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Inorganic sulfide solid electrolytes for all-solidstate lithium secondary batteries

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Liquid organic electrolytes are mostly used in commercial lithium-ion batteries, due to their advantages of high conductivity and excellent wetting of the electrode interface. However, liquid organic electrolytes are flammable and volatile, causing safety issues of commercial lithium-ion batteries in electric vehicles. Recently, all-solid-state lithium secondary batteries have attracted great attention owing to their high safety and increased energy density, and are considered the most promising next generation energy storage systems. The most essential components are solid electrolytes for all-solid-state lithium batteries. Among various inorganic solid electrolytes, sulfide solid electrolytes have received widespread attention because of their high ionic conductivity and good mechanical properties. Herein, we summarize the development of several typical sulfide solid electrolytes and the problems to be addressed in emerging all-solid-state lithium batteries. Finally, the future development directions of sulfide electrolytes and all-solid-state lithium batteries are briefly discussed.

1 Introduction

With the rapid development of new energy technologies, the demand for secondary battery systems with high energy density and high safety has become increasingly urgent. According to a worldwide technical goal, the energy density of secondary batteries needs to reach 500 W h kg⁻¹ in 2030. However, current lithium-ion batteries (LIBs) can hardly achieve this target. 1-3 Commercial LIBs mostly employ liquid organic electrolytes, which show flammable and volatile features compared to the solid electrolytes (SEs) with high safety. 4,5 Compared to traditional LIBs with liquid electrolytes, all-solid-state lithium secondary batteries using SEs theoretically have the following features: (1) higher safety due to the mechanical prevention of leaking and burning of SEs; (2) bi-function of SEs as separators and electrolytes in all-solid-state batteries; (3) better mechanical strength for ensuring long-term operation, compared with traditional polymer separators; (4) fewer side reactions between SEs and electrodes; (5) wider electrochemical window of SEs, as compared with liquid organic electrolytes; (6) high lithium ion migration number close to 1 in SEs. However, there are still great challenges for all-solid-state lithium secondary batteries compared to LIBs with liquid electrolytes: (1) poor wettability for solid electrolytes, resulting in poor contact between SEs and

active materials compared to liquid electrolytes; (2) unstable rigid interface between SEs and active materials due to the volume expansion and contraction of active materials during cycling, which can damage or terminate the battery; (3) unsuccessful commercialization SEs for all-solid-state batteries based on considerations of high conductivity, high stability and low cost.

SEs can be classified into two main groups: inorganic solid electrolytes and polymer solid electrolytes. Polymer solid electrolytes with good mechanical properties are helpful in improving the battery safety performance during production and operation. However, polymer solid electrolytes are still unsatisfactory, due to their low conductivity, narrow electrochemical window, and poor stability at elevated temperatures. 6-8 The inorganic solid electrolytes, also known as lithium fast ion conductors, can be mainly classified into two types: oxide solid electrolytes (hereinafter referred to as O-SEs) and sulfide solid electrolytes (hereinafter referred to as S-SEs). There are many types of O-SEs: natrium superionic conductors (NASICON), perovskites, garnets, γ-Li₃PO₄, and some amorphous oxides, including Li_2O-MO_x (M = Si, B, and P) and LiPON-related materials.9-13 The O-SEs have good electrochemical stability and thermal stability, but relatively low conductivity (10⁻⁷ to 10⁻⁴ S cm⁻¹ at room temperature) and rigid mechanical property, limiting their commercial application in battery systems.14-16 The S-SEs are mainly composed of Li₂S and sulfides (such as SiS₂, P₂S₅, and GeS₂). Compared with O-SEs, the electronegativity of S²⁻ in S-SEs is less than that of O²⁻, so the binding of lithium ions is weak and more free lithium ions migrate inside S-SEs. In addition, the radius of S²⁻

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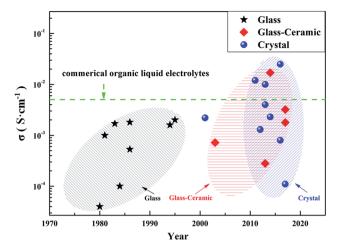


Fig. 1 A graph of lithium ion conductivities of typical SEs.

is larger than that of O2-, which is favourable for forming a large transmission channel of lithium ions. Therefore, S-SEs usually have higher lithium ion conductivity (10⁻⁵ to

 10^{-2} S cm⁻¹ at room temperature, Fig. 1) compared with O-SEs. Furthermore, S-SEs have better ductility than O-SEs, which is favourable for good contact between the electrode materials and S-SEs by simple cold pressing, as well as convenient for the manufacture of bulk all-solid-state batteries. 17,18 In this review, we summarize the development, intrinsic features, and applications of S-SEs in all-solid-state lithium secondary batteries. The emerging challenges and trends in all-solid-state lithium secondary batteries are also discussed.

Sulfide solid electrolytes 2

Lithium ion transport mechanism of S-SEs

S-SEs initially originated from Pradel's research on Li₂S-SiS₂ in 1986.19 There are three ways of sulfur accumulation in SEs: body-centred cubic (BCC) stacking, face-centred cubic (FCC) stacking, and hexagonal close packing (HCP). In BCC stacking (for example, Li₇P₃S₁₁ and Li₁₀GeP₂S₁₂), Li-ions migrate along the path connecting the two coplanar tetrahedral sites (T₁ and T₂, Fig. 2a) with a very low barrier of 0.15 eV, called the T-T path.

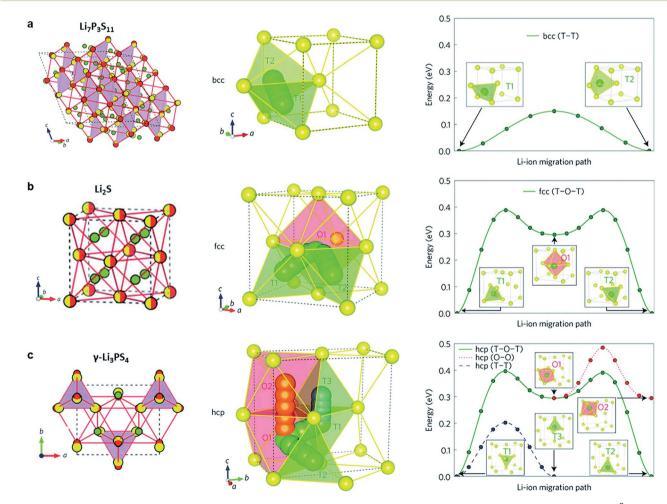


Fig. 2 (a-c) Crystal structures of the Li-ion conductors (a) $\text{Li}_7P_3S_{11}$, (b) Li_2S and (c) γ -Li $_3PS_4$. The Li ions, partially occupied Li^+ sites, S^{2-} anion, and PS₄ tetrahedral and GeS₄ tetrahedral sites (partially occupied in Li₁₀GeP₂S₁₂) are coloured green, green-white, yellow, purple and blue, $respectively. \ In \ both \ Li_{10} GeP_2S_{12} \ and \ Li_7P_3S_{11}, \ the \ sulfur \ anion \ sublattice \ can \ be \ closely \ mapped to \ a \ bcc \ framework \ (red \ circles \ connected \ by \ red \ red \ connected \ by \ red \$ lines). In Li₂S, the anion sublattice is an exact fcc matrix (yellow-red circles). The anion sublattices in γ -Li₃PS₄ and Li₄GeS₄ closely match to a hcp framework. Reprinted with permission. 15 Copyright@ 2015, Springer Nature.

In FCC stacking (like Li₂S), Li-ions move from a tetrahedral site (T_1) to another tetrahedral site (T_2) through an intermediate octahedral site (O1), which is called the T-O-T path, with a barrier of 0.39 eV (Fig. 2b). The T-O-T path can also be found in the a-b plane of the HCP lattice (T_1 to T_2 through O_1 in Fig. 2c) with almost the same activation barrier (0.40 eV). The migration of Li-ions along the c-axis in the HCP lattice is the T-T path through two face-sharing tetrahedral sites (T₁ and T₃, Fig. 2c) with a low barrier of 0.20 eV. Li-ions can also migrate across the path connecting two coplanar octahedral sites (O1 and O_2 , 0.19 eV, Fig. 2c) along the c-axis. However, the O-O path needs additional activation energy due to the instability of octahedral positions. Therefore, migration of Li-ions in the HCP lattice is likely to occur by an alternation of T-T and T-O-T paths. Therefore, the activation barrier of the lithium ion migration pathway in the body-centered-cubic anion framework is lower than that of other close-packed frameworks, 15 which is beneficial to achieve high ionic conductivity.

2.2 Crystalline state of S-SEs

According to their crystalline state, S-SEs can be divided into three categories: glass, glass-ceramic and crystal. Glassy electrolytes

have attracted much attention due to their isotropic ion conduction, zero grain boundary resistance and low cost. 20 The ionic conductivity of glassy electrolytes can reach about $10^{-4}~\rm S~cm^{-1}$ at room temperature. $^{21-24}$ Meanwhile, the glass-ceramic electrolytes obtained by crystallization from glassy electrolytes have higher conductivity, about $10^{-3}~\rm S~cm^{-1}$ (even up to $10^{-2}~\rm S~cm^{-1}$), at room temperature. $^{25-29}$ This is because the glassy electrolyte softens and reduces the grain boundary resistance during the crystallization process. In addition, the precipitation of partial crystallites also helps improve the lithium ion conductivity. The crystal electrolytes will be mentioned in the next section.

There are three main methods for preparing S-SEs: melt quenching, mechanical milling, and wet chemistry. Table 1 shows a comparison of the three preparation methods. Considering feasibility and safety, most S-SEs are prepared by mechanical milling. This work mainly classifies the electrolytes based on their crystalline structure. According to their structures, S-SEs can be divided into the following two categories: thio-lithium super ion conductors (thio-LiSICONs) and argyrodite type.

2.2.1 Thio-LiSICONs. Thio-LiSICONs were first discovered by replacing O^{2-} with S^{2-} in LiSICONs.³⁰ The thio-LiSICONs with the general formula of $Li_{4-x}Ge_{1-x}P_xS_4$ exhibit the highest

Table 1 Advantages and disadvantages of the three methods for preparing S-SEs

Method	Advantage	Disadvantage	
Melt quenching	Low equipment requirements	High temperature	
-	Easy to prepare bulk materials	Unsafe	
	Suitable for preparing glass, glass-ceramic and crystal SEs	Complicated operation	
Mechanical milling	Simple operation	Long working hours	
	High safety		
	Easy to prepare powder materials		
	Suitable for preparing glass, glass-ceramic and crystal SEs		
Wet chemistry	Controllable morphology	Residual organic waste	
	Easy to prepare powder materials	Strict preparation conditions	
	Suitable for crystal SEs		

Table 2 Characteristic parameters of typical solid-state electrolytes

Composition	State	Ionic conductivity (S cm ⁻¹)	Activation energy (eV)	Ref.
$60\text{Li}_2\text{S}-40\text{SiS}_2$	Glass	$5.3 imes 10^{-4}$	0.33	19
$67Li_2S-33P_2S_5$	Glass	10^{-4}	0.36	32
$\text{Li}_7\text{P}_3\text{S}_{11}$	Glass-ceramic	3.2×10^{-3}	0.125	26
$\text{Li}_7\text{P}_3\text{S}_{11}$	Glass-ceramic	$1.7 imes 10^{-2}$	0.18	21
Li ₃ PS ₄	Glass-ceramic	$2.8 imes 10^{-4}$	0.356	33 and 34
$78\text{Li}_2\text{S}-22\text{P}_2\text{S}_5$	Glass-ceramic	1.78×10^{-3}	0.31	35
80Li ₂ S-20P ₂ S ₅	Glass-ceramic	7.2×10^{-4}	0.25	33
Li ₇ Ge ₃ PS ₁₂	Crystal	1.1×10^{-4}	0.26	36
Li _{3.25} Ge _{0.25} P _{0.75} S ₄	Crystal	2.2×10^{-3}	0.207	30
Li _{9.54} Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3}	Crystal	$2.5 imes 10^{-2}$	0.238	37
Li ₁₀ GeP ₂ S ₁₂	Crystal	$1.2 imes 10^{-2}$	0.21	38
$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$	Crystal	4×10^{-3}	0.87	39
$\text{Li}_{10}\text{SiP}_2\text{S}_{12}$	Crystal	$2.3 imes 10^{-3}$	0.20	40
Li ₁₁ AlP ₂ S ₁₂	Crystal	$8 imes 10^{-4}$	0.263	41
Li ₆ PS ₅ Cl	Crystal	1.3×10^{-3}	0.33	42
Li ₆ PS ₅ Br	Crystal	10^{-2}	0.20	43

conductivity of 2.2×10^{-3} S cm⁻¹. The structure of most S-SEs is similar to the structure of Li_{4-x}Ge_{1-x}P_xS₄. Table 2 shows the characteristic parameters of typical S-SEs. According to the number of components, thio-LiSICONs can be mainly divided into binary systems of Li_2S-MS_n (M = P, Si and B) and ternary systems of $\text{Li}_2\text{S-P}_2\text{S}_5$ -MeS_n (Me = Si, Ge and Sn).

2.2.1.1 Binary systems of Li₂S-MS_n. Li₂S-B₂S₃ and Li₂S-SiS₂ were reported as the earlier binary systems of Li₂S-MS_n. However, their ion conductivity is still unsatisfactory, although the conductivity can be improved to a certain extent by doping $\text{Li}_{r}\text{MO}_{v}$ (M = Si, Ge, P). ⁴⁴ As the optimized binary system of Li_{2}S -MS_n, the Li₂S-P₂S₅ system has good physical and chemical properties and is widely used in all-solid-state batteries. In particular, Li₂S-P₂S₅ has a high ionic conductivity of 0.1 to 1 \times 10⁻³ S cm⁻¹ at room temperature²⁵⁻²⁹ and a wide electrochemical window.

There are two typical compounds with high ionic conductivity in the binary system of Li₂S-P₂S₅: Li₃PS₄ (75% Li₂S-25% P₂S₅ molar ratio) and Li₇P₃S₁₁ (70% Li₂S-30% P₂S₅ molar ratio). Li₃PS₄ was first discovered in 1984 (ref. 45) and is considered the most stable compound in the binary system of Li₂S-P₂S₅.46 Usually, Li₃PS₄ exists as γ -Li₃PS₄ with a conductivity of 3 \times $10^{-7} \text{ S cm}^{-1}$ at room temperature. When heated to 195 °C, γ - Li_3PS_4 is converted to $\beta\text{-Li}_3\text{PS}_4$ with a conductivity of 9 \times 10^{-7} S cm⁻¹.⁴⁷ The crystalline structure of β -Li₃PS₄ is shown in Fig. 3a, where the PS₄ and LiS₄ tetrahedra are dominant. There have been many effective attempts for improving the conductivity of β-Li₃PS₄ in the past. After preparation by mechanical ball milling and subsequent heat treatment at 230 °C, Li₃PS₄ presents a high conductivity of 2.8 \times 10⁻⁴ S cm⁻¹ at room temperature.³³ A special β-Li₃PS₄ with nanopores (about 100 nm), prepared by wet chemistry, shows a conductivity of 1.6 \times 10⁻⁴ S cm⁻¹ at room temperature, which is nearly 3 orders of magnitude higher than that of crystalline Li₃PS₄. Meanwhile, the nanoporous Li₃PS₄ exhibits good compatibility with lithium and has a wide electrochemical window of 5 V.34 A plate-like Li₃PS₄ (about 3 μm in length, 500 nm in width, and 100-200 nm in thickness), prepared by liquid-phase shaking, presents a conductivity as high as 2.0 × 10⁻⁴ S cm⁻¹ at room temperature.48

In general, Li₇P₃S₁₁ is obtained in the 70% Li₂S-30% P₂S₅ composition and is an extremely important member of the binary system due to its very high ionic conductivity (up to 1.7 \times 10⁻² S cm⁻¹ at RT).^{21,49} Some types of fast ion conductors are derived from the original $\text{Li}_7\text{P}_3\text{S}_{11}$ structure. Usually, $\text{Li}_7\text{P}_3\text{S}_{11}$ is unstable at high temperatures. When the temperature is increased to 420 °C, Li₇P₃S₁₁ decomposes into two fast ion conductors: β-Li₃PS₄ and Li₄P₂S₇.⁵⁰ In Fig. 3b, Li₇P₃S₁₁ is shown as a triclinic structure consisting of PS₄ tetrahedra and P₂S₇ double tetrahedra, where Li-ions are located in the polyhedral cavity.26 Different preparation methods are reported for the Li₇P₃S₁₁ structure. Li₇P₃S₁₁ obtained by mechanical ball milling and subsequent heat-treatment at 280 °C shows a high conductivity of $3.2 \times 10^{-3} \, \mathrm{S \, cm^{-1}}$ at room temperature and low activation energy.⁵¹ Afterward, the conductivity of Li₇P₃S₁₁ can be gradually increased by optimizing the preparation method. The optimized Li₇P₃S₁₁ prepared by hot pressing has a high

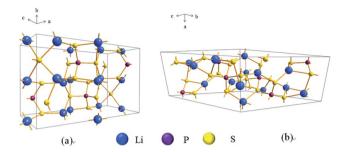


Fig. 3 The framework of (a) β-Li₃PS₄ and (b) Li₇P₃S₁₁ lattices.

conductivity of $1.7 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature, almost equivalent to that of liquid organic electrolytes. 21 The low grain boundary resistance during the heat treatment could be the main reason for the high conductivity of the optimized Li₇P₃S₁₁. Another important example for preparing Li₇P₃S₁₁ is the wet chemistry method by a two-step reaction: (1) the formation of solid Li₃PS₄·ACN phase and amorphous "Li₂S-P₂S₅" phase in liquid phase and (2) the subsequent conversion between the two phases. The conductivity of the as-prepared Li₇P₃S₁₁ sample reaches as high as $8.7 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.⁵²

Although positive and effective progress has been made to enhance the conductivity of Li₂S-P₂S₅ binary systems, some problems still remain at present: (1) poor chemical stability: S-SEs are extremely sensitive to moisture and easily react with steam in the air to produce toxic H₂S gas and destroy the structure of sulfides.17 (2) The cost of S-SEs with Li2S as raw material is high. (3) Compatibility between S-SEs and the cathode materials of lithium secondary batteries is poor, which will be further discussed in a following section. Therefore, regulating the components of S-SEs by introducing oxides and phosphate is an effective way to increase the chemical stability. For example, Li₂O-Li₂S-P₂S₅ prepared by replacing partial Li₂S with Li2O could effectively inhibit the generation of H2S gas.53 70% Li₂S-29% P₂S₅-1% Li₃PO₄ system, after doping Li₃PO₄ into 70% Li₂S-30% P₂S₅, shows a high conductivity of 1.87 \times 10⁻³ S cm⁻¹ at room temperature and enhanced chemical stability.27 As for cost, seeking new raw materials or exploring new preparation methods could be fundamental solutions.

2.2.1.2 Li₂S-P₂S₅-MeS₂ ternary system. Recently, typical thio-LiSICON structure Li₁₀GeP₂S₁₂ (abbreviated as LGPS afterward) was developed, with an extremely high conductivity of 1.2 \times 10⁻² S cm⁻¹ at 27 °C, which is comparable to or higher than those of the liquid organic electrolytes currently used in commercial Li-ion batteries.38 As indicated in Fig. 4a, LGPS consists of (Ge_{0.5}P_{0.5})S₄ tetrahedra, PS₄ tetrahedra, LiS₄ tetrahedra and LiS₆ octahedra. (Ge_{0.5}P_{0.5})S₄ and LiS₆ form a 1D chain along the c-axis by sharing a common edge. These 1D chains are connected to each other by the PS₄ tetrahedra, which are connected to the LiS6 octahedra through a shared angle. Fig. 4b shows the 1D conduction pathways of Li-ions along the c-axis in superionic conductors. Indeed, the addition of Ge element in Li₂S-P₂S₅ system could greatly improve the conductivity. However, at the same time, the stability of LGPS against metal lithium is reduced due to the oxidation property of Ge⁴⁺. This

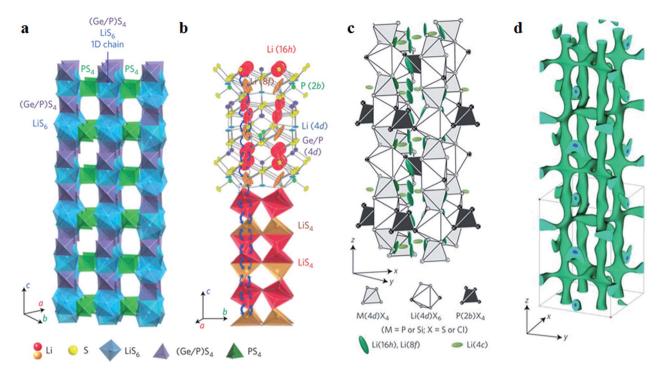


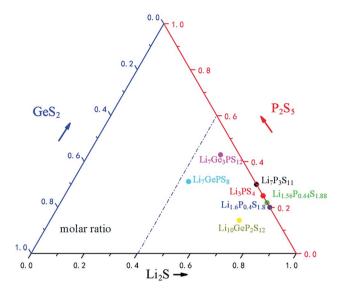
Fig. 4 (a) Framework structure of LGPS; (b) Li $^+$ conduction pathways in LGPS; (c) crystal structure of Li $_{9.54}$ Si $_{1.74}$ P $_{1.44}$ Si $_{1.7}$ Cl $_{0.3}$; (d) nuclear distributions of Li atoms in Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3} at 25 °C. Reproduced with permission.^{37,38} Copyright© (2011, 2016), Springer Nature.

means that the interfacial stability against metal lithium is still limited for LGPS.28

Of course, the cost factor is important for wide application of S-SEs in batteries and the price of Ge element is still high.⁵⁴ From theoretical calculations, the isovalent cation substitution of Ge⁴⁺ has minor impact on the intrinsic properties of LGPS.⁵⁵ Therefore, the replacement of Ge with tetravalent cations may reduce the cost of S-SEs. Here, $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$ and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ have similar structure, electrochemical stability and Li-ion conductivity to LGPS. After replacing Ge⁴⁺ with Sn⁴⁺, Li₁₀SnP₂S₁₂ shows a high conductivity of 4×10^{-3} S cm⁻¹ at room temperature and the cost is only one-third that of the Li₂S-GeS₂-P₂S₅ system.³⁹ The Ge can be also replaced with Si by high pressure method and the obtained Li₁₁Si₂PS₁₂ shows a high conductivity of 2.3 \times 10⁻³ S cm⁻¹ at room temperature.⁵⁶ Multi-components could be a good strategy for manipulating the conductivity of S-SEs. In particular, halogen elements in the multi-components are demonstrated to be effective for improving the conductivity. For example, the multi-component Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3} with a remarkably high conductivity of $2.5 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C was reported, which was the highest value so far for thio-LiSI-CONs.37 It was demonstrated from the anisotropic thermal displacement of lithium (Fig. 4c) and nuclear density distribution (Fig. 4d) that three-dimensional (3D) conduction pathways of Li ions (1D along the c-axis and 2D in the a-b plane) can be formed in Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, superior to the unique 1D pathway of the LGPS family. Therefore, the formation of widely distributed 3D conduction pathways in Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3} may contribute to its highest ionic conductivity at room temperature.

The distribution of commonly used ternary S-SEs in the Li₂S-GeS₂-P₂S₅ ternary phase diagram is illustrated in Fig. 5. Clearly, the Li₂S is dominant in the commonly used sulfide electrolytes (\geq 50% molar ratio); lower P_2S_5 and GeS_2 contents are used here to manipulate the crystallographic structure and intrinsic features. Among all the S-SEs, thio-LiSICONs are the most promising electrolytes for all-solid-state lithium secondary batteries, due to their unique structures and high ionic conductivity at room temperature. Although the conductivity of thio-LiSICONs is comparable to or even higher than those of organic liquid electrolytes, their chemical stability and compatibility with cathode materials are still unsatisfactory, which could undermine the practical application of S-SEs in allsolid-state batteries and urgently needs to be solved.

2.2.2 Argyrodite type. The mineral argyrodite, with a cubic structure and a typical chemical formula of Ag₈GeS₆, has the high ionic conductivity of Ag-ions. When Ag-ions are replaced by other cations, the original cubic structure still remains for argyrodite type compounds.57-67 So far, a novel "Li argyrodite" compound in the form of Li₇PS₆ has a high ionic conductivity. Here, Li₇PS₆ exists as a cubic phase at high temperatures (HT) and is converted to an orthorhombic phase at low temperatures. The partial substitution of S^{2-} by halogen anions can stabilize the cubic HT phase at room temperature, resulting in good conductivity of about 10⁻³ S cm⁻¹.68-70 Typical examples are the halogensubstituted argyrodites Li₆PS₅X (X = Cl, Br, and I). First, argyrodite-type solid electrolytes Li₆PS₅X were prepared by Deiseroth et al.71 As shown in Fig. 6, the stacking structure in Li₆PS₅X is made of regular octahedral Li₆S and tetrahedral PS₄ units.⁷² The preparation method of Li₆PS₅X is similar to that of thio-LiSICONs



Li₂S-P₂S₅-GeS₂ ternary phase diagrams.

and most are prepared by ball milling. For the Cl-substituted sample, Li₆PS₅Cl prepared by ball milling could reach 1.33 × 10⁻³ S cm⁻¹ at 25 °C and have an electrochemical window as high as 7 V (vs. Li/Li⁺).⁴² In the meantime, Li₆PS₅X compounds could also be prepared by mechanical milling with subsequent annealing at 550 °C for 5 h.73-79 In this preparation process, only Li₂S, P₂S₅ and LiX components can be observed after mechanical milling. The conductivities of Li₆PS₅Cl, Li₆PS₅Br and Li₆PS₅Cl before annealing are 3.3 \times 10⁻⁵, 3.2 \times 10⁻⁵ and 2.2 \times 10⁻⁴ S cm⁻¹, respectively, at room temperature. After subsequent annealing, the argyrodite phase is finally formed by transformation and crystallization. The conductivities of annealed $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$ increase to 1.9 \times 10⁻³ and 6.8 \times 10⁻³ S cm⁻¹, respectively, at room temperature, while that of $\text{Li}_6\text{PS}_5\text{I}$ is reduced to 4.6 \times 10⁻⁷ S cm⁻¹. Here, the activation energy for Li-ion diffusion in Li₆PS₅Cl and Li₆PS₅Br is lower, contributing to the high conductivities. It is also reported that Cl and Br⁻ can disorder S²⁻ to promote Li-ion mobility, while I⁻ cannot exchange with S2- due to its large size. Therefore, Li6PS5I cannot be comparable with Li₆PS₅Cl and Li₆PS₅Br on conductivity.75 In particular, the Li₆PS₅Cl and Li₆PS₅Br obtained by solidstate sintering processes with an excess of Li₂S are demonstrated to be superior, exhibiting higher conductivities of 1.8×10^{-3} and 1.3×10^{-3} S cm⁻¹, respectively, at room temperature.⁸⁰

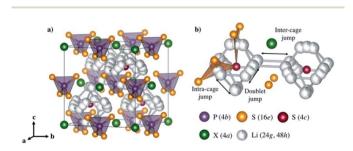


Fig. 6 (a) Crystal structures of Li_6PS_5X with X = Cl, Br, and I. (b) Lithium ion transport mechanism. Reproduced with permission. 72 Copyright@ 2017, American Chemical Society.

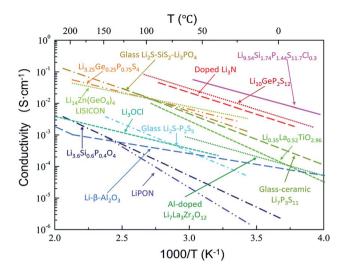


Fig. 7 Thermal evolution of ionic conductivity for different types of solid electrolytes. Reprinted with permission.81 Copyright@ 2018, Royal Society of Chemistry.

Argyrodite type solid electrolytes are very promising for allsolid-state batteries based on the considerations of conductivity and cost. However, similar to most S-SEs, the argyrodite type solid electrolytes are very sensitive to moisture, which should be the main focus for future applications.

To sum up, a wide variety of S-SEs with high conductivities has been reported, with thermal evolution of ionic conductivity drawn in Fig. 7. Here, high conductivity (higher than 10^{-3} S cm $^{-1}$ at room temperature) is a primary concern for solid electrolytes to be used in all-solid-state lithium secondary batteries. It can be seen that there are only a few electrolyte systems that can meet the demand of high conductivity: Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, Li₁₀GeP₂- S_{12} , doped- Li_3N , $Li_{3,25}GeP_{0,75}S_4$, $Li_2S-SiS_2-Li_3PO_4$, $Li_{14}Zn(GeO_4)_4$, and Li₇P₃S₁₁. Among all the electrolytes, Li₁₄Zn(GeO₄)₄ is stable, but not ideal due to its excessive hardness and poor compatibility with electrode materials. For the doped-Li₃N sample, ion conductivity is satisfactory, but the low decomposition voltage and extreme sensitivity toward moisture are insurmountable at present. The applications of obtained Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, Li_{3.25}GeP_{0.75}S₄ and Li₂S-SiS₂-Li₃PO₄ are largely limited due to their hard preparation processes and complex elemental components. It seems that every family of these electrolytes has problems currently. Comparatively speaking, Li₁₀GeP₂S₁₂ and Li₇P₃S₁₁ are the most promising solid electrolytes for high performance allsolid-state lithium secondary batteries due to their high conductivities and simple preparation process. Of course, there is still great room for improvement of conductivity in solid electrolytes, so it is necessary to explore new electrolyte systems based on the requirement of high conductivity.

S-SE's application in all-solid-state lithium batteries

With constant progress in highly conductive solid electrolytes, the developments in all-solid-state lithium secondary batteries

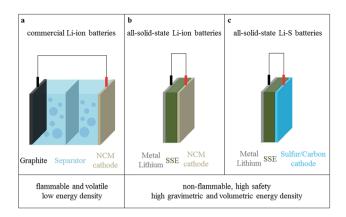


Fig. 8 Comparison of (a) commercial Li-ion batteries, (b) all-solidstate Li-ion batteries and (c) all-solid-state Li-S batteries.

change rapidly. The schematic structures of three commonly used lithium batteries with solid electrolytes are shown in Fig. 8.82 The first advantage of all-solid-state batteries is high safety, due to their simplified structure and the excellent mechanical properties of solid electrolytes. Another outstanding advantage of all-solid-state lithium batteries is their high theoretical energy density.83-85 The energy density of all-solid-state lithium batteries could reach 300-600 W h kg⁻¹, which is much higher than commercial liquid batteries at about 200 W h kg^{-1} .85-88 The reasons are as follows:

- (1) Lithium has the lowest electrode potential and the lowest molar mass and its theoretical specific capacity can reach 3860 mA h g^{-1} . 89,90 The compatibility of the S-SEs with lithium is better than that of liquid electrolytes with lithium, because of fewer side reactions on the interface. Therefore, lithium can be used as the anode in all-solid-state batteries, which is helpful to increase the volumetric and gravimetric energy densities of allsolid-state batteries.
- (2) Solid electrolytes usually have a wide electrochemical window. When combined with suitable cathode materials, the battery could provide a high operation voltage to improve the energy density.38,87,88

Although the ionic conductivity of S-SEs is competitive to those of liquid electrolytes, the electrochemical performance of all-solid-state lithium batteries is still unsatisfactory, highly depending on the interface issues between electrodes and S-SEs.⁹¹ There are several key issues of S-SE application in allsolid-state lithium batteries: (1) A solid-solid contact interface is formed between the electrode and electrolyte, but is not stable enough; (2) the volume change of the electrode during charge and discharge is unavoidable, which further destroys the electrode/electrolyte interface; (3) the chemical stability of S-SEs is poor. It was mentioned above that the chemical stability can be effectively improved to a certain extent by manipulating the composition of the electrolytes and optimizing the preparation process. However, the issue of solidsolid interfaces between electrodes and electrolytes is unavoidable in all-solid-state batteries92 and should be paid more attention.

3.1 Interface layer and interface impedance

In all-solid-state lithium batteries, the interface between the electrolytes and electrodes has significant influence on the working mechanism and electrochemical performance.93-97 In particular, no wettability exists among solids; the contact between solid and solid is not comparable with that of solid and liquid, leading to large interfacial impedance between solid electrolytes and electrodes. The space charge layer model, proposed by Takada et al., is popular to explain the interfacial impedance between the S-SEs and oxide cathode materials in all-solid-state lithium batteries.98 Another explanation for the interface phenomenon is mutual diffusion of different elements in oxide electrodes and S-SEs.99

Problems and current situation of the interface between oxide cathodes and sulfide solid electrolytes

The concept of a space charge layer was initially proposed based on a pioneering work on solid-state reactions, where the interface between two F ion conductors of BaF2 and CaF2 was studied. It was demonstrated that partial F ions can be transferred from one side to the other to reach equilibrium state under the driving force of different chemical potentials, resulting in the formation of vacancies and interstitial ions. Both the vacancies and interstitial ions help enhance ion conduction at the interface. This phenomenon was referred to as "nanoionics". 100,101

Takada et al. introduced the nanoionic phenomenon into the interface between oxide electrodes and S-SEs, forming a space-charge layer.91 The space-charge layer on the interface between oxide cathodes and S-SEs is harmful for cation transfer. This is a common feature of good ionic conductivity for both cathode materials and S-SEs. However, the electron insulation is absolute for S-SEs, while the good electron conductivity is also suitable for cathode materials. Currently, commercial cathode materials with large capacity are generally Ni-rich oxides with high electrode potentials. When contacting both oxide cathode materials and S-SEs, Li-ions move from S-SEs to the oxide under the driving force of chemical potential difference between the two materials. Correspondingly, the migration of Li-ions results in formation of the space-charge layer on the interface between S-SEs and oxide cathode. Specifically, the composition and structure of S-SEs on the interface are changed, leading to lower ion conductivity and increasing the interfacial resistance. However, the space charge layer on the cathode side of the oxide interface disappears rapidly because electrons simultaneously neutralize excess Li-ions. Therefore, the space charge layer is usually formed in the S-SE side on the interface between cathode and S-SE (as shown in Fig. 9).98 The formation of the space charge layer has great impact on the performance of allsolid-state lithium batteries.

Thus, to improve the electrochemical performance of allsolid-state lithium batteries, reducing the impact of the space charge layer is imperative. Takada proposed a buffer layer to alleviate development of the space charge layer.84 Inserting an additional oxide layer as an ion-conductive and electroninsulated buffer layer between the oxide cathode and S-SEs is

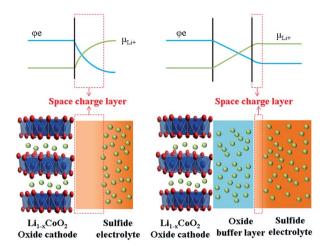


Fig. 9 Formation of the space charge layer and a modification mechanism with a buffer layer.

an effective way to slow the impact of the space charge layer. 91,102 Correspondingly, two interfaces are formed after introducing the buffer layer: one between the mixed-conducting oxide cathode and ion-conductive oxide and the other between the ion-conductive oxide and S-SEs. The space charge layer at both interfaces could be inhibited to a certain extent. The additional oxide layer avoids direct contact between oxide cathode and S-SEs as a buffer, so it is called a buffer layer. Take LiCoO2 and S-SEs as examples, as shown in Fig. 9. The space charge layer is largely developed when S-SEs are in direct contact with the LiCoO₂. With a buffer layer between LiCoO₂ and S-SEs, the space charge layer is greatly suppressed.

Therefore, it is important to search for suitable buffer layer materials to improve the performance of all-solid-state batteries. Electrodes in all-solid-state lithium batteries are usually mixtures of active materials, conductive additives and S-SEs. Here, the buffer layer should be formed on the surface of active materials before mixture. The current investigation shows that the mass ratio of Li₁₀GeP₂S₁₂ and LiCoO₂ in the composite cathodes is usually between 20/80 and 30/70 for better electrochemical performance. 92 In the future, the content of S-SEs as inactive materials in the electrode should be manipulated as low as possible to maintain the high energy density of all-solid-state lithium batteries. For effective transport of ions and conduction of electrons, the interface between electrodes and S-SEs could be constructed as a gradient. This special gradient transition layer would help stabilize the interface and improve the performance of all-solid-state lithium batteries. Fig. 10 shows more details about the interface structure and gradient transition layer for all-solid-state lithium batteries, as well as the composite cathode, Li anode and S-SEs.

Next, the interfacial problems between S-SEs and oxide cathodes will be discussed for different oxide cathodes in allsolid-state lithium batteries.

3.2.1 Layered LiCoO₂ cathode material. LiCoO₂ is commonly used as a cathode material for lithium-ion batteries in portable devices due to its electrochemical stability, high structural stability and high tap density. 103-105 Many attempts to

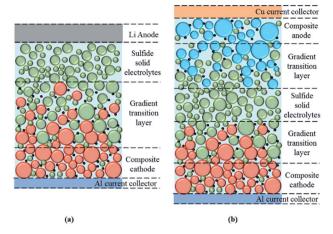


Fig. 10 All-solid-state lithium batteries with (a) metal anode and (b) powder anode.

reduce the interfacial resistance by inserting different buffer materials on LiCoO2 have been made in the past. LiNbO3 is demonstrated to be a typical buffer material due to its high ionic conductivity. All-solid-state batteries are usually assembled with LiNbO₃-coated LiCoO₂ as cathode, Li_{3,25}Ge_{0,25}P_{0,75}S₄ as electrolyte and In-Li alloy as anode.98,106 The interface resistance is reduced by two orders of magnitude after coating with LiNbO3, contributing to the great improvement of the electrochemical performance of the batteries. Similarly, all-solid-state batteries can be also built with Li₁₀GeP₂S₁₂ as electrolyte, In-Li alloy as anode, and TaO3-coated LiCoO2 as cathode. 107 The interface resistance is reduced from 3 imes 10⁵ to 4 imes 10³ Ω cm⁻² after coating the TaO₃ buffer layer on the cathode. In addition, Li₂SiO₃ can be considered as a buffer layer to deposit on LiCoO₂. It was shown that a buffer layer of 0.06 wt% Li₂SiO₃ effectively reduces the interface impedance and improves the electrochemical performance of the all-solid-state battery with Li₂S-P₂S₅ as electrolyte (Fig. 11a and b).99,108 As characterized by STEM (Fig. 11c and d), a thick interfacial layer is formed between LiCoO2 and Li₂S-P₂S₅, leading to large interfacial impedance and poor electrochemical performance due to mutual diffusion and interactions of Co, P, and S. After coating the Li₂SiO₃ buffer layer, a small interfacial impedance and large discharge capacity can be simultaneously obtained. Importantly, the interface of LiCoO₂/ Li₂S-P₂S₅ layer is thin and clean with the appearance of Si.

In a similar way, S-SEs can be coated onto active materials to form a favourable electrode-electrolyte interface and increase the electrochemically active surface area. 109 As shown in Fig. 12, S-SEs-coated LiCoO2 exhibits larger discharge capacity and better rate performance compared to a simple mixture of LiCoO2 and S-SEs. The effects of different grain size and composition of active materials on the electrochemical performance of all-solid-state batteries are also explored. In particular, the composition of 10 : 1 weight ratio of 10 μ m to 1.7 μ m LiCoO₂ helps to show better performance, for which the solidsolid contact/interface should be optimized.

3.2.2 Spinel cathode materials. Spinel cathode materials (LiMn₂O₄ and LiNi_{0.5}Mn_{1.5}O₄) possess the advantages of low

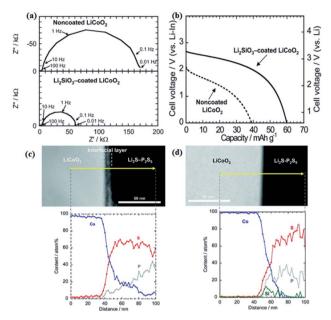


Fig. 11 (a) Impedance profiles of the all-solid-state cells In/Li₂S-P₂S₅ with solid electrolyte non-coated and Li₂SiO₃-coated LiCoO₂ at -30 °C after charging to 3.6 V vs. Li-In. (b) Discharge curves of the allsolid state cells under the current density of 0.064 mA cm⁻² at 30 °C. (c) Cross-sectional HAADF-STEM image of LiCoO2 electrode/Li2S-P₂S₅ solid electrolyte interface after initial charging and crosssectional EDX line profiles for Co, P, and S elements. (d) Crosssectional HAADF-STEM image of the Li₂SiO₃-coated LiCoO₂/Li₂S-P₂S₅ interface after initial charging and cross-sectional EDX line profiles for Co, P, S, and Si elements. 99,108 Reproduced with permission. Copyright@ (2009, 2010), American Chemical Society.

cost, good safety and high voltage platform as high as 4.7 V.¹¹⁰⁻¹¹² For application of spinel cathodes in all-solid-state batteries, a buffer layer is still essential. For example, LiMn₂O₄ can be coated with Li₄Ti₅O₁₂ by sol-gel method. Correspondingly, the interfacial impedance of cathode/ electrolyte can be greatly reduced after coating with Li₄Ti₅O₁₂ film and the electrochemical performance of the assembled In/ 80Li₂S-20P₂S₅/LiMn₂O₄@Li₄Ti₅O₁₂ batteries is improved as well. Amorphous-Li₃PO₄-deposition on LiMn₂O₄ cathode by pulsed laser deposition is also effective for decreasing the interfacial resistance and releasing a larger reversible capacity of 62 mA h $\rm g^{-1}.^{114}$ As for the high voltage $\rm LiNi_{0.5}Mn_{1.5}O_4$ cathode, LiNbO3 seems to be a more suitable buffer layer material based on safety considerations.115

3.2.3 Layered ternary oxide cathode materials. The ternary oxide cathode materials of the general formula LiNixCov- $M_{1-x-y}O_2$ (M = Mn, Al) have been popular in recent years due to their advantages of high specific capacity, low cost, and environmental friendliness.117-119 Specifically, nickel-rich oxide cathode (NCM811) with multi-electron reaction and high reversible capacity was introduced into all-solid-state batteries.116 As presented in Fig. 13, the capacity loss of NCM811 cathode in the first cycle is serious, caused by a change in the chemical composition at the S-SEs/cathode interface and shrinkage of NCM particles during delithiation. It means that

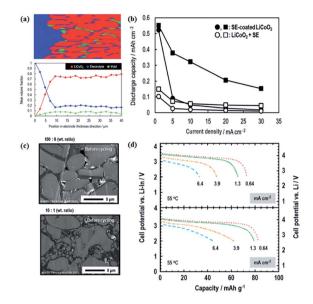


Fig. 12 (a) Volume fractions of respective materials along the electrode thickness; (b) electrochemical performance of S-SE-coated $LiCoO_2$ and $LiCoO_2 + S-SE$; (c) S-SE-coated $LiCoO_2$ particles with different grain sizes; (d) electrochemical performances of different cathode compositions. Reproduced with permission.109 Copyright© 2017, Royal Society of Chemistry.

the destruction at the S-SEs/cathode interface in the first cycle is final and not correctable in the following cycles, resulting in the rapid drop of the reversible capacity of NCM811 cathode without any coating buffer layer. After coating the LiAlO2 buffer layer on LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM333) by sol-gel method and ultrasonic treatment, the battery with LiAlO2-coated NCM333 as cathode, Li₃PS₄ as electrolyte and Li_{4.4}Si alloy as anode was assembled and investigated. 120 It is demonstrated that 1.0 mol%

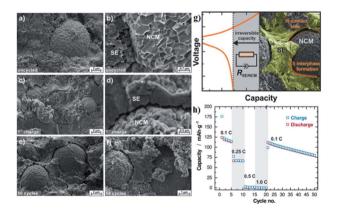


Fig. 13 (a and b) Scanning electron micrographs of the cathode composite of NCM811 and β -Li₃PS₄ as prepared in a solid-state cell but without the application of current or potential. (c and d) SEMs of a Li-In|β-Li₃PS₄|NCM-811 batteries after single charging to 4.3 V vs. Li/ Li⁺ at 0.1 C. (e and f) SEMs of a given cell after 50 full battery cycles in the discharged state. (g) Schematic diagram of performance degradation mechanism in all-solid-state batteries. (h) Rate test and longterm cyclability for the all-solid-state batteries. Reproduced with permission. 116 Copyright 2017, American Chemical Society.

LiAlO₂ coating is good enough for NCM333 cathode to release a high initial discharge capacity of 134 mA h g⁻¹ and to retain good capacity after 400 cycles.

The nickel-rich oxide LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) cathode is also verified in all-solid-state batteries. As shown in Fig. 14, after coating a thin layer of Li₂O-ZrO₂ (8 nm), ¹²¹ all-solid-state batteries with Li₂O-ZrO₂-coated NCA as cathode, 80Li₂S-20P₂S₅ as electrolyte, and In-Li alloy as anode can be charged/ discharged repeatedly with good capacity retention. The NCA can be also coated with Li₄Ti₅O₁₂ (LTO) for verification in allsolid-state batteries.122 The battery with Li4Ti5O12-coated NCA cathode shows a discharge capacity of about 110 mA h g-1, superior to that (70 mA h g⁻¹) of the non-coated cathode.

The effects of the particle size and structure defects of oxide cathodes in all-solid-state batteries are also important. First, reducing the particle size of the cathode materials by ball milling is helpful to form sufficient contact between the electrolytes and cathode. 123,124 Secondly, a subsequent heat treatment on the ball-milled cathode materials can further reduce structural defects on the surface of the cathode materials. Thereby, the electrochemical performance of the all-solid-state battery can be improved to some extent. Typically, all-solidstate batteries with NCA, ball-milled NCA, and heat-treated NCA as cathodes are built. The interface impedances are 652, 480 and 198 Ω cm⁻² and the initial discharge capacities of the cathodes are 46.7, 89 and 146 mA h g⁻¹, respectively.

In all-solid-state lithium ion batteries, the interface compatibility between the oxide cathode materials and S-SEs should be a key issue. It is imperative to probe the reaction mechanism of the interface and find a strategy for stabilizing the interface. The commonly used buffer layer materials are summarized in the following categories according to their structure and composition (Fig. 15): spinel oxides, perovskite oxides, lithium salts, and general oxides. At first, the commonly used buffer materials have been general oxides. Although the development of the space charge layer can be suppressed to a certain extent, the rate performance of the battery is undermined due to the insulating properties of the oxide buffer layer. Compared with general oxides, lithium salts have good ionconducting properties, leading to better rate performance of all-solid-state batteries. According to the above classification, typical examples of the three types are Li₄Ti₅O₁₂, Li₃PO₄ and LiNbO₃. A certain amount of Li₄Ti₅O₁₂ coating on the cathode surface could effectively suppress the formation of the space

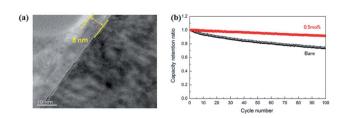


Fig. 14 (a) TEM image of a cross section of a 0.5 mol% LZO coated NCA particle. The right hand (dark) side corresponds to NCA; (b) cycle characteristics of bare and 0.5 mol% LZO coated NCA at 25 °C. Reproduced with permission. 121 Copyright@ 2013, Elsevier B.V.

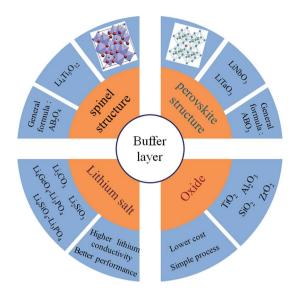


Fig. 15 Summary of buffer layer materials. Produced from experimental data.

charge layer.125 But due to its low ionic conductivity $(10^{-9} \text{ S cm}^{-1})$, the resistance of the coating layer itself became predominant in the electrode resistance, thus limiting the electrochemical performance of all-solid-state batteries. Li₃PO₄ has a higher ionic conductivity of 10⁻⁸ S cm⁻¹; thus, a Li₃PO₄ buffer layer could lead to better performance.126 LiNbO3 is an excellent material for the buffer layer in place of Li₄Ti₅O₁₂ and Li₃PO₄ because of its extremely high ionic conductivity of 10⁻⁵ to 10⁻⁶ S cm⁻¹ in amorphous state and its good stability. 102 It effectively reduces interfacial resistance and improves the highrate capability of all-solid-state batteries. For buffer layer materials, high ionic conductivity, good chemical stability and electrochemical passivation feature should be considered, as well as low cost and insensitivity to moisture. Of course, LiNbO₃ seems to be effective as a buffer layer for all the oxide cathode materials in all-solid-state lithium ion batteries.

S-SE application in all-solid-state lithium-sulfur battery

4.1 Lithium-sulfur battery

Sulfur is a light-weight element which can react with lithium to form Li₂S through a two-electron reaction, leading to the high theoretical specific capacity of 1672 mA h $\rm g^{-1}$, $^{127-131}$ which is about five times that of current commercial transition metal oxide cathode materials. 132-137 However, there are several major problems in conventional liquid lithium-sulfur (Li-S) battery: (1) poor ionic conductivity and electrical conductivity of sulfur and its discharge product Li_2S ; (2) large volume expansion (\sim 79%) from S to Li₂S; (3) dissolution of intermediate polysulfide, resulting in a shuttle effect and poor cycle performance; (4) flooded organic electrolyte, leading to low energy density; (5) flammability and leakage of the organic electrolyte. In order to improve the electrochemical performance, energy density, and safety, it is effective to build all-solid-state Li-S batteries. S-SEs could be good

candidates for an all-solid-state Li-S battery. In particular, there is good compatibility between S-SEs and sulfur, without the space charge layer effect mentioned in the previous section.

4.2 Research progress on all-solid-state lithium-sulfur battery

Although solid electrolytes can effectively suppress the shuttle effect of soluble intermediate polysulfide, there are still some problems with all-solid-state Li-S battery. First, due to the immobile nature of the solid electrolyte, the volume expansion caused by sulfur in the charge and discharge processes induces great stress at the electrode/electrolyte interface, damaging the structure of the interface. Second, the electron conductivities of S and Li₂S are extremely poor, severely limiting the electrochemical performance of the all-solid-state Li-S battery. Third, the contacts among S/Li₂S, conductive additives and solid electrolytes are insufficient. Therefore, it is urgent to search for suitable materials or modified methods to solve these problems in the all-solid-state Li-S battery.

Building nanocrystals and nanostructures is an effective way to improve the above problems. 138 First, the nanostructure has a large specific surface, so sufficient contact between the active materials and solid electrolytes can be formed based on the large surface. Second, although the poor conductivity of S and Li₂S limits the depth of the electrochemical reaction, nanocrystals with many active sites can improve the utilization of sulphur active material. In the meantime, the nanostructure can accommodate the pressure introduced during repeated cycling.

4.2.1 Sulfur cathode. Due to the poor electronic and ionic conductivities of sulfur, electronic conductive materials and solid electrolytes should be homogeneously mixed with the sulfur. 139,140 Generally, carbon materials have good electrical conductivity and large specific surface area, so the combination of carbon materials and sulfur could be a good choice for improving the conductivity of the composite cathode. Previously, common carbon materials have been reported for the allsolid-state Li-S battery, including acetylene black (AB),141 Ketjen black (KB),142 activated carbon (AC),143 and vapor grown carbon fibers (VGCF).144

Sulfur-AB composite cathodes prepared by ball-milling were used to build all-solid-state batteries. 145 The all-solid-state battery, assembled with a sulfur-AB composite cathode, can deliver a large capacity of 996 mA h g⁻¹ at 0.64 mA cm⁻² and retain a capacity of 853 mA h $\rm g^{-1}$ at 1.3 mA cm $^{-2}$ after 200 cycles. After further optimization with small particle size and sufficient contact between S and AB,146 the sulfur-AB composite cathode shows a large initial discharge capacity of 1087 mA h g⁻¹ with a coulombic efficiency of 97% and maintains a reversible capacity of 1050 mA h $\rm g^{-1}$ at 0.064 mA cm $^{-2}$ after 50 cycles. In addition, the composite cathodes using VGCF144 and AC147 as conductive additives also exhibit better electrochemical performance. Similar to carbon materials, metal sulfides (such as CuS₂)¹³⁹ and conductive polymers (such as polyacrylonitrile)148 are also commonly used to construct composite cathodes.

4.2.2 Li₂S cathode. Similar to sulfur, Li₂S has a high theoretical capacity of ~1166 mA h g⁻¹. In addition, Li₂S is highly sensitive to moisture and oxygen, which makes the preparation process of the cathode materials more complicated. 130,138,149,150

As mentioned above, constructing a composite cathode with conductive additive, solid electrolytes and Li2S is a good solution to improve the performance of Li₂S. The optimal preparation process of the composite cathode with Li₂S, AB and S-SEs is explored by mechanical ball milling.138 As indicated in Fig. 16, the Li₂S-AB-S-SEs composite cathode can be prepared by ball milling, which is superior for capacity and cycle stability compared with manual grinding. Specifically, the Li₂S-AB-S-SEs cathode has a discharge platform of 2 V (vs. Li), which corresponds to the reaction of $Li_2S = S + 2Li^+ + 2e$, proving the generation of polysulfide is suppressed. The initial charge and discharge capacities of the all-solid-state batteries with the Li₂S-AB-S-SEs composite cathode are 1010 and 920 mA h g⁻¹, respectively. To increase the utilization of the Li₂S active material, the effects of the particle size of Li₂S active materials on the reversible capacity and rate performance of all-solid-state batteries are also investigated. Clearly, reducing the particle size of Li2S active materials is helpful to improve the electrochemical performance of all-solid-state Li-S batteries.

It is also feasible to improve the performance of Li₂S by designing a special structure. A core-shell structure with nano-Li₂S as the core and Li₃PS₄ as the shell is obtained and has an ionic conductivity of 10⁻⁷ S cm⁻¹ at 25 °C, almost 6 orders of magnitude higher than that of bulk Li_2S ($\sim 10^{-13} \text{ S cm}^{-1}$). ¹⁵¹ As demonstrated in Fig. 17, the all-solid-state battery assembled with the LSS cathode shows an initial discharge capacity of 848 mA h g^{-1} (based on Li₂S) and a capacity retention of about 70% after 100 cycles. The good performance of LSS is ascribed

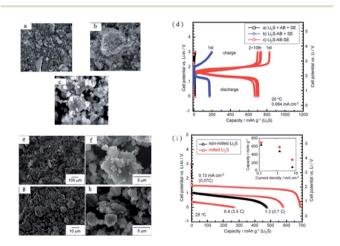


Fig. 16 SEM images of (a) $Li_2S + AB + S-SEs$, (b) $Li_2S-AB + S-SEs$, and (c) Li₂S-AB-S-SEs electrodes. (d) Charge-discharge curves of allsolid-state cells Li-In/80Li₂S-20P₂S₅ glass-ceramic/Li₂S using Li₂S + AB + S-SEs, $Li_2S - AB + S-SEs$, and $Li_2S-AB-SEs$ as cathodes. SEM images of (e) non-milled Li₂S, (f) Li₂S particles milled for 20 h, and Li₂S-AB-S-SEs electrodes using (g) non-milled Li₂S and (h) milled-Li₂S. (i) Charge-discharge curves for the first cycle of all-solid-state cells with Li₂S-AB-S-SEs electrodes prepared using (e) non-milled and (f) milled Li₂S particles. Reproduced with permission. ¹³⁸ Copyright© 2012, Royal Society of Chemistry.

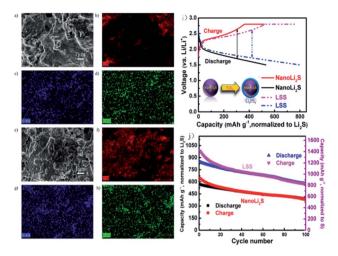


Fig. 17 SEM images and elemental maps of the cathode before and after cycling at 60 °C: SEM images of the cathode (a) before cycling and (e) after 100 cycles; (b), (c), and (d) are elemental maps of carbon, sulfur, and phosphorus before cycling; (f), (g), and (h) are elemental maps of carbon, sulfur, and phosphorus after 100 cycles. (i) The schematic diagram of the core-shell structure and voltage-capacity curve of the battery. (j) Electrochemical cycling performance of nano-Li₂S and LSS as the cathode materials for all-solid-state Li-S batteries at the rate of C/10 and 60 °C. Reproduced with permission.151 Copyright© 2013, American Chemical Society.

to its enhanced ionic conductivity after coating with Li₃PS₄ and reduced interfacial resistance between the electrodes and electrolytes. The high lithium-ion conductivity of LSS results in excellent cycling performance for the all-solid-state Li-S battery, also promoting safety during cycling.

In summary, the insulation of S/Li₂S is the main problem hindering the development of the all-solid-state Li-S battery. Intimate contact among electrode components is effective to reduce the particle size and improve the conductivity of composite electrodes to solve the above problems.

4.2.3 Metal sulfides cathode. Recently, transition metal sulfides with unique nanostructures (such as NiS, 152 TiS2, 153 and FeS¹⁵⁴) have been used as active materials in all-solid-state lithium batteries. These cathodes not only have moderate operating voltages and high theoretical specific capacity, but also better interfacial compatibility and stability with S-SEs. Furthermore, excellent solid-solid interface contact can be achieved by reducing the size of the active material to the nanometer scale. Therefore, transition metal sulfides are promising for high energy density electrode materials.

In order to achieve intimate contact between sulfide electrodes and S-SEs, Fe₃S₄@Li₇P₃S₁₁ is prepared by in situ coating $\text{Li}_7P_3S_{11}$ on Fe_3S_4 . The Fe_3S_4 @ $\text{Li}_7P_3S_{11}$ nanocomposites are employed to construct all-solid-state batteries. The all-solidstate batteries (Li/75% Li₂S-24% P₂S₅-1% P₂O₅/Li₁₀GeP₂S₁₂/ Fe₃S₄(a)Li₇P₃S₁₁) show superior cycling stability. As shown in Fig. 18, after 200 cycles, the discharge capacity remained a high value of 1001 mA h g⁻¹ at a current density of 0.1 A g⁻¹. Subsequently, sulfide nickel anchored carbon nanotube (NiS-CNT) nanocomposites are prepared by a facile hydrothermal

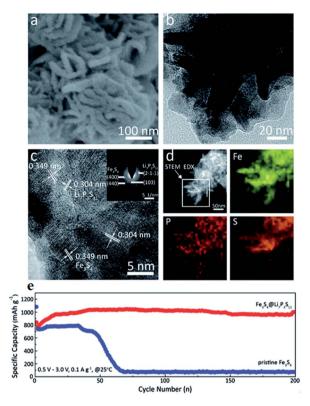


Fig. 18 (a) High magnification SEM, (b) TEM, and (c) HRTEM images of Fe₃S₄@Li₇P₃S₁₁ nanocomposites; the inset in (c) is the SAED pattern; (d) STEM-EDS elemental mapping images of Fe₃S₄@Li₇P₃S₁₁ nanocomposites, marked by the rectangular region, for Fe, P, and S. (e) Comparison of the electrochemical performance between Fe₃S₄@-Li₇P₃S₁₁ and pristine Fe₃S₄. Reproduced with permission. Copyright© 2017.155 Royal Society of Chemistry.

method.3 The all-solid-state batteries with NiS-CNT as cathode also deliver high reversible capacity and excellent cycling stability.

Current situation of the interface between anode/S-SEs

5.1 Characteristics of metal lithium

Metal lithium is an ideal anode material due to its low standard electrode potential (-3.04 V vs. standard hydrogen electrode), low density (0.53 g cm⁻¹) and high theoretical specific capacity of 3862 mA h g⁻¹.89 Conventional lithium batteries with organic liquid electrolytes have poor compatibility with metal lithium. Metal lithium is extremely reactive and easily forms uncontrolled lithium dendrites at the anode surface, thus leading to internal short-circuiting and serious safety issues.97,156,157 In allsolid-state lithium batteries, all components are solid. The solid electrolyte has good mechanical properties which can weaken the growth of lithium dendrites during charge/discharge cycling. Therefore, metal lithium can be employed as an anode in all-solid-state lithium batteries with high energy density. Although S-SEs have good mechanical properties, they are electrochemically unstable to metal lithium. 158 It implies

that the interface change between the anode and S-SEs could be serious and strongly related to the performance of all-solid-state batteries. This part will discuss the interfacial problem from two aspects: electrochemical stability and mechanical stability.

5.2 Electrochemical stability of the interface between metal lithium and S-SEs

In fact, most highly-conductive S-SEs (such as Li₇P₃S₁₁, Li₁₀- GeP_2S_{12} , and $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$) are unstable against active lithium metal.37,113,159 To improve electrochemical stability between S-SEs and lithium and to reduce the decomposition of S-SEs, lithium alloys are introduced as anodes. 160,161 Among all the alloys, Li-In alloy with a flat potential platform of 0.62 V (vs. Li/Li⁺) and a high specific capacity is widely used in all-solid-state lithium batteries to suppress interfacial reactions and the decomposition of solid state electrolytes. 160 Of course, the energy density of all-solid-state batteries can be slightly reduced due to low battery voltage with Li-In alloy as anode. In addition, cost should be a concern for a battery with indium as anode material. Therefore, improving the interfacial stability between the lithium metal and S-SEs to inhibit the growth of Li dendrites is critical for utilization of S-SEs in all-solid-state lithium secondary batteries.

The electrochemical stability can be improved by doping anions into S-SEs. Li₇P₂S₈I, prepared by doping LiI in Li₃PS₄, shows extremely high electrochemical stability to a metal lithium anode. ¹⁶² Improving the interface between lithium metal anode and S-SEs could be done through the following three aspects: (1) modification on the surface of S-SEs; (2) modification on the surface of metal lithium; (3) introduction of a buffer layer between S-SEs and metal lithium. ³⁵ Among these, the buffer layer solution is the most commonly used. Therefore, the characteristics of different buffer layer materials are explored. 20 nm Si-deposited metal lithium is obtained by laser pulse deposition ¹⁶³ and the LiCoO₂|Li₂S-P₂S₅|Li battery is then assembled. Here, the battery with bare lithium anode presents a capacity retention rate of 76% after 100 cycles, while the

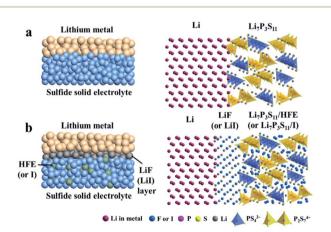


Fig. 19 Schematic diagrams of (a) $\text{Li}/\text{Li}_7\text{P}_3\text{S}_{11}$ interface of ASSLIBs and (b) modified interface with a uniform thin LiF (or LiI) interphase layer and HFE (or I solution) infiltrated sulfide electrolyte. Reprinted with permission. ¹⁶⁴ Copyright© 2018, Elsevier B.V.

battery with Si-deposited lithium anode is cycled without capacity decay almost for 1000 cycles. Subsequently, different deposited layers of Si, Al and Sn on the surface of metal lithium are studied. The all-solid-state batteries with Si-deposited lithium anode exhibit optimized electrochemical performance. Employing LiF (or LiI) as a buffer layer at the interface between metal Li and S-SEs and penetrating methoxyper-fluorobutane (HFE) or I solution inside S-SEs could effectively suppress Li dendrite growth (Fig. 19). A LiCoO2@LiNbO3/Li-P3S11/Li all-solid-state battery employing HFE-penetrated Li-P3S11 glass-ceramic as electrolyte and LiF-coated Li metal as anode shows a high reversible discharge capacity of 118.9 mA h g $^{-1}$ at 0.1 mA cm $^{-2}$ and retains 96.8 mA h g $^{-1}$ after 100 cycles.

5.3 Mechanical stability of the interface between metal lithium and S-SEs

Another important problem is the formation of Li dendrites along the voids and grain boundaries in solid electrolytes, although these materials have much stronger mechanical strength than Li metals. ¹⁵⁷ In fact, there are problems similar to lithium dendrite growth in solid electrolytes. The mechanism for dendrite formation and growth in solid electrolytes is still unclear and controversial.

Metal lithium reacts and grows along grain boundaries and cracks inside the S-SEs.¹⁵⁷ However, lithium dendrites are still formed and grown in the glassy sulfide electrolytes without a grain boundary.¹⁶⁵ In order to suppress the growth of Li

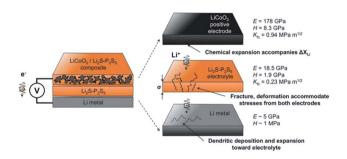


Fig. 20 Summary of mechanical performance data for $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ (LPS) in the context of all-solid-state batteries. Reprinted with permission. ¹⁶⁶ Copyright© 2017, John Wiley and Sons.

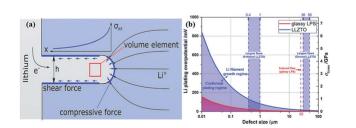


Fig. 21 (a) The effect of stress accumulation on lithium growth; (b) inverse square root dependence of Li plating over-potential and crack-extension stress ($\sigma_{0,max}$) on defect size of glassy LPS and LLZTO. Reproduced with permission.¹⁶⁵ Copyright© 2017, John Wiley and Sons.

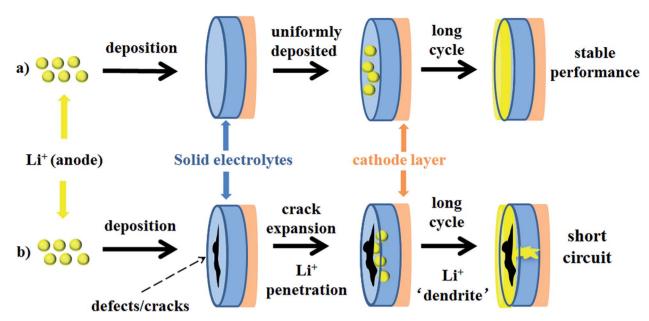


Fig. 22 Schematic diagrams of the mechanism of penetration of Li-ions into solid electrolytes. (a) Li-ions are uniformly deposited on the surface of the defect-free electrolyte; (b) penetration of Li-ions into the solid electrolyte layer forming 'dendrites' through defects, causing short circuit. Produced with permission. Copyright@ 2017, John Wiley and Sons.

dendrites, it is necessary to prevent the interfacial reaction between the solid electrolyte and Li. Therefore, it is necessary to understand the mechanical parameters of sulfide solid electrolytes to analyse interface problems. The Young's modulus, hardness, and fracture toughness of glassy 70Li₂S-30P₂S₅ solid electrolytes were determined to be 18.5 \pm 0.9 GPa, 1.9 \pm 0.2 GPa, and 0.23 \pm 0.04 MPa m^{1/2}, respectively. ¹⁶⁶ As illustrated in Fig. 20, L₂S-P₂S₅-type electrolytes are more compliant and brittle than crystalline oxide electrolytes. The low stiffness of the glassy electrolytes indicates that the electrolytes can accommodate mismatch in interfacial stress in all-solid-state batteries. But their ability is easily affected by low fracture toughness and cycling-generated flaws.

Monroe and Newman propose that solid electrolytes with sufficiently high shear modulus (about twice that of Li, which has shear modulus of 4.2 GPa)167 could suppress the formation of Li dendrites. 168,169 However, this theory cannot explain the phenomenon that appeared in Porz et al.'s work.165 There is still a disturbance by metal lithium dendrite growth in glassy Li₂S-P₂S₅ with a shear modulus of 8.3 GPa. The growth mechanism of lithium dendrites in four types of solid electrolytes, glassy Li₂S-P₂S₅, β-Li₃PS₄, and polycrystalline and single crystal LLZTO, is studied by galvanostatic electrodeposition experiments combined with in situ and ex situ microscopy. As shown in Fig. 21a, a model is proposed to explain the effect of stress accumulation on lithium dendrite growth. An electrochemomechanical model for growth of lithium-filled cracks is developed. Fig. 21b shows the relationship between the minimum over-potential and the defect size for glassy Li₂S-P₂S₅ and LLZTO. The relationship between maximum stress and defect size is also plotted. When studying the mechanism of lithium metal penetration through glassy Li₂S-P₂S₅, lithium

metal is uniformly deposited in the region of the glassy Li₂S-P₂S₅ with no crack and gradually propagates laterally from the electrode contact point as shown in Fig. 22a. However, when lithium metal is deposited near the precracked area, cracks are formed and extended into the sample, causing structural damage and even short-circuit as the experiment progressed, as in Fig. 22b. It is concluded that stabilization of the interfaces between solid electrolytes and lithium metal will require minimizing interface defects. The factors governing lithium penetration through brittle electrolytes are investigated by performing lithium electrodeposition on single-crystal Li₆La₃-ZrTaO₁₂ garnets. 170 It is concluded that the risk of lithium metal penetration can be reduced by designing the battery with a larger cathode, smaller anode and small thickness/width

Conclusions and prospects

All-solid-state batteries are the most promising energy storage system for next generation applications, due to their good safety, high energy density and wide operating temperature. Among all the solid electrolytes, S-SEs have received extensive attention owing to their high conductivity, wide electrochemical window, and good mechanical properties. However, there are still great challenges for the application of S-SEs in all-solidstate batteries: (1) S-SEs are extremely sensitive to moisture and easily react with water in the air to produce toxic H₂S gas and therefore destroy the structure of the electrolyte; (2) problems of the interface between electrode/electrolyte still need to

This work mainly reviews the research progress of S-SEs and their applications in all-solid-state lithium and all-solid-state Li-S batteries. The future development of emerging all-solidstate batteries should focus on the following aspects: (1) exploring new types of S-SEs or new preparation methods to improve the conductivity of Li-ions to meet practical applications; (2) enhancing the chemical and thermal stabilities of sulfide electrolytes; (3) improving the interface between the solid electrolytes and the electrodes; (4) optimizing the preparation process of all-solid-state batteries.

As the most promising energy storage system, there is still a long way to go in realizing the commercialization of all-solidstate batteries based on the requirements of safety, energy density and cycle stability.

Conflicts of interest

There are no conflicts to declare.

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