfide electrolytes with the corresponding structures is presented in Table 2.

Sulfide glasses

The conduction pathways of sulfide glasses are isotropic and the grain boundary resistances are easy to eliminate. Therefore, sulfide glasses are generally considered to possess higher ionic conductivity than their corresponding crystalline materials. A detailed investigation of xLi_2S-$(100-x)P_2S_5$ (mol%) binary systems with different Li_2S fractions was carried out by Dietrich *et al.*[62] and Hayashi *et al.*[45] The results showed a single glass phase can form between $x = 0.4$ and 0.8. Furthermore, the relationship between the local structure of the thiophosphate building blocks and the ionic conductivity was revealed in their work. As represented in Figure 4, a continuous change can be observed from dominant di-tetrahedral $P_2S_7^{4-}$ to mono-tetrahedral PS_4^{3-} with increasing Li_2S content. The $75Li_2S$-$25P_2S_5$ glass material with only PS_4^{3-} tetrahedra delivered the highest ionic conductivity of 2.8×10^{-4} S cm^{-1} at RT. Moreover, xLi_2S-$(100-x)SiS_2$ and xLi_2S-$(100-x)B_2S_3$ glass materials with wide composition ranges have been reported with ionic conductivities of $\sim10^{-4}$ S cm^{-1}[63,64].

Doping lithium salts into glass electrolytes is a common method to enhance the Li^+ carrier concentration and thus improve the ionic conductivity of glasses. The addition of small amounts of Li_xMO_y (e.g., Li_4SiO_4, Li_3BO_3, Li_3GeO_4 and Li_3PO_4) in xLi_2S-$(100-x)SiS_2$ glass materials can enhance their stability against crystallization and maintain the level of ionic conductivity at $\sim10^{-3}$ S cm^{-1}[65,66]. In addition, LiX (X = Cl, Br or I) is usually applied to enhance the ionic conductivity of glasses. For instance, the Li_2S-B_2S_3-LiI and Li_2S-SiS_2-LiI systems presented ionic conductivities of 1.7×10^{-3} and 1.8×10^{-3} S cm^{-1}, respectively[67,68]. In contrast, the addition of lithium halides narrows the electrochemical stability window of glass materials because of their decomposition. Furthermore, with $LiBH_4$ as a doping agent, the Li_2S-B_2S_3-$LiBH_4$ system

Table 1. Ionic conductivities of representative sulfide electrolytes prepared by different methods

Material	Conductivity (S cm^{-1})*	Preparation method	Ref.
70Li$_2$S-30P$_2$S$_5$ glass	9.2×10^{-5}	Melt quenching	[16]
Li$_2$S-P$_2$S$_5$-LiI glass	~10^{-3}	Melt quenching	[36]
70Li$_2$S-30P$_2$S$_5$ glass	8.0×10^{-5}	Melt quenching	[18]
β-Li$_3$PS$_4$	1.6×10^{-4}	Liquid phase (THF)	[22]
Li$_3$PS$_4$	2.3×10^{-6}	Liquid phase (N-methylformamide)	[37]
Li$_3$PS$_4$	3.3×10^{-4}	Liquid phase (ethyl acetate)	[38]
Li$_7$P$_3$S$_{11}$	1.0×10^{-3}	Liquid phase (ACN)	[39]
Li$_7$P$_3$S$_{11}$	2.7×10^{-4}	Liquid phase (DME)	[21]
Li$_7$P$_3$S$_{11}$	9.7×10^{-4}	Liquid phase (ACN/THF/CAN + THF)	[19]
Li$_7$P$_3$S$_{11}$	8.7×10^{-4}	Liquid phase (ACN)	[40]
Li$_6$PS$_5$Cl	1.4×10^{-5}	Liquid phase (ethanol)	[41]
Li$_6$PS$_5$Cl	6.0×10^{-5}	Liquid phase (ethanol and ethyl acetate)	[42]
Li$_6$PS$_5$Cl	2.4×10^{-3}	Liquid phase (THF and ethanol)	[43]
Li$_6$PS$_5$Br	1.9×10^{-4}	Liquid phase (ethanol)	[23]
Li$_6$PS$_5$Br	3.9×10^{-3}	Liquid phase (THF and ethanol)	[44]
Li$_{5.5}$PS$_{4.5}$Cl$_{1.5}$	3.9×10^{-3}	Liquid phase (THF and ethanol)	[43]
Amorphous Li$_3$PS$_4$	2.0×10^{-4}	High-energy ball milling	[45]
Li$_3$PS$_4$	1.0×10^{-3}	Mechanical milling	[46]
Li$_7$P$_3$S$_{11}$	3.2×10^{-3}	Mechanical milling	[47]
Li$_6$PS$_5$Cl	6.2×10^{-4}	High-energy ball milling	[27]
Li$_6$PS$_5$I	1.9×10^{-4}	High-energy ball milling	[27]
Li$_{6.24}$P$_{0.823}$Sn$_{0.177}$S$_{4.58}$I$_{0.9}$	3.5×10^{-4}	High-energy ball milling	[48]
Li$_{5.5}$PS$_{4.5}$Cl$_{1.5}$	1.0×10^{-2}	Ultimate-energy mechanical alloying	[25]
Li$_6$PS$_5$I	7.9×10^{-4}	Ultimate-energy mechanical alloying	[28]
Li$_{5.6}$PS$_{4.6}$I$_{1.4}$	2.0×10^{-3}	Ultimate-energy mechanical alloying	[34]
Li$_2$S-P$_2$S$_5$-Li$_3$N glass	5.8×10^{-4}	Mechanical milling	[26]
Li$_2$S-P$_2$S$_5$-Li$_3$N glass ceramic	1.4×10^{-3}	Mechanical milling	[26]
Li$_{10}$Ge(P$_{0.925}$Sb$_{0.075}$)$_2$S$_{12}$	1.7×10^{-2}	Mechanical milling	[49]
Li$_{10}$SnP$_2$S$_{12}$	3.2×10^{-3}	Mechanical milling	[50]

*Unless otherwise specified, the ionic conductivity is tested at RT. THF: Tetrahydrofuran; ACN: acetonitrile; DME: 1,2-dimethoxyethane; RT: room temperature.

delivered a high ionic conductivity of 1.6×10^{-3} S cm^{-1} and a stable electrochemical window up to 5 V[69].

Sulfide glass ceramics

Glass ceramics consist of amorphous and crystalline phases, which are usually prepared through heat treatment of the glass phase. The types of crystals formed depend on the composition of the glass and the conditions of the heat treatment. Currently, research into glass-ceramic electrolytes is mainly focused on the Li$_2$S-P$_2$S$_5$ system. Different crystalline phases are generated in xLi$_2$S-(100-x)P$_2$S$_5$ (mol%) glass materials depending on the x value, as displayed in Figure 5[70]. For instance, at $x < 70$ mol%, the formation of Li$_2$P$_2$S$_6$ or Li$_4$P$_2$S$_6$ phases with low ionic conductivity decreases the overall conductivity of the glass ceramic[71,72]. However, for $x \geq 70$ mol%, the crystalline phases of Li$_{3.25}$P$_{0.95}$S$_4$ and Li$_7$P$_3$S$_{11}$ with high ionic conductivity precipitate in the glass materials and significantly increase the ionic conductivity[29,31,73]. Very recently, a high-energy ball-milling method was utilized to produce glass-ceramic electrolytes in a one-pot process. The prepared glass ceramics displayed an ionic conductivity of ~10^{-3} S cm^{-1}[27,34,74].

Table 2. Ionic conductivities of representative sulfide electrolytes and the corresponding structures

Material	Structure	Conductivity (S cm^{-1})*	E_a (eV)	Ref.
Li_3PS_4	Glass	2.0×10^{-4}	0.35	[45]
$0.4LiI\text{-}0.6Li_4SnS_4$	Glass	4.1×10^{-4} (30 °C)	0.43	[52]
$Li_2S\text{-}P_2S_5\text{-}LiI$	Glass	$\sim 10^{-3}$	0.30	[36]
$Li_7P_3S_{11}$	Glass ceramic	1.7×10^{-2}	0.18	[18]
$Li_7P_{2.9}Sb_{0.1}S_{10.75}O_{0.25}$	Glass ceramic	1.6×10^{-3}	0.28	[53]
$Li_{5.6}PS_{4.6}I_{1.4}$	Glass ceramic	2.0×10^{-3}	0.31	[34]
$Li_{6.5}In_{0.25}P_{0.75}S_5I$	Glass ceramic	1.0×10^{-3}	0.28	[28]
$Li_7Ag_{0.1}P_3S_{11}I_{0.1}$	Triclinic	1.3×10^{-3}	0.23	[54]
$Li_{9.6}P_3S_{12}$	Tetragonal	1.2×10^{-3}	0.26	[10]
Li_4SnS_4	Orthorhombic	7.0×10^{-5}	0.41	[55]
$Li_{3.334}Ge_{0.334}As_{0.666}S_4$	Orthorhombic	1.1×10^{-3}	0.17	[56]
$Li_{3.25}Ge_{0.25}P_{0.75}S_4$	Monoclinic	2.2×10^{-3}	0.21	[57]
$Li_{10}GeP_2S_{12}$	Tetragonal	1.2×10^{-2}	0.25	[51]
$Li_{10}SnP_2S_{12}$	Tetragonal	4.0×10^{-3} (27 °C)	0.27	[58]
$Li_{10}SiP_2S_{12}$	Tetragonal	2.0×10^{-3} (27 °C)	0.30	[59]
$Li_{10}Si_{0.3}Sn_{0.7}P_2S_{12}$	Tetragonal	8.0×10^{-3}	0.29	[59]
$Li_{10}Ge(P_{0.925}Sb_{0.075})_2S_{12}$	Tetragonal	1.7×10^{-2}	0.27	[49]
$Li_{5.5}PS_{4.5}Cl_{1.5}$	Cubic	9.4×10^{-3}	0.29	[33]
$Li_{6.7}Si_{0.7}Sb_{0.3}S_5I$	Cubic	1.1×10^{-2}	0.26	[11]
$Li_{5.3}PS_{4.3}ClBr_{0.7}$	Cubic	2.4×10^{-2}	0.155	[12]
$Li_{6.25}PS_{4.75}N_{0.25}Cl$	Cubic	1.5×10^{-3}	0.26	[60]
$Li_{6.3}P_{0.7}Sn_{0.3}S_{4.4}O_{0.6}I$	Cubic	2.3×10^{-4} (30 °C)	0.32	[61]

*Unless otherwise specified, the ionic conductivity is tested at room temperature.

Figure 4. Raman and ^{31}P magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectra of $xLi_2S\text{-}(100\text{-}x)P_2S_5$ glasses with different Li_2S contents. Reproduced with permission[62] (Copyright 2017, Royal Society of Chemistry).

Nonetheless, the appearance of the crystallization region leads to an increase in the grain boundary impedance. To improve the conductivities of glass-ceramic materials, Seino *et al.*[18] performed a hot-pressing process to eliminate the grain boundaries in $70Li_2S\text{-}30P_2S_5$ glass ceramics. The obtained electrolytes
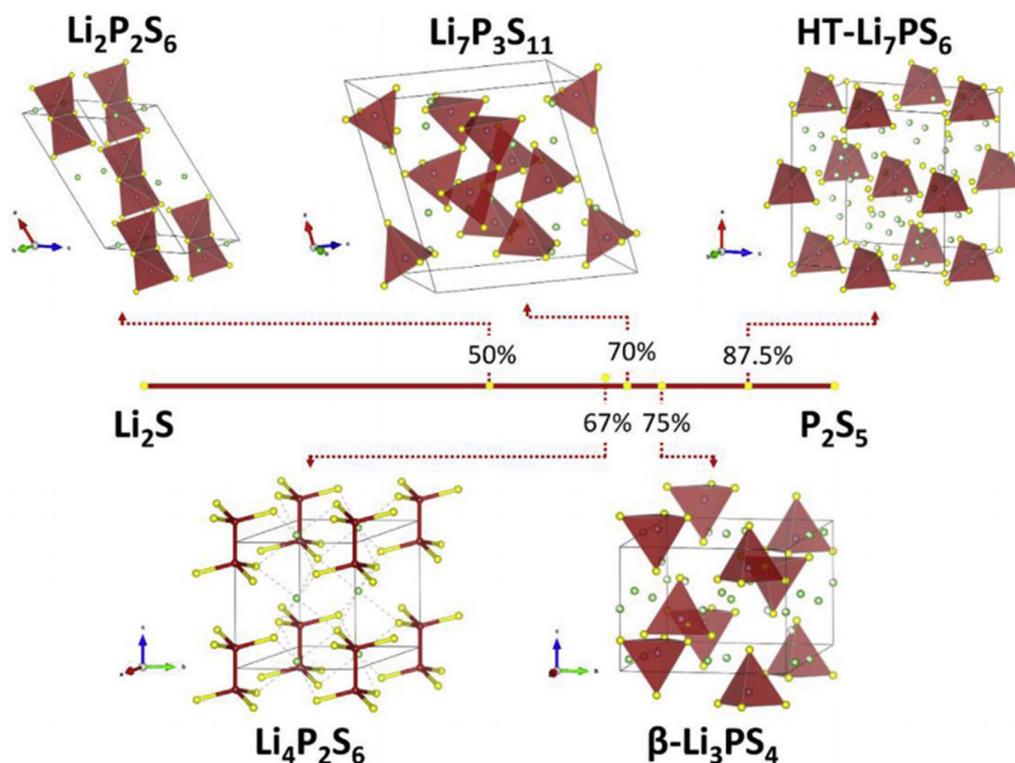
Figure 5. Different crystalline phases generated within the Li_2S-P_2S_5 binary system. Reproduced with permission[70] (Copyright 2018, Elsevier).

showed a superior conductivity of 1.7×10^{-2} S cm^{-1}. In addition, a doping strategy was used to enhance the ionic conductivity of glass ceramics. It was reported by Xu *et al.*[35] that replacing P^{5+} with Mo^{4+} ions could not only generate point defects to improve the ionic conductivity but also broaden the Li^+ transport channels. As a consequence, the Mo-doped $70Li_2S$-$30P_2S_5$ glass-ceramic electrolyte represented a high ionic conductivity of 4.8×10^{-3} S cm^{-1}[35]. Mn and I co-doping was also applied in their later work to optimize the $Li_7P_3S_{11}$ glass ceramic. The prepared $Li_7P_{2.9}Mn_{0.1}S_{10.7}I_{0.3}$ glass-ceramic electrolyte possessed a high ionic conductivity (5.6×10^{-3} S cm^{-1}) and a wide electrochemical window (up to 5 V)[75].

SULFIDE CRYSTALLINE ELECTROLYTES
Thio-LISCIONs
The thio-LISICON structures found in the Li_2S-GeS_2, Li_2S-GeS_2-Ga_2S_3 and Li_2S-GeS_2-ZnS systems were derived from a LISICON-type γ-Li_3PO_4 electrolyte by replacing O with S[76]. S possesses lower electronegativity and a larger radius than O, and is therefore capable of reducing the Li^+ binding energy and broadening the Li^+ migration channels. Therefore, thio-LISICON electrolytes are expected to have higher ionic conductivity than oxide electrolytes[13,51]. Six materials [Li_4GeS_4, Li_2GeS_3, Li_2ZnGeS_4, $Li_{4-2x}Zn_xGeS_4$, Li_5GaS_4 and $Li_{4+x+\delta}(Ge_{1-\delta'-x}Ga_x)S_4$] were discovered by Kanno *et al.*[76] to possess the thio-LISICON structure. Among these thio-LISICON electrolytes, orthorhombic $Li_{4+x+\delta}(Ge_{1-\delta'-x}Ga_x)S_4$ exhibited the highest ionic conductivity of 6.5×10^{-5} S cm^{-1} at RT. The orthorhombic Li_4GeS_4 electrolyte displayed a low ionic conductivity (2.0×10^{-7} S cm^{-1}) at RT[76], while the Li_4GeS_4 thin film was discovered to possess a high ionic conductivity of 7.5×10^{-5} S cm^{-1}[77]. Moreover, the Li_4SnS_4 electrolyte, possessing an ionic conductivity of 7.5×10^{-5} S cm^{-1}, is also defined as thio-LISICON. Furthermore, with As or Sb aliovalent doping, $Li_{3.833}Sn_{0.833}As_{0.166}S_4$ and $Li_{3.85}Sn_{0.85}Sb_{0.15}S_4$ electrolytes showed enhanced ionic conductivities of 1.4×10^{-3} and 8.5×10^{-4} S cm^{-1}, respectively[78,79].

A more detailed investigation of the thio-LISICON structure was carried out for the Li_2S-GeS_2-P_2S_5 system. Kanno *et al.*[57] obtained $Li_{4-x}Ge_{1-x}P_xS_4$ ($0 < x < 1$) by partial substituting Ge^{4+} with P^{5+} in the Li_4GeP_4 electrolyte. The aliovalent P doping could introduce lithium vacancies into the crystal structure to improve the ionic conductivity significantly. As displayed in Figure 6A and B, the crystal structure is based on the parent structure of Li_4GeS_4. The X-ray diffraction (XRD) pattern illustrated that $Li_{4-x}Ge_{1-x}P_xS_4$ ($0 < x < 1$) electrolytes could be regarded as a solid solution between γ-Li_3PS_4 and Li_4GeS_4[2]. According to the appearance of superlattice reflections, the $Li_{4-x}Ge_{1-x}P_xS_4$ ($0 < x < 1$) system can be divided into three types, namely, the orthorhombic thio-LISICON I region ($0 < x \leq 0.6$), the monoclinic thio-LISICON II region ($0.6 < x < 0.8$) and monoclinic thio-LISICON III region ($0.8 \leq x < 1$). Among these regions, the $Li_{3.25}P_{0.75}Ge_{0.25}S_4$ electrolyte in the thio-LISICON II region displayed the highest ionic conductivity of 2.2×10^{-3} S cm^{-1}[57]. Furthermore, Nishino *et al.*[80] evaluated the activation energy and the diffusion coefficient of $Li_{4-x}Ge_{1-x}P_xS_4$ thio-LISICON by long-time quantum molecular dynamics simulations. The lithium vacancies or excess lithium atoms from doping triggered a new diffusion pathway and drastically decreased the activation energy through the lithium vacancy or interstitial mechanism[80]. Various LiSiCON (oxide) and thio-LISICON (sulfide) materials with their conduction mechanisms and ionic conductivities are summarized in Figure 7[57].

$Li_{11-x}M_{2-x}P_{1+x}S_{12}$ (M = Ge, Sn or Si)

In order to achieve ASSLBs with high energy density, it is essential to develop a sulfide electrolyte with ultrahigh ionic conductivity. The tetragonal $Li_{10}GeP_2S_{12}$ (LGPS) electrolyte with a brand-new three-dimensional (3D) framework structure was reported by Kamaya *et al.*[51] in 2011. LGPS is the first sulfide electrolyte that exhibits an extremely high ionic conductivity (1.2×10^{-2} S cm^{-1}) comparable to that of liquid organic electrolytes. As exhibited in Figure 8, the ternary LGPS electrolyte is composed of $(Ge_{0.5}P_{0.5})S_4$ tetrahedra, PS_4 tetrahedra, LiS_4 tetrahedra and LiS_6 octahedra. The $(Ge_{0.5}P_{0.5})S_4$ tetrahedra and LiS_6 octahedra form a one-dimensional (1D) Li^+ conduction framework along the c axis by sharing a common edge. These 1D chains are interconnected via PS_4 tetrahedra, which share a common corner with the LiS_6 octahedra. Furthermore, the 1D Li^+ conduction channel consists of LiS_4 tetrahedra sharing a common edge in the 16h and 8f sites[51].

It was speculated that the Li ions in LGPS migrate through 1D diffusion pathways along the c axis. However, further investigation into the LGPS electrolyte by advanced characterization techniques and density functional theory (DFT) calculations overturned this suggestion. A variety of complementary techniques were employed by Kuhn *et al.*[81] to characterize the structure and Li^+ dynamics of the LGPS electrolyte. No strong anisotropic signs of diffusivity were found in the material. Therefore, it was concluded that the exceptionally high ionic conductivity of LGPS electrolyte should be attributed to nearly isotropic Li hopping processes in the bulk lattice with an E_a value of ~0.22 eV[81]. Also, it was demonstrated by Mo *et al.*[82] that the LGPS electrolyte is a 3D conductor rather than a 1D conductor. The reason is that 1D conductors cannot maintain good conductivity due to inevitable channel blocking defects. Thus, some crossover between 1D channels is required to bypass these defects[83].

Unfortunately, the high cost of Ge raw materials hinders the application of the LGPS electrolyte. Replacing Ge with low-cost elements (e.g., Sn or Si) is an effective approach to reduce the production costs of LGPS. A $Li_{10}(Ge_{1-x}M_x)P_2S_{12}$ (M = Sn or Si) mixed cation system was synthesized by Kato *et al.*[84] to evaluate the effect of Sn and Si substitution. It was found that Sn and Si substitution reduces the ionic conductivity of the system, indicating that the lattice volume is not the only factor that affects the ionic conductivity[84]. The Sn analog $Li_{10}SnP_2S_{12}$ electrolyte displayed an ionic conductivity of 7×10^{-3} S cm^{-1}, in good agreement with theoretical calculations. The $Li_{10}SiP_2S_{12}$ electrolyte was expected to possess an enhanced ionic conductivity (2.3×10^{-2} S cm^{-1}) and lower activation energy (0.20 eV) compared to the pristine LGPS electrolyte according
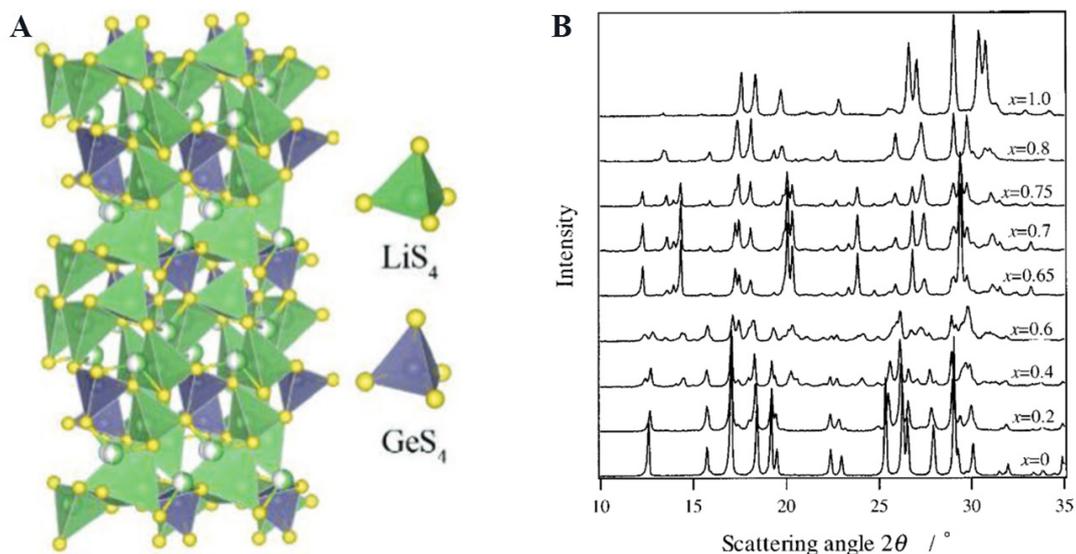
A   **B**

Figure 6. (A) Structure of thio-LISICON based on the parent structure of Li_4GeS_4. (B) XRD patterns of $Li_{4-x}Ge_{1-x}P_xS_4$. Reproduced with permission[2] (Copyright 2019, Wiley-VCH). XRD: X-ray diffraction.
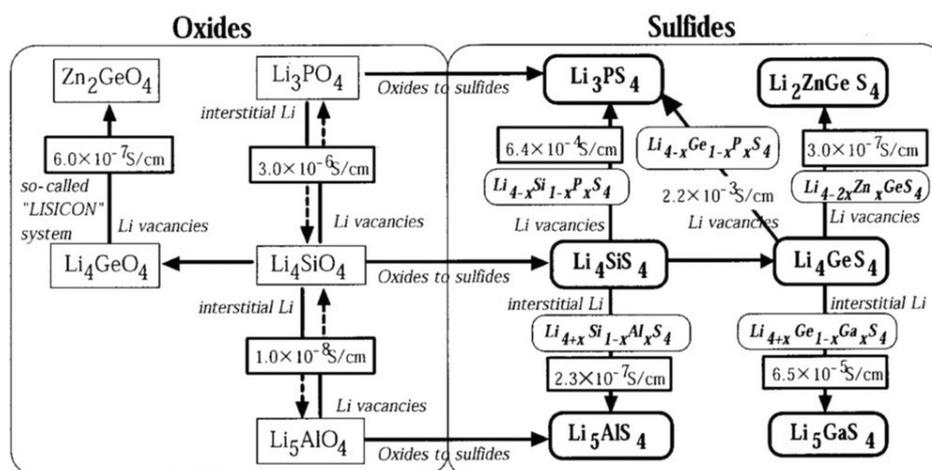

Figure 7. LISICON and thio-LISCION family maps with listed lithium-ion conduction mechanisms and ionic conductivity values. Reproduced with permission[57] (Copyright 2001, Electrochemical Society).

to theoretical calculations[85]. However, the experiment results demonstrated that crystalline $Li_{10}SiP_2S_{12}$ only has a low ionic conductivity of 2.3×10^{-3} S cm^{-1}[86]. The reason behind this contradiction has not yet been revealed. Furthermore, in the LGPS family, two newly prepared electrolytes, namely, $Li_{10.35}Si_{1.35}P_{1.65}S_{12}$ and $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, exhibit ultrahigh ionic conductivities of 2.0×10^{-2} and 2.5×10^{-2} S cm^{-1}, respectively[10,87].

Li_6PS_5X (X = Cl, Br or I)

Ag_8GeS_6 is the first known solid electrolyte with an argyrodite structure (space group F4̄3m). The Ag_8GeS_6 electrolyte has a high ionic conductivity and mobility of Ag$^+$ ions due to its highly disordered cation arrangements[88]. The Ag$^+$ ions in this electrolyte can be substituted by Cu$^+$ ions and the argyrodite structure is still maintained[89]. Considering that the ionic radii of Li$^+$ (73 ppm) and Cu$^+$ (74 ppm) are similar, Li_6PS_5X (X = Cl, Br or I) electrolytes were proposed by substituting Cu$^+$ with Li$^+$ and substituting Ge^{4+} with P^{5+} and X$^-$[88]. In the Li_6PS_5X (X = Cl, Br or I) system, three different jump processes occur, including doublet jumps
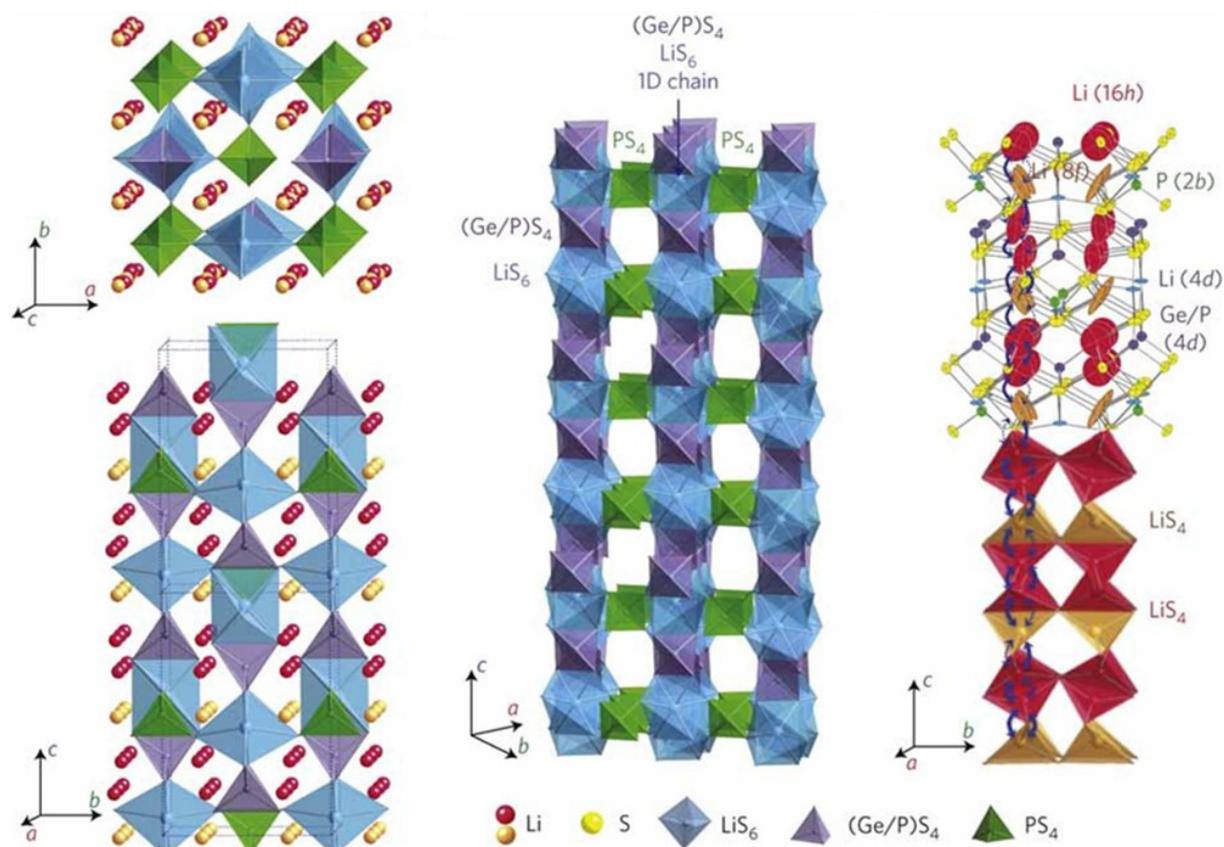
Figure 8. Crystal structure of $Li_{10}GeP_2S_{12}$. Reproduced with permission[51] (Copyright 2011, Springer Nature Publishing AG).

(48 h-24 g-48 h), intracage jumps (48 h-48 h) and intercage jumps, as shown in Figure 9A and B[90]. It was demonstrated by de Klerk *et al.*[91] that the intercage jumps dominate long-range Li^+ transport and the site disorder between the 4a and 4c sites has a significant impact on the ionic conductivity. The argyrodite-type electrolytes Li_6PS_5Cl, Li_6PS_5Br and Li_6PS_5I exhibited ionic conductivities of 1.9×10^{-3}, 6.8×10^{-4} and 4.6×10^{-7} S cm^{-1}, respectively[92].

Numerous studies have shown that the differences in ionic conductivity in argyrodite-type electrolytes originate from the different degrees of S^{2-}/X^- anion disorder. In Li_6PS_5Cl and Li_6PS_5Br, the S^{2-} and Cl^-, or S^{2-} and Br^- ions, at the 4a and 4c sites are partially disordered because of their relatively close ionic radii[93]. However, the large I^- ions can only occupy the 4a sites and are not able to swap with S^{2-} ions at the 4c site, thus resulting in a fully ordered anion framework[94]. The Li_6PS_5Cl and Li_6PS_5Br electrolytes with various S^{2-}/X^- anion-site disorders were investigated by first-principles molecular dynamics calculations. It was found by Morgan *et al.*[95] that the degree of S^{2-}/X^- anion disorder determines the diffusion pathways of the active Li^+. For anion-ordered systems, the lithium motion is restricted and orbits around the S positions because the critical site-site pathways are inactive and disconnected. In contrast, for anion-disordered systems, the active site-site pathways can form a 3D diffusion network, which enables the long-range diffusion of Li^{+}[95].

Therefore, considerable efforts have been made to improve the ionic conductivity by increasing the degree of site disorder. It was discovered by Zhao *et al.*[48] that replacing P^{5+} with larger cations not only broadens the unit cell but also induces site disorder, which is conducive to the transport of Li^+. By substituting Sn, the
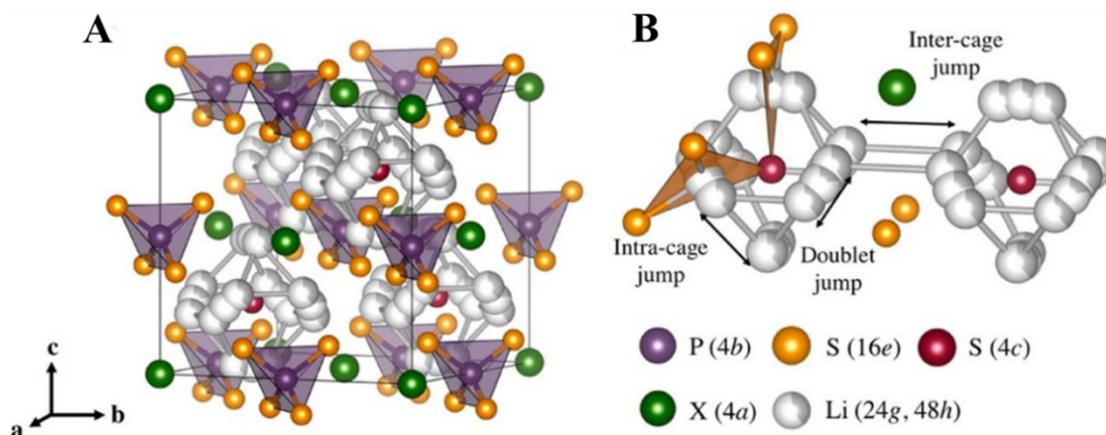
Figure 9. (A) Crystal structure of Li_6PS_5X (X = Cl, Br or I). (B) Li positions forming localized cages in which multiple jump processes are possible. Reproduced with permission[90] (Copyright 2017, American Chemical Society).

optimized $Li_{6.24}P_{0.823}Sn_{0.177}S_{4.58}I_{0.9}$ electrolyte delivered a high ionic conductivity of 3.5×10^{-4} S cm^{-1}, which was 125 times higher than that of the pristine Li_6PS_5I electrolyte[48]. The influence of Ge substitution on $Li_{6+x}P_{1-x}Ge_xS_5I$ electrolytes was also systematically explored by Kraft *et al.*[90]. The anion site disorder could be induced by the substitution of Ge. As a result, the $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ electrolytes displayed an ionic conductivity of 5.4×10^{-3} S cm^{-1} after cold-pressing and 1.84×10^{-2} S cm^{-1} after sintering at 298 K[96]. A three-fold increase in the ionic conductivity of the $Li_{6.35}P_{0.65}Si_{0.35}S_5Br$ electrolyte could be observed compared to that of the unsubstituted sample.[97]

Furthermore, increasing the halogen content in Li_6PS_5X (X = Cl, Br or I) electrolytes can also effectively improve the anion disorder and enhance their ionic conductivity[34,98,99]. The argyrodite $Li_{5.3}PS_{4.3}Cl_{1.7}$ and $Li_{5.3}PS_{4.3}Br_{1.7}$ electrolytes have ionic conductivities of 1.7×10^{-2} and 1.1×10^{-2} S cm^{-1} upon sintering, respectively[98,99]. Recently, Patel *et al.*[12] explored a mixed-halide argyrodites with the formula $Li_{6-x}PS_{5-x}ClBr_x$. The results showed that Cl$^-$, Br$^-$ and S^{2-} co-occupied the 4a/4c sites. A maximum ionic conductivity of 2.4×10^{-2} S cm^{-1} in a sintered state could be observed in the $Li_{5.3}PS_{4.3}ClBr_{0.7}$ electrolyte, which is so far the highest value in the argyrodite family. The $Li_{5.3}PS_{4.3}ClBr_{0.7}$ electrolyte also possessed an extremely low activation energy of 0.155 eV, providing a promising possibility for its application under low-temperature conditions[12]. In addition, introducing structural disorder in the crystalline Li_6PS_5I electrolyte by a soft mechanical treatment can also enhance its ionic conductivity[100].

STABILITY OF SULFIDE ELECTROLYTES
Electrochemical stability window
In addition to ionic conductivity, the electrochemical stability window of sulfide electrolytes is a crucial factor that affects the overall performance of sulfide-based ASSLBs. The decomposition of sulfide electrolytes results in high interfacial resistance and reduces the capacity of the batteries. Initially, the electrochemical stability window of sulfides was measured by cyclic voltammetry. Early experiments demonstrated that most sulfide electrolytes possess a remarkable electrochemical stability window up to 5 V *vs.* Li metal[27,75,101,102]. For instance, the electrochemical window of Li_6PS_5X (X = Cl, Br or I) argyrodites was characterized by Boulineau *et al.*[27] with a Li/BM-Li_6PS_5X/stainless steel cell. There was a total absence of any electrochemical response, which illustrated that the Li_6PS_5X (X = Cl, Br or I) electrolytes could remain stable at a voltage of 0.5-7 V *vs.* Li metal[27]. Moreover, by applying a similar testing method, the iodide-based $Li_7P_2S_8I$ electrolyte and the oxygen-substituted $Li_{10}GeP_2S_{11.4}O_{0.6}$ electrolyte were discovered to display a stable electrochemical window up to 10 V *vs.* Li metal[101,102].

In contrast, recent studies have suggested that the electrochemical windows of sulfide electrolytes were overestimated because the poor contact between the inert metal and solid electrolyte limits the reaction kinetics and hinders the mobility of Li$^+$[103,104]. DFT calculations were applied by Mo *et al.*[101] and Bai *et al.*[102] to predict the electrochemical windows of typical sulfides. It was found that sulfides display much narrower electrochemical windows than previously suggested experimentally, as displayed in Figure 10[105,106]. A new Li/electrolyte/electrolyte-carbon cell configuration was proposed by Han *et al.*[103] to correct the discrepancy between the theoretical calculations and experimental measurements. Mixing an electrolyte and carbon could increase the overall electronic conductivity of electrodes, which was beneficial for amplifying the decomposition current signal and reflecting the intrinsic electrochemical windows of sulfide electrolytes. Based on cycling voltammetry of the Li/LGPS/LGPS-C/Pt cell, it was found that the LGPS electrolyte would be reduced at 1.7 V and oxidized at 2.1 V, consistent with the theoretical calculation results[103].

Chemical stability in humid air

The chemical stability against humid air is another concern regarding the application of sulfide electrolytes. Most sulfide electrolytes suffer from poor moisture stability and generate toxic H_2S gas upon contact with humid air. Therefore, the common preparation process of sulfide electrolytes is usually under the protection of inert gas (argon). Numerous surveys of the moisture stability of sulfide electrolytes have been carried out. For example, the air stability of the Li_6PS_5Cl electrolyte was characterized with XRD measurements. Several clear impurity peaks could be observed after exposing the Li_6PS_5Cl electrolyte to humid air for 10 min and its ionic conductivity deteriorated from 1.8×10^{-3} S to 1.56×10^{-3}, 1.43×10^{-3} and 8.7×10^{-4} S cm^{-1} after exposure to air for 10 min, 1 h and 24 h, respectively[107]. The chemical stability of sulfide electrolytes in the Li_2S-P_2S_5 system was also investigated by Muramatsu *et al.*[108] in humid atmosphere. There was no obvious structure change in the PS_4^{3-} ions after exposure to air, while the S^{2-} and $P_2S_7^{4-}$ ions displayed a clear structural change and significant amounts of toxic H_2S gases were generated. As a consequence, a conclusion was drawn that PS_4^{3-} ions possess higher chemical stability compared to other phosphate ions[108].

The hard-soft-acid-base theory has been proposed by Liang *et al.*[49] to explain the poor chemical stability of sulfide electrolytes and has been applied to inhibit their deterioration. In P-containing sulfide electrolytes, the hard acid (P) tends to bond with the hard base (O) in humid air to form P-O bonds rather than maintaining the pristine P-S bonds. Furthermore, S atoms tend to bond with the H atoms in humid air, resulting in the generation of H_2S. Therefore, replacing the soft base (S) with a hard base (O) or replacing the hard acid (P) with a soft acid is a feasible approach to improve the air stability of sulfide electrolytes according to the hard-soft-acid-base theory. Based on this, many successful experiments for improving the air stability of sulfides have been reported[48,49,109]. In the Li_2S-P_2S_5 glass electrolytes, substituting partial P_2S_5 with P_2O_5 could effectively reduce the release rate of H_2S gas, illustrating that the air stability of electrolytes was improved with O substitution[109]. In addition, replacing hard acid (P) with soft acid (Sb, Sn and so on) was a good choice to enhance the air stability[48,49]. Liang *et al.*[49] investigated the effect of Sb substitution in $Li_{10}Ge(P_{1-x}Sb_x)_2S_{12}$ electrolytes. As depicted in Figure 11A and B, Sb prefers to substitute P at the 4d site. It was discovered that there was no appearance of additional or broadening peaks after exposing the Sb-substituted electrolytes to humid air for 24 h. In addition, theoretical calculations and experimental tests demonstrated that Sn-substituted Li_6PS_5I electrolytes possessed better air stability than the pristine Li_6PS_5I electrolyte because of the stronger Sn-S bonds[48].

SULFIDE ELECTROLYTE/LI METAL ANODE INTERFACE

Challenges for the sulfide electrolyte/Li metal anode interface

Interfacial side reactions and Li dendrites are two concerns that have plagued the development of liquid-state lithium-metal batteries for a long time[110]. These issues also exist when applying lithium metal as the anode in an ASSLBs[111,112]. Similar to typical sulfide electrolytes, high-valent cations in anion clusters, such

Figure 10. Calculated electrochemical stability windows for a variety of solid electrolytes. The dashed lines mark the oxidation potentials to fully delithiate the material. Reproduced with permission[106] (Copyright 2015, American Chemical Society).

Figure 11. (A) Crystal structure of $Li_{10}Ge(P_{0.925}Sb_{0.075})_2S_{12}$. (B) XRD patterns of $Li_{10}Ge(P_{0.925}Sb_{0.075})_2S_{12}$ sample before and after air exposure. Reproduced with permission[49] (Copyright 2020, American Chemical Society). XRD: X-ray diffraction.

as P^{5+}, Ge^{4+}, Sn^{4+} and so on, can easily react with Li metal [Figure 12B], resulting in an enhancement in Ohmic resistance and a decrease in Coulombic efficiency (CE)[113]. Theoretically, dendrite growth should be prohibited in solid electrolytes for the reason that the bulk modulus of solid electrolytes is higher than that of Li metal. However, the issue of dendrites tends to be severer in ASSLBs[114,115]. The theory of dendrite growth in solid electrolytes is diverse and is introduced in detail below. Unlike liquid electrolytes, which can directly wet the electrodes, the solid/solid contact in ASSLBs is not satisfactory. Although sulfide electrolytes display a better contact than oxide electrolytes, the contact loss at the sulfide electrolyte/anode interface during Li stripping/plating enlarges the local current density and leads to rapid dendrite growth[116].

Interfacial reactions

Li metal has the lowest reduction potential (-3.04 V *vs*. SHE), which means it has excellent potential in the application of energy storage systems. However, the low reduction potential of Li metal also indicates that

Figure 12. (A) Types of interfaces between lithium metal and a solid lithium ion conductor: (I) a non-reactive and thermodynamically stable interface; (II) a reactive and mixed conducting interphase; (III) a reactive and metastable solid-electrolyte interphase (SEI). Reproduced with permission[117] (Copyright 2015, Elsevier). (B) Decomposition energy E_D of sulfide electrolyte as a function of applied voltage Li. Reproduced with p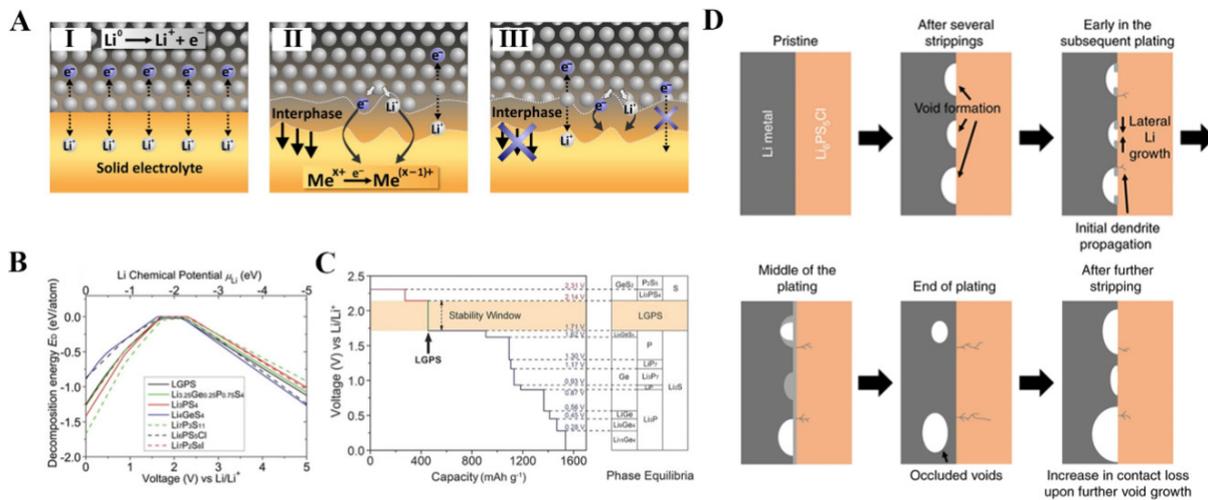ermission[106] (Copyright 2015, American Chemical Society). (C) First-principles calculation results of the voltage profile and phase equilibria of LGPS during lithiation and delithiation. Reproduced with permission[103] (Copyright 2016, Wiley-VCH). (D) Schematic of Li metal/Li_6PS_5Cl interface cycled at an overall current density above the CCS. Reproduced with permission[116] (Copyright 2019, Springer Nature Publishing AG).

the interfacial reactions between an electrolyte and Li metal are almost inevitable. Typically, in organic electrolyte research, Li metal is oxidized by solvents or Li salts to form an SEI, which can protect Li metal from further corrosion. In solid electrolytes, the property of the interphase is more complex.

Three types of Li/solid-state electrolyte interphase have been identified according to the mainstream theory [Figure 12A][117]. Type I includes all the thermodynamically stable solid electrolytes against Li metal. In this case, no interfacial reactions occur. For instance, several researchers have reported that LIPON and Li are in thermodynamic equilibrium. Unfortunately, sulfide electrolytes are included this type because their anionic clusters are easily reduced by Li metal.

The type II interphase is unique and arises from the reaction between Li and solid electrolytes containing metal ions. The reaction products consisting of electronic conductors (Li alloys) and ionic conductors continue to react with electrolytes. The so-called mixed conducting interphase is common in sulfide electrolytes. During the cycling of Li || LGPS || Li symmetric cells, the voltage polarization keeps rising due to continuous side reactions. By analyzing the X-ray photoelectron spectroscopy (XPS) spectra of the Li || LGPS interphase, Li-Ge alloys, which are the reaction products from Li and GeS_4^{4-} should be the origin of the unstable interphase[118]. Furthermore, a theoretical study has predicted the reaction products of Li and GeS_4^{4-} [Figure 12C].

For type III, the interphase reaction still occurs between Li and solid electrolytes but the reaction products that are thermodynamically stable against Li could prevent the reaction from proceeding. This type of interphase plays a similar role as the SEI. For example, Li_6PS_5Cl and Li react to form Li_2S, Li_3P and $LiCl$[60,116]. The resistance of Li-Li symmetric cells incorporated with Li_6PS_5Cl does not continue to increase because the reaction products of Li and Li_6PS_5Cl are rather stable against Li. The side reactions between Li and electrolytes lead to a drop in CE and present a bottleneck in the development of high-energy-density Li-metal batteries (LMBs). In particular, for sulfide electrolytes containing relatively unstable anionic clusters,

the interphase of type II should be avoided and the influence of type III should be limited to a certain level.

Li dendrites

Li dendrites are central factors that hinder the commercial application of LMBs. These needle-like crystals pierce the membrane and cause short-circuit to the whole-cell effortlessly[119]. Thermodynamically, the growth regimes of dendrites are linked with the intrinsic energetic properties of metal surfaces[120]. Therefore, the epitaxial and mossy growth of bare Li during the electrochemical process is inevitable.

Ideal solid electrolytes with high ionic conductivity and no electronic conductivity are proposed to take the place of traditional membranes and liquid electrolytes in LMBs. Compared to soft and porous membranes, ideal solid electrolytes possess high bulk moduli and are obviously denser after applying pressure[121]. Moreover, it is well known that the organic electrolytes utilized in liquid-state LMBs are combustible, yet the ignition points of solid electrolytes are much higher. Although, this initially inspired significant research into the commercialization of ASSLBs, the dendrite problem is not solved by solid electrolytes[115,122]. Recently, the growth of Li dendrites in solid electrolytes was clearly displayed by a high-resolution *in-situ* optical microscope, implying that solid electrolytes still had the conditions for dendrite growth[122]. By experimental observation, the voids in solid electrolytes provide a suitable environment for Li dendrites to grow. Furthermore, it has been reported that the grain boundaries of solid electrolyte may support dendrite growth due to their different nature from the bulk crystal[115,123,124]. Recently, Han *et al.*[125] tested the electronic conductivity of typical oxide, LIPON, and sulfide electrolytes and found that the role of electronic conductivity in dendrite growth could not be ignored. Neutron depth profiling was also applied to visualize dendrite growth. By correlating the critical current densities with electronic conductivity, they proposed a criterion where the electronic conductivity of the solid electrolyte should be considered when designing practical solid electrolytes.

Contact loss at the sulfide/anode interface

Solid-solid contact remains a key issue in ASSBs. Sulfide electrolytes, due to their soft characteristics, possess good interphase compatibility with Li metal. The pellets of sulfide electrolytes can be directly assembled into cells without any treatment. However, during the process of Li stripping/plating, the interphase initially in close contact becomes loose. The explanation for this phenomenon can be briefly concluded by the rate of Li creeping. Pits and holes form when Li is stripped from the bulk. These pits and holes can be filled to some extent by the creeping of Li metal, but the reality is that the rate of Li creeping is far lower than the rate of Li stripping. Thereafter, the next Li plating process is affected by the existence of pits and holes, resulting in insufficient contact between the Li and sulfide electrolytes. Therefore, when the external current density is constant, the contact loss between sulfide electrolytes and Li metal leads to an exponential rise in local current density at the contact point of the sulfide and Li metal.

According to Sand's theory, the rate of dendrite growth is positively related to current density[126]. It is not arduous to draw the conclusion that the contact loss of sulfide/Li interphase plays a major role in the failure of ASSLBs. Kasemchainan *et al.*[116] carried out detailed research on the relationship between the morphology of the interphase and cell performance. Via characterization of cross-sectional SEM and *in situ* X-ray computed tomography, voids were shown to form after several stripping cycles. Though the process of Li plating could decrease the number of voids, some occluded voids still existed when the current density was above the critical stripping current. After further stripping, the voids grow and the contact loss at the Li/sulfide interphase is severer. Once the local current density is above the threshold for dendrite formation, short circuit and cell failure occur as a result [Figure 12D]. The contact loss of the sulfide/Li interphase may be the reason that dendrite problems have still not been solved in sulfide-based ASSBs.

Strategies to stabilize the sulfide electrolyte/Li metal anode interface

Benefiting from our successful experience and methods in liquid-state Li-metal batteries and sodium-ion batteries[127-129], improving the interphase compatibility between sulfides and Li metal is achievable[130,131]. So far, the strategies to stabilize the sulfide/Li metal interphase can be considered as tuning the composition of sulfide electrolytes or anodes and constructing an artificial SEI or interlayer[2,132]. Although none of these methods thoroughly solve the dilemma of interphase incompatibility, the theory and experience generated during the process of inquiry are certainly worthwhile. A summary of the performance of Li-Li symmetric cells using sulfide electrolytes is given in Table 3.

Composition tuning of sulfide electrolytes

According to Sand's theory, the origin of dendrite growth starts from uneven Li deposition[126]. In ASSLBs, promoting the rate of Li diffusion could release the Ohmic polarization. On this basis, a more homogenous Li deposition can be realized. Considering that interfacial side reactions are closely related to the properties of sulfide electrolytes, the targets for the composition tuning of sulfides should not only focus on enhancing the ionic conductivity. Indeed, improving the diffusion rate of Li^+ could somehow promote a more homogenous Li^+ flux during Li plating/stripping, but sulfide electrolytes doped with high-valent metal ions can form an unstable mixed conductive interphase. Hence, maintaining high ionic conductivity while decreasing the overall side reactions represents a conventional route for modifying the composition of sulfide electrolytes to obtain better anodic stability[145].

The investigation of Li/sulfide interphases by XPS and the calculation of the grand potential phase diagram have proved that sulfur anion clusters centered on high-valent cations (e.g., PS_4^{3-}, BS_4^{5-}, SiS_4^{4-}, GeS_4^{4-} and so on) are responsible for side reactions[146]. For non-metal high-valent cations with less reduction activity, replacing partial S atoms with O atoms could decrease the side reactions. A theoretical phase diagram study proposed that Li_3PO_4 is metastable against Li metal[147]. Thus, Tao *et al.*[30] added certain amounts of P_2O_5 into $75Li_2S-25P_2S_5$ glass-ceramic electrolytes to improve the ionic conductivity and anodic stability. It was discovered that the glass-ceramic electrolytes substituted with 1 mol% P_2O_5 had good electrochemical performance. The Li||Li symmetric cells incorporated with modified electrolytes displayed a lower polarization and longer cycling life than the cells using $75Li_2S-25P_2S_5$ glass-ceramic electrolytes at a current density of 0.1 mA cm^{-2} and a cutoff capacity of 0.1 mAh cm^{-2}, indicating that both the side reactions and dendrite growth were suppressed. Ideally, the side reactions between sulfide electrolytes and Li metal should be eliminated. However, with the existence of sulfur anion clusters centered on high-valent cations, prohibiting the decomposition of sulfide electrolyte in anodic sides by tuning its composition is almost impossible. Thus, it is worthy of consideration to select a proper doping component that can generate a robust passivation layer on the surface of Li metal.

LiX (X = F, Cl, Br or I) is widely used as a dopant in sulfide electrolytes due to its mechanical and electronical properties[90]. Han *et al.*[135] introduced different amounts of LiI into a $75Li_2S-25P_2S_5$ glassy system to regulate its reactivity and ionic conductivity. The glass electrolyte with a composition of $0.7(Li_2S-P_2S_5)-0.3LiI$ possessed high ionic conductivity and a critical current density (CCD) above 1 mA cm^{-2}. The promoted anodic stability was attributed to the introduction of LiI into the Li/electrolyte interphase. LiI could help to lower the electronic conductivity of the interphase based on a larger bandgap of LiI (6.4 eV) compared to that of Li_3P (0.7 eV). Furthermore, incorporating LiI into interphase increase the ionic conductivity of the interphase so that the mobility of Li atoms could be improved.

LiF is an essential component in traditional LIBs to stabilize the interphase. By DFT calculations, it was reported that LiF possesses a strong ability to suppress dendrite growth. Though the ionic conductivity of bulk LiF is relatively low, researchers have found that nano-LiF distributed in the interphase displayed a

Table 3. Summary of the performance of Li-Li symmetric cells using sulfide electrolytes

No.	Cell configuration	Critical current density (mA cm^{-2})	Cut-off capacity (mAh cm^{-2})	Test temperature	Ref.
1	Li/Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$/Li	3.0	3.0	50 °C	[133]
2	Li/Li$_{6.25}$PS$_{4.75}$ClN$_{0.25}$/Li	1.52	1.52	RT	[60]
3	Li/Li$_6$PS$_5$Cl$_{0.3}$F$_{0.7}$/Li	6.37	5.0	RT	[134]
4	Li/0.7(Li$_2$S-P$_2$S$_5$)-0.3LiI/Li	3.9	3.9	100 °C	[135]
5	Li/G-LGPS-G/Li (50 MPa)	10.0	0.25	RT	[136]
6	Li/Li$_7$P$_{2.88}$Nb$_{0.12}$S$_{10.7}$O$_{0.3}$/Li	1.16	1.16	RT	[8]
7	Li/Li$_3$N-LiF//Li$_3$PS$_4$//Li$_3$N-LiF/Li	6.0	6.0	RT	[137]
8	Li/LiMg22/LGPS/LiMg22/Li	1.3	1.3	RT	[138]
9	Li/LiFSI@Li$_3$PS$_4$/Li	2.0	2.0	RT	[121]
10	Li-Bp-DME/Polyoxyethylene (PEO)/Li$_3$PS$_4$ /PEO/Li-Bp-DME	17.78	17.78	30 °C	[139]
11	Li/Graphite-Li$_6$PS$_5$Cl-LGPS-Li$_6$PS$_5$Cl-Graphite Li	20.0	0.25	55 °C	[140]
12	Li/Li$_7$P$_3$S$_{11}$/Li	0.76	0.76	RT	[141]
13	Li/0.75Li$_2$S-0.25P$_2$S$_5$/Li	0.4	0.4	RT	[135]
14	Li/0.6Li$_2$S + 0.32SiS$_2$ + 0.12PS$_{5/2}$/Li	1.50	1.50	RT	[142]
15	Li/Li$_6$PS$_{4.7}$O$_{0.3}$Br/Li	0.90	0.90	RT	[143]
16	Li/Li$_6$PS$_5$Cl/Li	0.55	0.55	RT	[144]
17	Li/Li$_7$P$_{2.9}$Si$_{0.05}$S$_{10.85}$/Li	0.80	0.80	RT	[141]

RT: Room temperature.

satisfactory ionic conductivity[148]. Recently, Zhao *et al.*[134] reported a F-containing sulfide electrolyte to derive the formation of a functional SEI layer with a high concentration of LiF. Li$_6$PS$_5$Cl was selected as a host material to realize F doping in their work. The Li symmetric cells incorporated with an optimized electrolyte Li$_6$PS$_5$Cl$_{0.3}$F$_{0.7}$ delivered a stable cycle performance at an ultrahigh current density of 6.37 mA cm^{-2} and a cut-off capacity of 5 mA cm^{-2}. A detailed investigation of interphase by XPS depth profiling and time of flight-secondary ion mass spectrometry proved the existence of LiF throughout the interphase. Compared to unmodified Li$_6$PS$_5$Cl, the F-containing electrolytes effectively passivate the interphase and suppress dendrite growth.

Moreover, accompanied by the success of Li$_3$N-rich SEI in LMBs using organic electrolytes, Liu *et al.*[60] substituted partial Cl atoms in Li$_6$PS$_5$Cl with N atoms. On this basis, an *in-situ* formed Li$_3$N-rich interphase was introduced. By galvanostatic cycling Li symmetric cells at step-increased current densities, the electrolyte with a composition of Li$_{6.25}$PS$_{4.75}$ClN$_{0.25}$ displayed a CCD over 1.5 mA cm^{-2}. Based on DFT calculations, N atoms near the Li/electrolyte interphase are not easily pulled into the lattice of metallic Li to form Li-N bonds [Figure 13A and B]. In addition, incorporating Li$_3$N into the interphase can fasten the transport of Li$^+$. On this basis, homogenous Li plating was realized.

Very recently, an unconventional work has brought inspiration to the composition tuning of sulfides. Although it is true that metal cations in sulfides can easily react with Li metal, when the doped metal cations are not the dominant components, the disadvantages can be compensated for. Taklu *et al.*[133] reported a sulfide super-conductor Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$ with high stability against Li. Despite the existence of Cu$^+$, the Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$ electrolyte with much lower electronic conductivity and better interphase compatibility than typical Li$_6$PS$_5$Cl. Thus, the dendrite growth would be prohibited. The released interphase incompatibility and low electronic conductivity compensated for the effects of side reactions. Consequently, the CCD of Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$ can reach 3 mA cm^{-2} at 50 °C, which is four times higher than that of typical
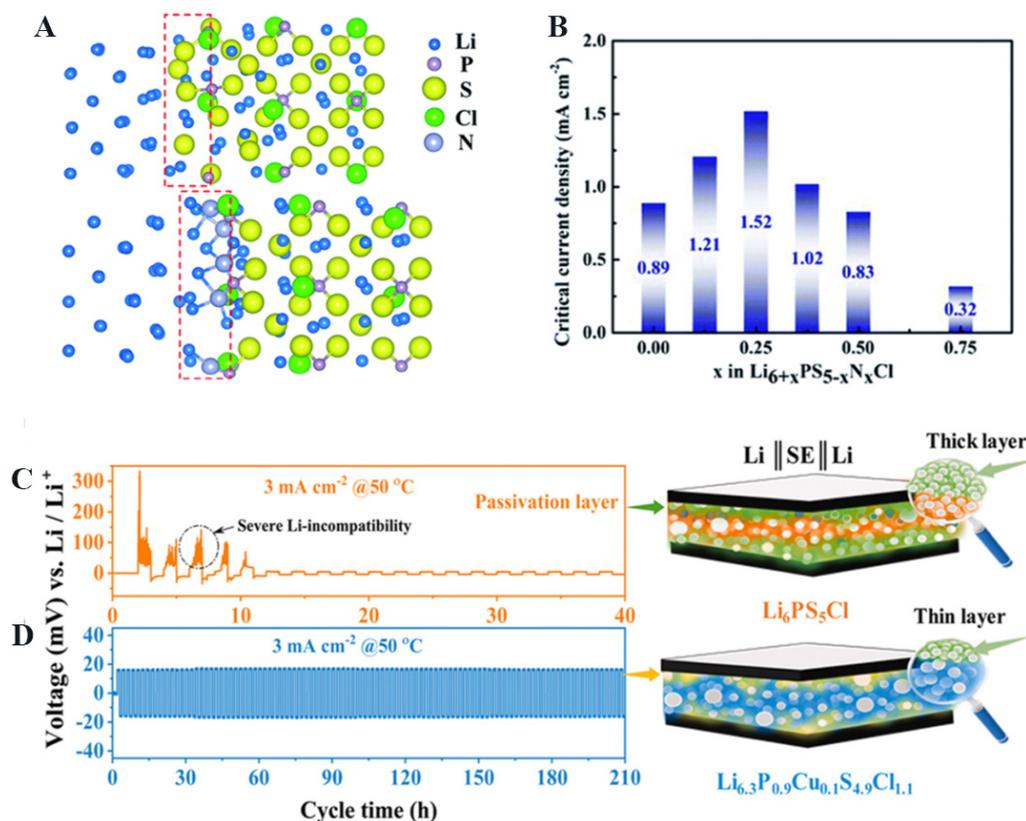
Figure 13. (A) Interface configuration for Li/Li$_6$PS$_5$Cl (top) and Li/N-doped Li$_6$PS$_5$Cl (below) after structure relaxation by DFT calculations. (B) Critical current densities of Li$_{6+x}$PS$_{5-x}$N$_x$Cl electrolytes as a function of N content x. Reproduced with permission[60] (Copyright 2021, Royal Society of Chemistry). Galvanostatic symmetric cell, Li | SE | Li voltage profiles at 50 °C. (C) and (D) Li plating and stripping performance of Li$_6$PS$_5$Cl and Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$ at 3 mA cm^{-2}, respectively. Reproduced with permission[133] (Copyright 2021, Elsevier).

Li$_6$PS$_5$Cl. In addition, when cycling the symmetric cells at a current density of 3 mA cm^{-2}, the performance of Li$_{6.3}$P$_{0.9}$Cu$_{0.1}$S$_{4.9}$Cl$_{1.1}$ is much better than that of Li$_6$PS$_5$Cl [Figure 13C and D].

Composition tuning of anodes
It is clear that employing pure Li metal as an anode acquires high energy density, but it is also acceptable to sacrifice part of the energy density in exchange for stability. Through DFT calculations and experimental observations, Li alloys have relatively high reduction potentials compared to Li metal[149]. Therefore, the side reactions between the anode and sulfide electrolyte will not proceed violently. Furthermore, it is also proved that the diffusion rate of Li$^+$ on some Li alloys is higher than that on Li metal[150]. A fast diffusion rate of Li$^+$ on anodes could decrease the growth of dendrites. Li-In alloys, for instance, are widely used as anodes in assembling ASSLBs[151]. The reduction potential of Li-In alloys is ~0.6 V above Li metal. For this reason, the side reactions between anodes and electrolytes are prohibited[152]. Moreover, the soft nature of Li metal does not change significantly in Li-In alloys, which ensures good contact between the Li and electrolytes[153]. However, it is not practical to use Li-In alloys got commercialization given that In is not affordable for large-scale generation. Furthermore, the high density of In and high reduction potential of Li-In alloys decrease the overall energy density of ASSLBs. Therefore, only experimental work investigating cathodic or anodic unstable electrolytes would apply Li-In as anodes.

Lee *et al.*[154] demonstrated a silver/carbon composite anode that could mitigate the problems of low CE and dendrite growth in ASSLBs at high current densities. It was proved by cross-sectional SEM and corresponding energy dispersive spectroscopy that nano-Ag particles can be alloyed with Li during the process of Li plating. In addition, partial Ag was found to move to the current collector side, which assisted the uniform and dendrite-free plating of Li metal. The Ag-C/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) pouch cells exhibited high energy density (> 900 Wh L^{-1}) and stable cycling for over 1000 times. Recently, Tan *et al.*[155] developed a micro-silicon anode to realize high-energy-density ASSLBs. During the lithiation process of micro-silicon, the formation of Li-Si alloys can propagate throughout the anode, benefiting from the good ionic and electronic contact between Li-Si and micro-silicon particles. The assembled micro-silicon/NMC811 full cell could deliver a capacity retention of ~80% after 500 cycles at a current density of 5 mA cm^{-2}, demonstrating the robustness of the constructed micro-silicon anodes. Choi *et al.*[156] proposed Ag-Li alloy anode via a mass-producible roll-pressing method [Figure 14A]. The *in-situ* formed Ag-Li intermetallic layer mitigated uneven Li plating, as confirmed by the improved cycling performance of Ag-Li/Ag-Li symmetric cells [Figure 14B]. ASSLBs with Ag-Li anodes displayed a capacity retention of 94.3% for 140 cycles, while the cells with unmodified Li metal showed frequent initial short-circuit. In addition, Su *et al.*[136] applied a Li/graphite composite as the anode, where the graphite served as a protective layer to suppress the side reactions between Li and LGPS. Under a pressure of 250 MPa, the symmetric cells with Li-graphite composite anodes could cycle at a current density of 10 mA cm^{-2} with no occurrence of short circuit or dendrite growth.

In addition to the construction of Li alloy anodes, Peng *et al.*[139] prepared a liquid lithium solution anode by putting Li metal into a biphenyl/DME solution at 60 °C. It has been reported that the contact loss between a sulfide and Li metal causes dendrite problems. The introduction of the liquid lithium solution anode continuously ensured the contact between anode and electrolytes, thus prohibiting dendrite growth. As a result, the symmetric cells incorporated with liquid lithium solution anodes, a Li$_3$PS$_4$ pellet and polyoxyethylene (PEO) protective layers [Figure 14C] achieved a record-high CCD of > 17.78 mA cm^{-2} [Figure 14D]. The repeatability and strictness of the CCD measurement was proved by adding stable cycling for three times at some particular current densities into the step-increase test of CCD for a Li-Bp-DME/PEO/LPS/PEO/Li-Bp-DME cell [Figure 14E]. An ultrahigh current density of 10.16 mA cm^{-2} was achieved with a per-cycle plating areal capacity of 3.81 mAh cm^{-2}, thereby confirming that the cell has a superior lithium dendrite suppression ability.

Construction of artificial SEIs

Artificial SEIs have proved to be effective in suppressing side reactions and dendrite growth in liquid-state LMBs. The experience obtained from the design of appropriate artificial SEIs in previous research on liquid-state LMBs also aids the design of artificial SEIs in ASSLBs. The success of high concentration electrolytes in liquid-state LMBs is attributed to anion-derived SEIs[157]. Based on this, Fan *et al.*[121] processed Li with 6 M LiFSI in DME to form a LiF-rich interphase between Li and a sulfide electrolyte. After drying the organic electrolytes, galvanostatic charging/discharging tests on symmetric cells using Li$_3$PS$_4$ as an interlayer were performed. The symmetric cells incorporated with the LiF-rich interphase displayed a CCD value of > 2 mA cm^{-2}, indicating that this interphase effectively prohibited the growth of dendrites. Zhang *et al.*[158] proposed a surface phosphating method of Li metal to suppress the side reactions between Li and LGPS. Symmetric cells with a LiH$_2$PO$_4$-rich interphase could maintain stability at 0.1 mA cm^{-2} for over 950 h without obvious polarization. Furthermore, Liang *et al.*[159] constructed a SEI consisting of amorphous Li$_x$SiS$_y$ by two steps of liquid phase reactions on Li metal [Figure 15A]. Through thermogravimetric analysis of the anodes, the modified anodes were verified to be air stable. The amorphous Li$_x$SiS$_y$ coated on Li metal enabled fast Li diffusion, thereby preventing the formation of voids and cracks. As a result, symmetric cells with Li$_x$SiS$_y$-coated Li could stably cycle at a current density of 0.1 mA cm^{-2} and 0.5 mAh cm^{-2} for over
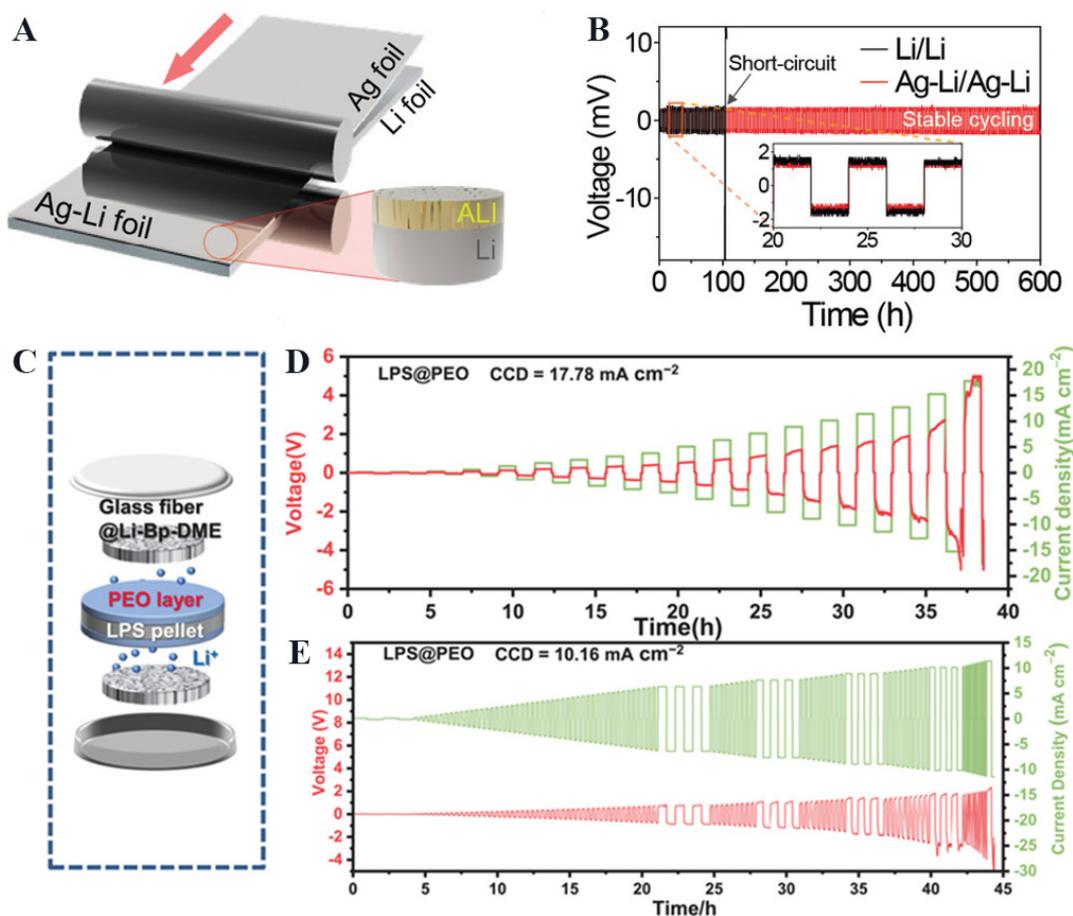
Figure 14. (A) Experimental scheme for preparing Ag Li alloy foil. (B) Voltage profiles of Li/Li and Ag Li/Ag Li symmetric cells at 0.5 mA cm^{-2} with a fixed capacity of 1 mAh cm^{-2}. Reproduced with permission[156] (Copyright 2021, Wiley-VCH). (C) Schematic illustration of the symmetric coin cell used for CCD detection. (D) Voltage profiles of the symmetric cell using PEO protective layer at step-increased current densities and the cell cycled once under each current density. (E) Voltage profiles of the symmetric cell using PEO protective layer at increased current densities and the cell cycled three times under some particular current densities. Reproduced with permission[139] (Copyright 2021, Wiley-VCH). CCD: Critical current density; PEO: polyoxyethylene.

2000 h [Figure 15B], while the symmetric cells with bare Li could only cycle at the same conditions for less than 20 h.

Recently, based on a theoretical study of the mechanical and chemical properties of typical SEI components. Ji *et al.*[137] designed a Li$_3$N-LiF hybrid coating on Li$_3$PS$_4$ to assure a high ionic conductivity and interphase energy. As a consequence, a record-high CCD value of > 6 mA cm^{-2} was achieved. Furthermore, according to the experimental results and DFT calculations, the criteria for designing SEIs in ASSLBs were proposed in their work. Firstly, a good SEI should be electrochemically stable to metal Li to avoid additional side reactions. It should also have high ionic conductivity to enable the homogenous and fast diffusion of Li$^+$ and have low electronic conductivity to block the transport of electrons through the interphase. The high interphase energy of SEI could help to suppress dendrite growth. These criteria cannot only guide the design of artificial SEIs but could also provide a standard to evaluate the interphases between Li and solid electrolytes.
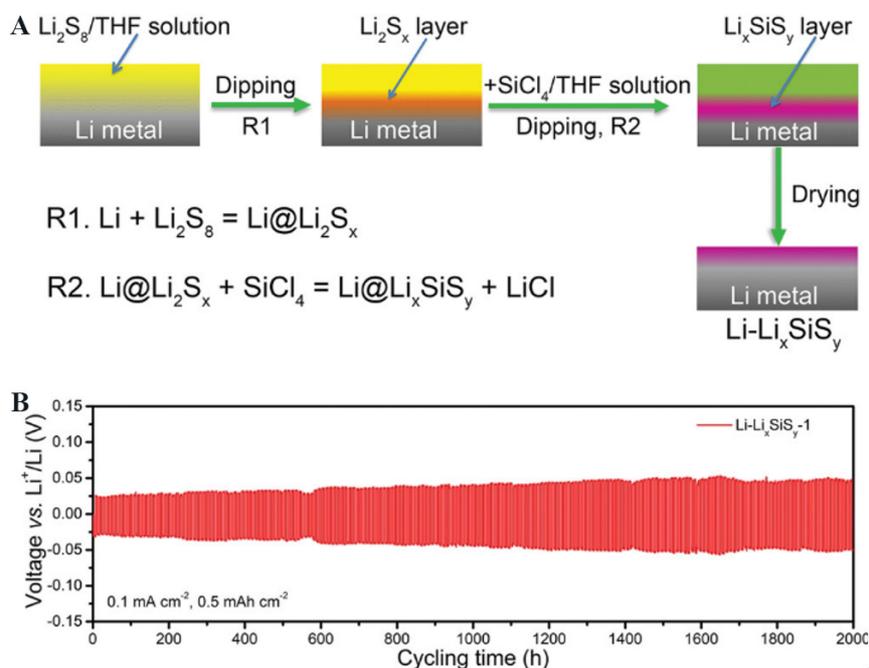
Figure 15. (A) Reaction scheme for the formation of Li-Li$_x$SiS$_y$ and the characterization of the Li-Li$_x$SiS$_y$-1 electrode. (B) Long-term cycling performance of symmetric Li-Li$_x$SiS$_y$ cells. Reproduced with permission[159] (Copyright 2019, Wiley-VCH).

It is noteworthy that most previous work on the construction of artificial SEIs did not consider contact loss. Yang *et al.*[160] performed large-scale molecular dynamics simulations to investigate the interphases between Li and solid electrolytes. The interphase failure started with the formation of nanosized pores by their observations. By correlating the interphase behavior and interfacial adhesion energy, it was discovered that the interphases between Li and solid electrolytes with higher interfacial adhesion energy displayed a better ability to avoid contact loss. Incoherent Li-solid electrolyte interphases with high interfacial adhesion energy require less applied external pressure. Therefore, future research into interphases should focus more on adhesion energy since the contact loss plays a significant part in dendrite growth.

Construction of interlayers
The construction of interlayers is a new perspective in ASSLBs. Firstly, it was found that ASSLBs incorporated with bilayer inorganic composite electrolytes displayed good cycling behavior during discharging and charging. In particular, for the electrolytes that have unsatisfactory anodic or cathodic stability, constructing another protective interlayer is effective. Based on DFT calculations, sulfide electrolytes containing iodine suffer from low cathodic stability. It is well known that sulfide electrolytes containing high-valent metal ions can easily react with Li metal. Therefore, Zhao *et al.*[48] applied bilayer inorganic composite electrolytes when assembling ASSLBs. The Li-S ASSLBs with bilayer inorganic electrolytes could obtain a capacity retention of 96% after 200 cycles. Recently, Ye *et al.*[140] designed a structure of a less stable LGPS electrolyte sandwiched between more stable electrolytes of Li$_6$PS$_5$Cl, which could prohibit dendrite growth through localized decomposition in the LGPS layer. To explain this, they proposed a mechanism analogous to the expansion screw effect, which is, any cracks in LGPS would be filled by dynamically generated decompositions. When utilizing graphite-covered Li as an anode, the symmetric cells could stably cycle over 1800 h at a current density of 0.25 mA cm^{-2} at RT. Moreover, this kind of symmetric cell could also cycle at an ultrahigh current density of 20 mA cm^{-2}. This effect could partially explain why well-designed bilayer inorganic composite electrolytes have good electrochemical performance.

Secondly, the building of polymer electrolyte layers between the Li and sulfide electrolytes is of great importance in solving the dilemma of contact loss during Li plating/stripping. Polymer electrolytes have a certain degree of fluidity, which can ensure the wetting of Li metal during cycling. Furthermore, altering the components of the polymer electrolytes provides a new strategy for constructing SEIs in ASSLBs. Inspired by the moderation and long duration of sustained release drug-carriers in the biomedicine, Chen *et al.*[161] prepared LiTFSI/PPC polymer electrolytes. During cycling, PPC decomposes into PC to release LiTFSI, which reacts with Li metal [Figure 16A]. As a consequence, a LiF-rich interphase forms to suppress dendrite growth. As a result, symmetric cells containing polymer-coated Li displayed stable cycling and relatively low polarization at a current density of 0.5 mAh cm^{-2} for over 300 h [Figure 16B and C].

Li *et al.*[162] also synthesized a gel electrolyte originating from the polymerization of 1,3-dioxolan initiated by lithium difluoro(oxalato)borate. By adding certain amounts of LiPO$_2$F$_2$ as a SEI forming agent, a robust SEI containing Li$_3$PO$_4$ and LiF was obtained. The side reactions and dendrite growth were efficiently suppressed by the synthesized gel electrolytes. At a current density of 0.5 mA cm^{-2} and a cut-off capacity of 0.5 mAh cm^{-2}, the symmetric cells with polymer/LGPS layers could cycle for 500 h without almost any polarization compared to the symmetric cells with only LGPS as the interlayer, which indicated that the severe side reactions between Li and LGPS were prohibited. Using backscattered electron imaging characterization, a clear black spot appeared in LGPS without the protection from polymer electrolytes, while there was no obvious change in the LGPS electrolytes protected by synthesized polymer electrolytes. The appearance of black spots means dendrite growth through the observed area because the electron conductivity of Li is much higher than the electrolyte.

SULFIDE ELECTROLYTE/CATHODE INTERFACES

Challenges for sulfide electrolyte/cathode interfaces

The challenges facing sulfide electrolyte/cathode interfaces originate from the sharp electrochemical window of sulfides and insufficient contact between cathode particles and sulfides. Firstly, based on the above-mentioned DFT calculation results, sulfide electrolytes are not able to sustain high-voltage environments. Therefore, oxidation compositions of sulfides occur during the process of charging. Moreover, contact loss between solid and solid particles during cycling and violent volume change of cathodes contribute significantly to the failure of ASSLBs. Finally, the formation of the space charge layer in the interphase between sulfides and cathode particles hinders the transport of charge carriers.

Space charge layers

The space charge layer is a concept that originated from semiconductors. It is formed when two materials with different chemical potentials are brought into contact with each other and the charge carriers in two materials cannot migrate to establish local charge neutrality. Theoretically, both electrons and atoms would be driven to the material with the lowest chemical potential near the interphase. However, the insulating nature of solid electrolytes makes it difficult for electrons to transport. The only charge carrier between the electrolyte and electrode in ASSLBs is Li$^+$, which creates a space charge layer[163,164].

The role that the space charge layer plays in the interphase between solid electrolyte/cathode can be controversial. In the early research on the interphase between cathodes and solid electrolytes, space charge layers have been indicated to be several micrometers in thickness, which would cause an enormous interphase resistance. Recently, Wang *et al.*[165] characterized the LiCoO$_2$/Li$_6$PS$_5$Cl interphase by *in-situ* differential phase contrast scanning transmission electron microscopy (DPC-STEM) to investigate the net-charge-density distribution. It was found that a Li$^+$ deficient negative-charge-density region would form once the LiCoO$_2$ cathode and Li$_6$PS$_5$Cl came into contact on the Li$_6$PS$_5$Cl side of the interphase. The STEM
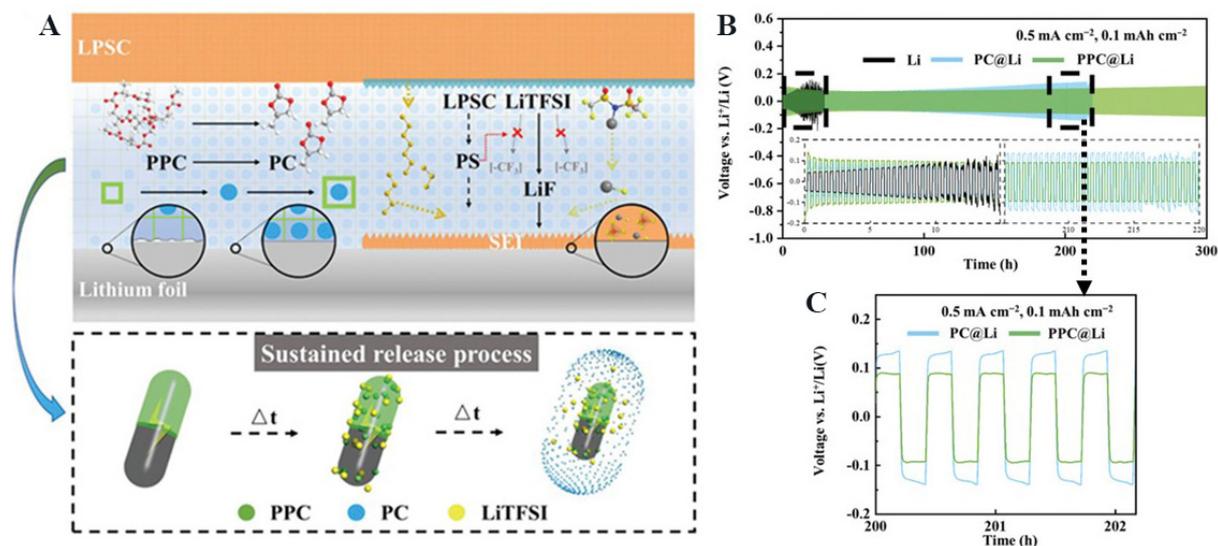
Figure 16. (A) Schematic illustration of *in situ* sustained release effect of poly(propylene carbonate) between Li_6PS_5Cl and Li anode. (B, C) Galvanostatic discharge/charge voltage profiles of Li/Li_6PS_5Cl/Li (Li) and PPC@Li/Li_6PS_5Cl/PPC@Li (PPC@Li) symmetric cells at a current density of 0.5 mA cm^{-2} and a cut-off capacity of 0.1 mAh cm^{-2} at RT. Reproduced with permission[161] (Copyright 2020, Wiley-VCH). RT: Room temperature.

image of pristine $LiCoO_2$/Li_6PS_5Cl interphase displayed that the space charge layer was about several nanometers in thickness, which was an order of magnitude thinner than previously expected. Furthermore, in the process of studying the Li^+ kinetics by solid-state nuclear magnetic resonance (SS-NMR), Yu *et al.*[166] surprisingly concluded that interphase resistances were only a few Ω cm^{-2} over pristine electrode-electrolyte interphases. This favored the observation that the thickness of space charge layer was on the nanometer scale since such a thickness was unlikely to lead to a notable interphase resistance.

A recent study by Niek *et al.*[163] might put an end to the debate. They proposed a simple model to simulate the interphase capacitance and resistance caused by the space charge layer. This model is applied to $LiCoO_2$ in contact with LLZO ($Li_7La_3Zr_2O_{12}$) and LATP [$Li_{1.2}Al_{0.2}Ti_{1.8}(PO_4)_3$] solid electrolytes at several voltages. The results of the prediction demonstrated that the resistance of the space charge layer is negligible, except for the situation that layers completely depleted of Li^+ are formed in solid electrolytes. For the interphase between $LiCoO_2$ and Li_6PS_5Cl, the formation of layers completely depleted of Li^+ was observed by DPC-STEM at a bias voltage of 2.2 V, which hindered the transport of Li^+ to the cathode and increased the interphase resistance[165]. Therefore, the space charge layer could influence the sulfide/cathode interphase and should be considered when designing a proper electrolyte/electrode interphase.

Interfacial reactions

The interfacial reactions at the cathode/sulfide interphase mainly originate from sulfur. According to a first-principles study on the electrochemical window of sulfide electrolytes, the onset oxidation potential of sulfides was predicted to ~2.0-2.3 V (*vs.* Li^+/Li) due to the existence of S element[146]. For this reason, severe side reactions between sulfide and cathode would always occur during the process of charging. The oxidation of sulfide electrolytes near the cathode intends to form an ionic insulating layer to block the transport of Li^+, which in turn enhances the interphase resistance. Furthermore, the side reactions between sulfide and high-voltage oxide cathodes sometimes destroy the crystalline structure of oxides, resulting in an irreversible capacity loss[167].

Koerver *et al.*[168] presented a detailed study that revealed the interphase between an NMC811 cathode and β-Li_3PS_4 electrolyte by utilizing XPS and *in-situ* EIS. According to the discussion of reaction mechanism, they proposed that β-Li_3PS_4 electrolyte might be polymerized into $Li_2P_2S_6$, $Li_4P_2S_7$ and $Li_4P_2S_8$. Based on the results of XPS characterization, the redox activity of Li_6PS_5Cl in ASSLBs was investigated by Zhang *et al.*[169]. It was revealed that Li_6PS_5Cl would be oxidized into P_2S_5, LiCl and polysulfides in the cathode. Additionally, a $LiCoO_2$ cathode intended to react with Li_6PS_5Cl to produce phosphate upon cycling. Auvergniot *et al.*[170] then also carried out further research on the interphase stability of Li_6PS_5Cl towards different oxide cathodes. The XPS results displayed that P_2S_5, LiCl, phosphate and polysulfides were the general reaction products of oxide cathodes and the Li_6PS_5Cl electrolyte. Interestingly, the side reactions did not severely hinder the good cyclability of batteries since Li_6PS_5Cl could contribute to the reversible capacity. Moreover, Zheng *et al.*[171] unraveled the electrochemical stability of $Li_{10}SnP_2S_{12}$ in ASSLBs via solid-state NMR and XPS. It was demonstrated that $Li_{10}SnP_2S_{12}$ suffered from severe side reactions when preparing cathode composites by ball-milling. As shown in Figure 17A-C, the broad Li^+ peak indicated the generation of low ionic conductivity species. By the confirmation of ^{31}P and ^{119}Sn spectra in Figure 17B and C, Li_3PS_4, and Li_4SnS_4 would form when ball-milling $Li_{10}SnP_2S_{12}$ electrolytes and $LiCoO_2$ together [Figure 17D]. The detailed XPS investigation then indicated that $Li_{10}SnP_2S_{12}$ oxidized into S, SnS_2 and P_2S_5 when the ASSLBs were charged to 4.2 V. Though the interfacial reactions of sulfides on the cathodic sides may provide extra capacity, the initial low CE and the generation of low ionic conductivity species are detrimental to the electrochemical performance of ASSLBs. Thus, an appropriate method to protect sulfides from being constantly oxidized by cathodes is desperately required.

Mechanical instability

The contact between particles has always been a dilemma for the cathode of ASSLBs. Several kinds of solid/solid interphases, including cathode/cathode, cathode/electrolyte, cathode/electron conductor (carbon) and electrolyte/electron conductor (carbon), can initially form upon mixing the components of cathode together. The existence of various interphases on the cathode creates an arduous condition for the transport and exchange of ions and electrons. The insufficient solid/solid contact increases the interfacial resistance. During the process of charging and discharging, accompanied side reactions generate species of low ionic conductivity, which block the contact between cathode particles and sulfide electrolytes[171]. In addition, introducing an electron conductor to the cathode composite intends to strengthen the side reactions of sulfides[172]. Though the overall electron conductivity may be enhanced, the contact loss between sulfides and cathode particles hinders the diffusion of Li^+. Furthermore, the volume of cathode particles would expand or shrink when processing charging or discharging, which destroys the ionic- or electronic-conducting network[173]. The issue of volume expansion shrinking is especially severe in Li-S ASSLBs due to the violent volume difference between S particles and Li_2S. After long cycles, the accumulated side reactions induce the pulverization of cathode particles. For this reason, the complete crystal structure of the cathode is broken, which irreversibly decreases the capacity of ASSLBs[174].

Interfacial engineering

Due to the above-mentioned problems that exist in sulfide/cathode interphases, it is imperative to design an appropriate structure of a cathode composite. Synthesizing a relatively stable electrolyte against cathode particles is an alternative perspective. Wang *et al.*[175] found the correlation between the performance of ASSLBs with the sulfides having the same stoichiometry but different crystallinity. It was reported that glass/glass-ceramic sulfides displayed better electrochemical performances rather than crystalline sulfides due to reduced occurrence of contact loss. The crystalline sulfides possessing high partial electronic conductivity may be the reason for severe degradation in the cathode composite. Even with the same stoichiometry, the electrochemical and mechanical properties of sulfides can be different. Therefore, a considerable selection for sulfides with satisfactory electrochemical and mechanical properties would benefit
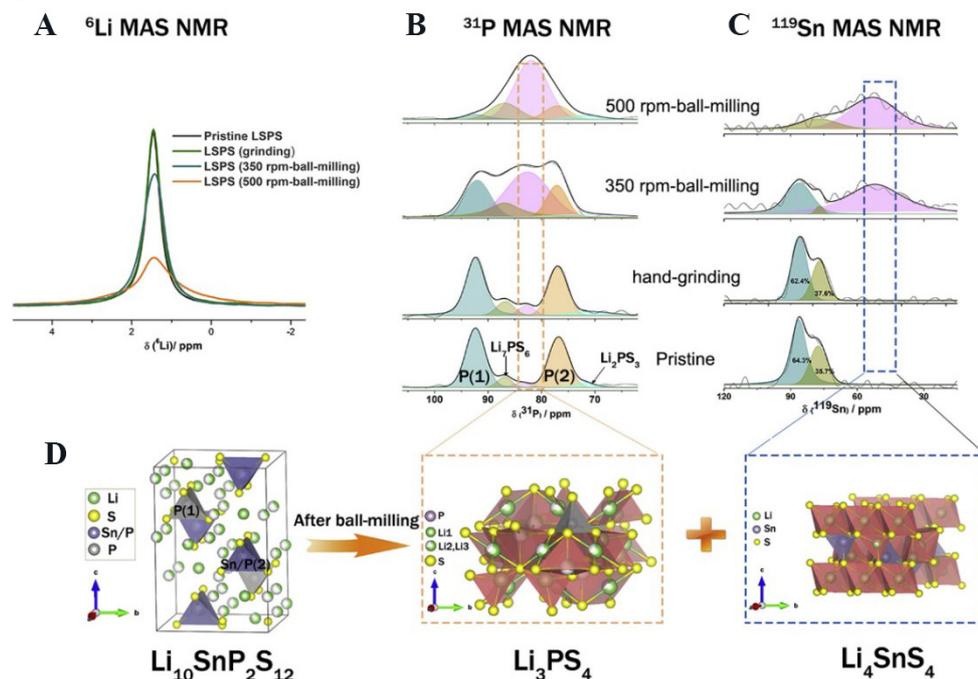
Figure 17. Solid-state NMR results of $Li_{10}SnP_2S_{12}$ before and after treatment. (A) ^6Li, (B) ^{31}P and (C) ^{119}Sn MAS NMR spectra of $Li_{10}SnP_2S_{12}$ powder with different treatments. (D) Decomposition mechanism of $Li_{10}SnP_2S_{12}$ powder after ball-milling. Reproduced with permission[171] (Copyright 2019, Elsevier).

the optimization of cathode composites.

In addition, Zhang *et al.*[172] found that the introduction of carbon into a cathode composite might have detrimental effects on the electrochemical performance. The cathode composite incorporated with LGPS electrolytes and carbon exhibited more severe degradation and larger volume change compared to the composite without carbon. Analysis by XPS indicated that carbon fastened the decomposition of sulfides by transferring the Li of low chemical potential in the charged state deeper into the electrolytes and expanding the decomposition region. Therefore, in their later work, a non-carbon $LiNi_{0.7}Co_{0.1}Mn_{0.2}O_2$ (NCM622) cathode composite was proposed. It was surprisingly detected that the crystal of NCM622 displayed a certain level of electronic conductivity. By carefully controlling the ratio of Li_6PS_5Cl and NCM622 without adding extra electronic conductors, both the ionic and the electronic conductivity of the cathode composite met the standards for normal application[176]. Recently, Liu *et al.*[173] presented in-depth research on the effects of the size and crystallinity of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) cathodes on the electrochemical performance. By combining the characterization methods of XPS, solid-NMR, *in-situ* EIS and focused ion beam-SEM, the electrochemical performance and electrochemomechanical behavior of polycrystalline NCM811, small-sized polycrystalline NCM811 and single-crystal NCM811 in $Li_{10}SnP_2S_{12}$-based ASSBs were compared. It was found that single-crystal NCM811 with good microstructural integrity performed better than polycrystalline and small-sized polycrystalline NCM811. However, the mechanism of the extraordinary performance of single-crystal NCM811 remains to be discovered.

As well as tuning the crystallinity of cathodes and electrolytes, coating a protective layer on cathode particles is a more common method to realize the reversible charging-discharging behavior of the cathode. Typically, $LiNbO_3$-coated $LiCoO_2$ was widely used as cathode materials in recent work. $LiNbO_3$ with high ionic conductivity, low electronic conductivity and relatively wide electrochemical window worked well as a

buffer layer. The resistance of the cathode composite incorporating $LiNbO_3$-coated $LiCoO_2$ was reduced and the side reactions were also prohibited. To realize high energy density in ASSLBs, Ni-rich oxide cathodes should be considered. Constructing a buffer layer on Ni-rich oxide cathodes is also proved to be effective to enhance electrochemical performance. Recently, Li *et al.*[177] successfully prepared $LiNbO_3$-coated NCM811 cathodes, with 1 wt.% $LiNbO_3$-coated NCM811 cathodes demonstrated a high initial discharge capacity of 203 mAh g^{-1} and excellent rate performance. Peng *et al.*[178] carried out an in-depth investigation on coating $LiNi_{0.7}Co_{0.1}Mn_{0.2}O_2$ (NCM712) with $LiNbO_3$. The $LiNbO_3$-coated NCM712 delivered an initial discharge capacity of 80.9 mAh g^{-1} at 5 C at RT with a capacity retention of 87.5% after 600 cycles. The coating effectively suppressed the volume change of cathode particles during cycling and prohibited the side reactions, which was confirmed by the results of XPS and TEM.

Moreover, Banerjee *et al.*[179] investigated the interfacial reactions between Li_6PS_5Cl and $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$ (NCA) by ab-initio molecular dynamics. It was found by radical distribution functions that PO_4^{3-} polyhedra form after cycling [Figure 18B and C]. The $LiNbO_3$ coating on NCA cathodes could effectively improve the thermodynamic stability between NCA and Li_6PS_5Cl by lowering the exothermic reaction energy [Figure 18A]. The initial charge plateau previously observed between 2.3 and 3.6 V at the 1st cycle vanished at the 2nd cycle in the ASSLBs using LNO-coated NCA, which confirmed that LNO could prevent the electrolytes from decomposing [Figure 18D]. As a consequence, the ASSLBs exhibited excellent cycling stability with a capacity retention of 93% at 100 cycles [Figure 18E]. Li *et al.*[180] constructed a nanoscale LATP protective layer on single-crystal $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622). The conformal LATP buffer layer with high-voltage stability decreased the oxidation decomposition of sulfides. The ASSLBs incorporated with LATP-coated single-crystal NCM622 presented a discharge capacity of 152.1 mAh g^{-1} with a capacity retention of 87.6% after 100 cycles at 0.1 C.

Aside from building a buffer layer on cathodes, Wang *et al.*[181] noticed that the incompatibility of sulfides and oxide cathodes could be eliminated by doping sulfur into the crystal structure of $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO). Compared with surface coatings, this new perspective required less arduous operation. Moreover, the ionic conductivity of LNMO particles was significantly improved by the introduction of sulfur. The S-doped LNMO/sulfide ASSLBs delivered a three-times higher initial discharge capacity and much higher capacity retention than the bare LNMO counterpart.

FABRICATION OF ASSLBS WITH HIGH CELL-LEVEL ENERGY DENSITY

Based on Ohm's law, the internal resistance of a battery is proportional to the Ohmic polarization when the current is constant. Considering that commercialized batteries are cycled at a relatively large current density in the actual application scenario, the electrolyte with high resistance will cause the proportion of Ohmic polarization to increase rapidly. Thus, employing electrolytes with low overall resistance in ASSLBs is a major concern.

The thickness and ionic conductivity of electrolytes are negatively proportional to the resistance. According to this, an ideal interlayer should be thin and of high ionic conductivity. Randau *et al.*[182] proposed a benchmark for the performance of ASSLBs recently. It was mentioned that the thickness of the thiophosphate solid electrolyte separator should be less than 40 μm under the condition that the area capacity of NCM cathode was 5 mAh cm^{-2} and the thickness of Li metal was 20 μm if the energy density of ASSLBs with NCM as cathodes is required to exceed 400 Wh kg^{-1}. However, the practical energy density of sulfide-based ASSLBs has not exceeded 200 Wh kg^{-1}. Either increasing the ratio of cathodes or decreasing the thickness of the interlayer would help to enhance the energy density. The high ionic conductivity of sulfide endows the potential of its application in the field of high energy-density ASSLBs. By the slurry
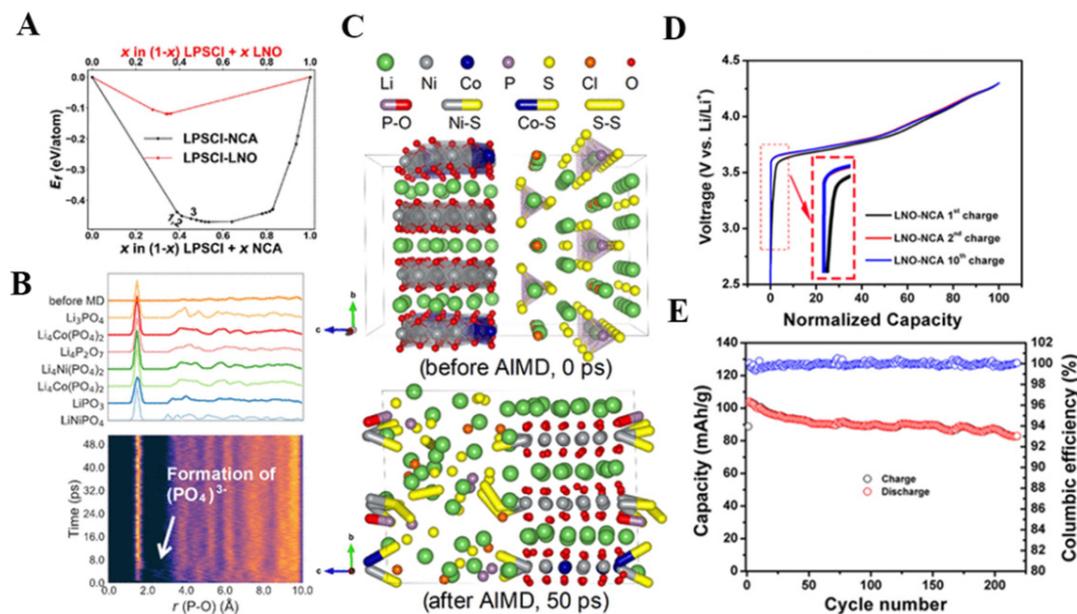
Figure 18. (A) Pseudo-binary phase diagram between Li_6PS_5Cl electrolyte and discharged NCA cathode at different mixing ratios, the red line indicates the case with $LiNbO_3$ coating. (B) Atomic structure of the half-charged NCA/Li_6PS_5Cl interface at 0 and 50 ps, which summarizes the key observations in the ab-initio molecular dynamics (AIMD) simulation. (C) Visualization of the formation of characteristic PO bonds in PO_4 polyhedra at the half-charged NCA/Li_6PS_5Cl interface using RDF. The charging profile (D) of LPSCl and NCA-LPSCl ASSBs at the 1st, 2nd and 10 th cycles. Cycling stability of (E) ASSBs for LNO-coated and bare NCA at the rate of C/3.5. Reproduced with permission[179] (Copyright 2019, American Chemical Society). NCA: $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$.

method, Wang *et al.*[183] prepared a Li_6PS_5Cl/poly(vinylidene difluoride) composite free-standing membrane with a thickness of 100-120 μm. The ionic conductivity of the sulfide composite membrane was 1×10^{-3} S cm^{-1}. Cycling stability of Li_6PS_5Cl electrolyte against Li metal was improved after adding poly(1,1-difluoroethylene) (PVDF), which was proved by longer cycling life and lower polarization of symmetric cell using the composite membrane as the interlayer in the galvanostatic tests at a current density of 0.2 mA cm^{-2}. Liu *et al.*[184] coated a 5 nm thick homogeneous polydopamine layer on Li_6PS_5Cl electrolyte and prepared a 35 μm thick free-standing electrolyte film by cold pressing the coated electrolytes. Zhu *et al.*[185] designed a free-standing sulfide film through a self-limited strategy. By employing a chemically compatible cellulose membrane as the skeleton, the thickness of SSE films was defined and the mechanical strength was also improved.

Zhang *et al.*[186] ball-milled a $Li_{5.4}PS_{4.4}Cl_{1.6}$ powder and polytetrafluoroethylene fiber to prepare a solid electrolyte membrane. The thickness of obtained sulfide membrane was 30 μm and the ionic conductivity of it exceeded 8×10^{-3} S cm^{-1}, which basically satisfied the benchmark of high-energy-density ASSLBs [Figure 19A]. An Al_2O_3 interphase was introduced to avoid the direct contact between Li and membrane for the purpose of suppressing side reactions and dendrites growth. Consequently, the ASSLBs configured with Al_2O_3-coated-Li/sulfide membrane/NCM exhibited capacity retention of 80.2% after 150 cycles with a high NCM mass loading of 11.6 mg cm^{-2} at 0.05 C [Figure 19B and C]. Moreover, Samsung fabricated a thin sulfide film using a doctor blade[154]. By modifying the composition and structure of anode and cathode, a 900 Wh L^{-1} level ASSLBs with superior cycle life (> 1000 times) was obtained. Very recently, Xu *et al.*[187] developed a water-stable sulfide membrane by spray coating LATP nanoparticles and fluorinated polysiloxane. The as-prepared coating can help sulfide membrane withstand extreme exposure conditions with water jetting in the ambient environment, which brings dawn to the large-scale production of sulfide-based ASSLBs in the future.
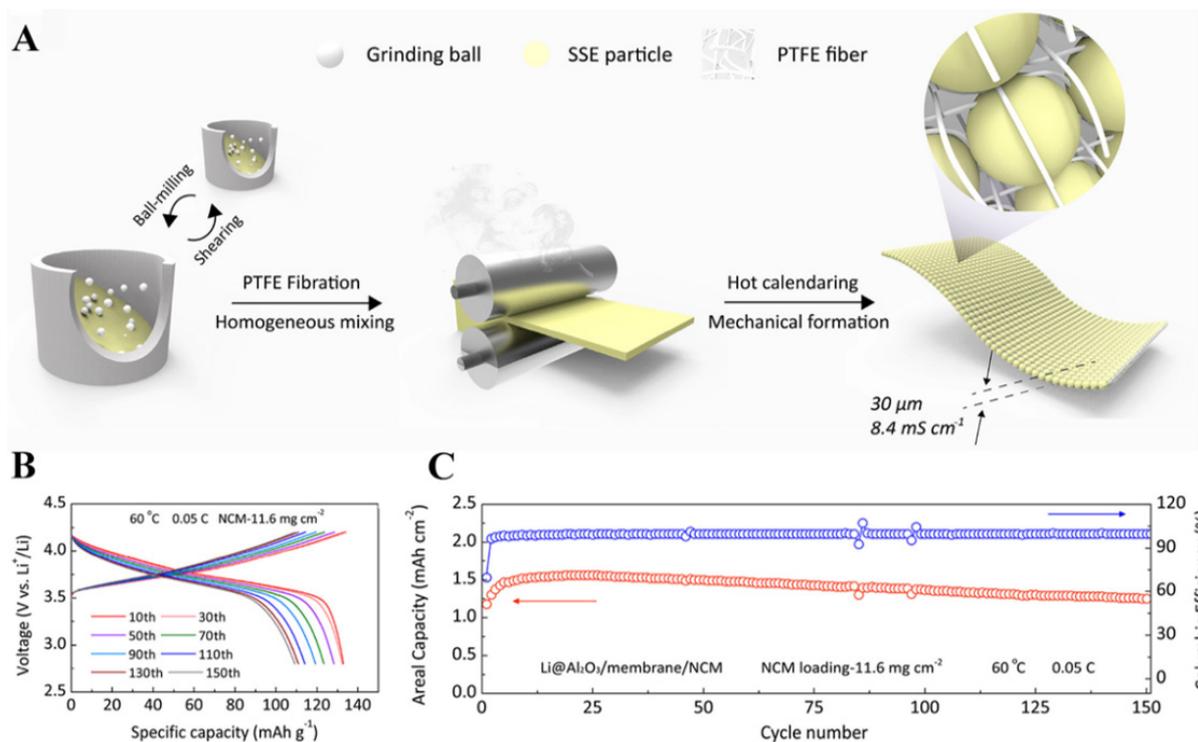
Figure 19. (A) Schematic illustration of ultrathin membrane fabrication. (B) Voltage profile and (C) cyclic performance of the NCM/Li ASSLBs with a high NCM mass loading of 11.6 mg cm^{-2} at 0.05 C (0.085 mA cm^{-2}). Reproduced with permission[186] (Copyright 2021, American Chemical Society).

SUMMARY AND OUTLOOK

As a hot research topic in recent years, solid electrolytes are recognized as being pivotal to the next-generation energy storage field due to their non-flammable properties and high Li$^+$ migration number. Among all the solid electrolytes, sulfides are proposed to be a promising family of materials due to their high ionic conductivity and good wettability with Li metal. Either glass, glass-ceramic or crystalline sulfide electrolytes have demonstrated their possibility to be applied as interlayers in ASSLBs. For glass and glass-ceramic sulfides, almost infinite possibilities are provided for altering their chemistry to obtain the desired properties. Although many of the facets of crystalline sulfides have been revealed, the mechanistic research by DFT has provided several theoretical guidance for designing crystalline sulfide electrolytes with ultrahigh ionic conductivity. Moreover, the synthesizing approaches of sulfides required fewer effort than that of oxide electrolytes. In particular, the liquid-phase synthesis approach is promising for large-scale industrialization. Furthermore, the high ionic conductivity of sulfides endows the potential of its application in the field of high energy-density ASSLBs. Cell-level high energy density sulfide-based ASSLBs with thin-film interlayers have come to reality.

Nonetheless, the S atoms in sulfides are sensitive to humid air. Consequently, H$_2$S-generation is inevitable when preparing sulfides outside the Ar-filled glove box. This drawback prevents the large-scale production of sulfides. Luckily, with the in-depth research on sulfides proceeding, some methods to improve the stability of sulfides to humid air have been discovered.

The sharp electrochemical window of sulfides leads to severe side reactions both on the cathode and anode sides. The side reactions between Li and electrolytes lead to the drop of CE and hinder the development of

high-energy-density LMBs. The oxidation of sulfide electrolytes near the cathode intends to form an ionic insulating layer to block the transport of Li^+, which in turn enhances the interphase resistance. In order to develop ASSLBs with long cycling life and high capacity retention, the influence of side reactions should be decreased to an ignorable level.

Dendrite growth is still major issue in sulfide-based electrolytes and the contact loss between Li/sulfides even deteriorates the situation. The compositional tuning of anodes and electrolytes and the construction of SEIs and interlayers have been proposed to solve the dilemma. At present, the highest CCD value of symmetric sulfide-based Li/Li cells could reach a level comparable to that of LMBs using organic electrolytes. With the combination of experimental results and theoretical study, practical criteria are built and would provide the guidance for further research on developing stable interphase between Li and sulfides.

The mechanical instability of sulfides hinders the complete charging/discharging behaviors of cathode materials while the formed space charge layer increases the interfacial resistance by hindering the transport of charge carriers. Detailed research into the properties of sulfide and cathode particles optimized the preparation methodology of cathode composites. Moreover, coating a protective layer on cathode particles is a more common method to realize the reversible charging-discharging behaviors of the cathode. Particularly, the method of mixing raw materials in a liquid phase is proposed as an alternative to mechanical mixing.

The recent progress of sulfide electrolytes for ASSLBs may provide guidance for future research. First of all, investigating the mechanism of improving the ionic conductivity of sulfide electrolytes will definitely create more candidates for the practical interlayer in ASSLBs. Secondly, in order to satisfy the needs of mass production, novel methods should be proposed to enhance the air stability of sulfide electrolytes. Moreover, the interphase problems constrain the electrochemical performances of sulfide-based ASSLBs. It is true that a lot of the strategies to modify the interphase of sulfide/cathode and sulfide/anode are proved to be effective. The next target of interphase modification should be focused on practicality. Finally, though the ionic conductivity of sulfides is the highest among solid electrolytes, it is also necessary to reduce the thickness of the interlayer to obtain high energy density ASSLBs. For this reason, future work should focus on improving the electrochemical performances of ASSLBs with high cell-level energy density.

DECLARATIONS
Authors' contributions
Conceived the manuscript: Su H, Jiang Z
Wrote the manuscript: Su H, Jiang Z
Reviewed the manuscript: Tu J, Su H
Contributed to the discussion of the manuscript: Su H, Jiang Z, Liu Y, Li J, Gu C, Wang X, Xia X, Tu J

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
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