Sulfide-based composite solid electrolyte films for all-solid-state batteries

Check for updates

Shenghao Li[1,4], **Zhihua Yang**[1,4], **Shu-Bo Wang**[1,4], **Mingqiang Ye**[1,4], **Hongcai He**[2], **Xin Zhang**[1] ✉,
Ce-Wen Nan[3] & **Shuo Wang** [1] ✉

All-solid-state batteries with non-flammable solid electrolytes offer enhanced safety features, and show the potential for achieving higher energy density by using lithium metal as the anode. Among various solid electrolytes, sulfides are favored for their high room-temperature ionic conductivity and low-temperature processing. However, making large-scale thin electrolyte films via pressing sulfide powder is still challenging. A polymer has recently been introduced as a binder or framework to obtain a flexible thin sulfide-based composite electrolyte film with high ionic conductivity. In this Review, we initially discuss the ionic transport mechanism of sulfide/polymer composite electrolyte films. Then, the preparation methods and the properties of sulfide-based composite electrolytes are introduced in detail, and the advantages and disadvantages of each method are also analyzed. We later discuss the application of composite electrolyte films in all-solid-state batteries. Finally, we provide a perspective on the future development direction of sulfide-based composite electrolyte films.

Lithium-ion batteries have become increasingly prevalent in various applications, such as grid electric storage, electric vehicles, and portable electronic equipment[1–3]. However, the currently used lithium-ion batteries use flammable organic electrolytes, and lithium dendrites can grow, especially during the high-current cycling, and penetrate the separator, leading to the short circuits of batteries[4,5], which would cause serious safety issues. All-solid-state batteries (ASSBs) with non-flammable solid electrolytes exhibit higher energy density and improved safety in comparison with commercial lithium-ion batteries, and thus ASSBs have attracted ever-increasing attention[6–9]. Solid-state electrolytes, as one of the most important components of a solid-state battery, could be classified into polymer-based electrolytes, oxides, sulfides, and halides[10–13].

Polymer-based solid electrolytes exhibit good processability and flexibility, but their low room-temperature ionic conductivity (around 10^{-5} S cm^{-1}) hinders their further applications[14,15]. Oxides show good air stability and wide electrochemical windows. However, their high sintering temperature and natural brittleness make them difficult to be applied in bulky batteries on a large scale[16,17]. Halide solid electrolytes have emerged as promising candidates due to their good deformability, high ionic conductivity, and oxidation stability. However, they also face some challenges due to their high density, expensive raw material cost, and instability in organic solvents[18,19]. In contrast, sulfide solid electrolytes, especially

some lithium argyrodites (e.g. Li_6PS_5Cl[20], $Li_{5.5}PS_{4.5}X_{1.5}$ (X = Cl, Br)[21,22], $Li_{5.5}PS_{4.5}Cl_{0.8}Br_{0.7}$[23]), have gained extensive attention due to their abundant raw materials and impressive room-temperature ionic conductivity which is comparable to that of liquid electrolytes[24–26].

Since crack formation easily occurs in the thin ceramic wafers formed by the cold pressing of sulfide solid electrolyte powders, the thickness of the electrolyte layer is typically between 0.6 and 1 mm, which will greatly sacrifice the energy density of the whole battery[27]. Therefore, reducing the thickness of the sulfide electrolyte layer is vital for achieving high specific energy. To fabricate a flexible sulfide electrolyte film with high ionic conductivity, combining sulfide electrolyte with polymer is an effective method[28]. The sulfide/polymer composite electrolytes include two types: one in which the polymer electrolyte acts as matrix and the sulfide serves as fillers, the other in which the sulfide electrolyte acts as matrix and the polymer serves as filler[29–31]. Due to the fact that polymer-based composite electrolyte films exhibit lower room-temperature ionic conductivity, typically at the level of 10^{-4} S cm^{-1}[32], this review mainly focuses on the research progress of sulfide-based composite electrolyte films.

In this review, we first illustrate the mechanism of ionic transport in sulfide/polymer composite electrolyte films. Subsequently, the preparation methods and corresponding properties of sulfide-based composite electrolytes are introduced in detail with an analysis of the advantages and

[1]Center of Smart Materials and Devices, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Material Science and Engineering, Wuhan University of Technology, 430070 Wuhan, China. [2]Qingtao Research Institute, Qingtao Energy Development Inc., Kunshan, China. [3]State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, 100084 Beijing, China. [4]These authors contributed equally: Shenghao Li, Zhihua Yang, Shu-Bo Wang, Mingqiang Ye. ✉e-mail: zhang-xin@whut.edu.cn; shuowang@whut.edu.cn

disadvantages of these methods. Then, the research progress of sulfide-based electrolyte films used in the ASSBs is presented. Finally, we provide insights into the future development direction of sulfide-based composite electrolyte films.

Ionic transport in composite electrolytes

For the composite electrolyte films in which sulfide acts as a matrix and polymer is filler, the sulfide phase is mainly responsible for the Li^+ transport. Since most polymer binders, such as NBR, poly(styrene-co-butadiene) rubber (SBR), are ionic insulators, if the binders wrap around the sulfide electrolyte particles, the contact between the sulfide particles will be blocked, which will impede the continuous and fast ionic transport in the sulfide phase (Fig. 1a)[32–34]. Therefore, the ideal situation is that the polymer binder fills the gaps between the stacked sulfide electrolyte particles and acts as an adhesive for these sulfide particles, which could minimize binder usage. In order to further improve the ionic conductivity of the sulfide composite electrolyte films, replacing the common insulating binders with ionically conductive polymer-based electrolytes is an alternative method. Some composite electrolyte films, such as $Li_6PS_5Cl/PEO–SiO_2–LiClO_4$ electrolyte[35], $Li_{3.25}Ge_{0.25}P_{0.75}S_4/PEO–LiTFSI–Pyr_{1,4}TFSI$ electrolyte[36], $Li_6PS_5Cl/NBR–LiG3$ gel polymer electrolyte[37] and $Li_6PS_5Cl/NBR–LiTFSI$ composite electrolyte[38] have been developed. NMR tests have confirmed that lithium ions could migrate through both the sulfide phase and polymer phase, and lithium ions preferably diffuse through the sulfide ceramic phase (Fig. 1b). Due to the higher room-temperature ionic conductivity of sulfide-based composite electrolyte films, this review mainly focuses on the recent progress of sulfide-based composite electrolyte films.

The preparation method of sulfide-based composite electrolyte

The typical preparation methods of sulfide-based composite electrolyte films include dry and wet processes. Among them, the wet process is a prevalent technique for film production.

Wet process

The preparation of composite electrolyte membrane by the wet process mainly includes wet mixing—cold (or hot) pressing, tape casting, and infiltration. Below is a brief introduction to the operation procedures, advantages and disadvantages of these methods.

Wet mixing—cold (or hot) pressing

Wet mixing-cold (or hot) pressing is a popular method used in the laboratory. The specific process is as follows. First of all, the polymer binder is partially dissolved in the organic solvent, then the sulfide electrolyte is added, followed by the solvent evaporation. Finally, the obtained composite electrolyte powder was cold (or hot) pressed into a freestanding pellet under a certain temperature and pressure (Fig. 2a). Through the wet mixing, the homogeneous dispersion of the polymer binder will be effectively improved, and the freestanding composite electrolyte membranes with a high ionic conductivity of about $0.5–1$ mS cm^{-1} and a thickness of about 100–120 μm will be obtained[28,39].

Meanwhile, the wet mixing-cold (or hot) pressing method also provides a new way for the development of high-energy density ASSBs. For example, Liu et al. successfully prepared a continuous and uniform coating

of polydopamine with a thickness of 5 nm on the Li_6PS_5Cl particles. Subsequently, a compact Li_6PS_5Cl-polydopamine film with a thickness of 35 μm and an ionic conductivity of 0.2 mS cm^{-1} was prepared by cold pressing of Li_6PS_5Cl@polydopamine particles. An ASSB with the Co_3S_4 as cathode and the above film as a separator was assembled. The cell delivered a high discharge capacity of 485.1 mAh g^{-1} with a high capacity retention of about 78.5% after 100 cycles at 0.1 C and 25 °C[40].

Though the wet mixing–cold (hot) pressing method is widely used in the laboratory, it still also faces many obstacles in practical applications. Excessive pressure during the process may lead to the rupture or deformation of the composite electrolyte membrane, while too low pressure may lead to weak bonding of the composite electrolyte powder. Additionally, the composite electrolyte membrane prepared with this method has limitations in terms of size. Larger dimensions would require a larger tonnage press. Therefore, this preparation method is largely constrained by the capabilities of the equipment used, posing challenges for large-scale preparation.

Tape casting

Compared to the wet mixing-cold (or hot) pressing method, tape casting is an efficient method to prepare composite electrolyte films on a large scale[41–44]. This preparation technique involves a series of following steps. To begin with, a binder is dissolved into a solvent to form a solution. Subsequently, the sulfide is added to the solution and mixed to form a sulfide electrolyte slurry. Next, the slurry with adjusted viscosity is uniformly cast on the substrate. After that, the solvent is removed from the slurry by drying. Finally, a composite electrolyte film is successfully obtained (Fig. 2b).

Tape casting is a prevalent composite film fabrication technique due to significant advantages, such as uniform preparation, as well as the ability to precisely control the thickness of the film[45]. In addition, the manufacturing process of this method is relatively mature and simple, making it suitable for large-scale production. However, it should be noted that lithium thiophosphates typically undergo severe reactions with polar solvents (Fig. 3a), such as dimethylformamide, leading to sulfide electrolyte decomposition and reduction of the ionic conductivity[46]. This is because sulfides will suffer from nucleophilic attack by the aldehydo group with lone-pair electrons at electronegative oxygen. Consequently, only solvents with low-polarity or non-polarity, such as toluene and xylene, are usually used during the wet process. This is because non (or low)-polar solvents exhibit chemical inertness in contact with lithium thiophosphates owing to their negligible donor ability (Fig. 3b and c)[46–48]. However, these solvents will limit the choice of polymer binder. Only a few binders that could be solved in the solvents with low-polarity or non-polarity, such as NBR and SBR, are viable options[49,50]. In addition, the sulfide electrolyte particles are easy to be encapsulated by polymers during the tape-casting process, which may lead to a low ionic conductivity of the composite film[51,52].

To address the above issues, the interactions among sulfide solid electrolytes, polymer binders, and solvents have been investigated to find an appropriate sulfide–polymer binder–solvent system. For example, Tan et al. analyzed the stability of $Li_7P_3S_{11}$ against various solvents by comprehensive methods. They found that p-xylene (XYL) exhibited good compatibility with $Li_7P_3S_{11}$. Additionally, styrene–ethylene–butylene–styrene (SEBS) polymers could be solved into the XYL. Based on the above optimal system, a $Li_7P_3S_{11}$-SEBS composite film with an ionic conductivity of 0.7 mS cm^{-1} and a thickness of 50 μm was successfully prepared via tape-casting

Fig. 1 | The ionic transport mechanism of sulfide/polymer composite electrolyte. a Li_6PS_5Cl-based composite electrolyte with NBR–LiG3 as the binder (NBR: nitrile-butadiene rubber; LiG3: triethylene glycol dimethyl ether). Lithium ions prefer to go through the Li_6PS_5Cl particles, and NBR–LiG3 also contributes to the Li^+ transport[37]. **b** Li_6PS_5Cl-based composite electrolyte with ionically insulating poly(vinylidene fluoride) (PVDF) as the binder. Li^+ can only migrate through the Li_6PS_5Cl particles[28].

- Li_6PS_5Cl
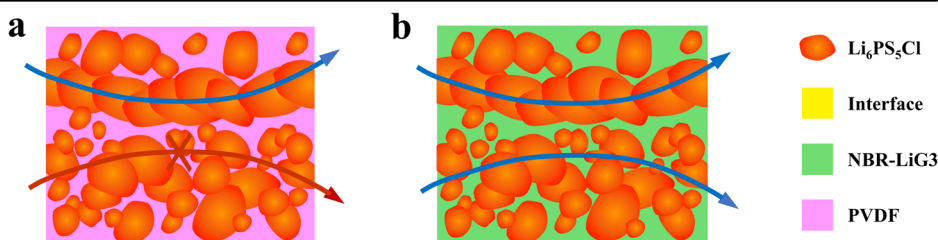- Interface
- NBR-LiG3
- PVDF

Fig. 2 | Schematic illustration of the preparation of composite electrolyte films via different wet processes. a The process of wet mixing—cold (or hot) pressing. **b** The process of tape casting.
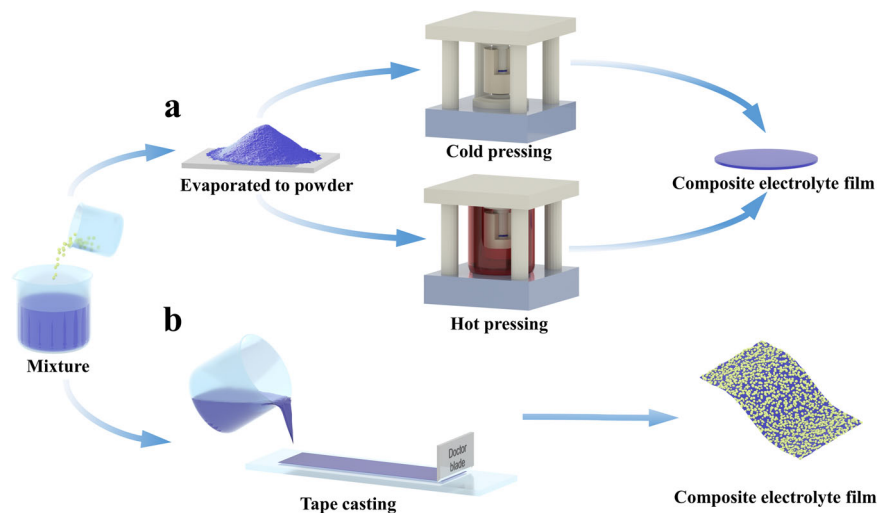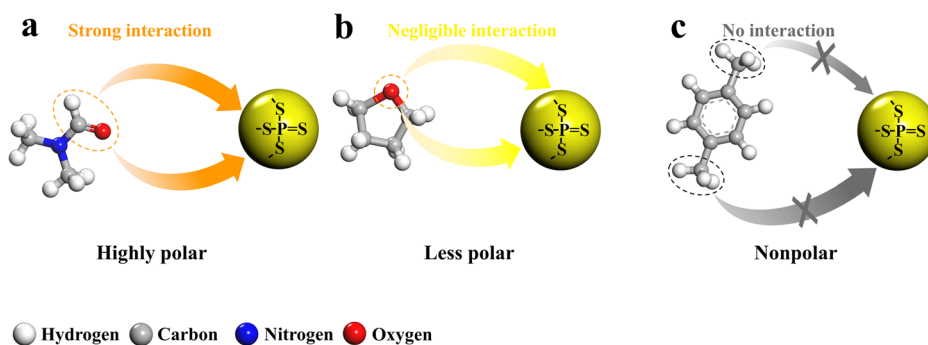

Fig. 3 | Schematic illustrating interactions between lithium thiophosphates and solvents with various polarity. a Severe interaction between the highly polar dimethylformamide and sulfides. **b** Negligible interaction between the less polar tetrahydrofuran and sulfides. **c** No interaction between the nonpolar paraxylene and sulfides.

method[51]. To further improve the ionic conductivity and reduce the thickness of the film, a sulfide electrolyte with higher ionic conductivity is chosen. An 8 μm thick $Li_{9.88}GeP_{1.96}Sb_{0.04}S_{11.88}Cl_{0.12}$−poly(methyl methacrylate)/n-butylacrylate composite film with high ionic conductivity of 1.9 mS cm^{-1} was successfully obtained via tape-casting[53].

Recent studies have found that some polar ester solvents with large volumes of alkyl groups can not only enhance the solubility of some binders (acrylate-type, NBR, SBR) and lithium salts but also can inhibit nucleophilic attacks on the sulfide electrolytes because of the steric hindrance effect. In recent studies, a co-solvent approach combining solvents with various polarity solvents has been implemented for the fabrication of sulfide-based composite electrolyte films[38,54]. For example, Kim et al. developed a co-solvent system composed of the highly polar hexyl butyrate (HB) and the less polar dibromomethane (DBM) to prepare a composite electrolyte film. The DBM solvent effectively suppressed the decomposition of sulfide electrolyte and dissolved NBR, while the HB solvent was used to dissolve lithium salts and adjust the dispersion of the NBR. Additionally, the HB solvent exhibited excellent stability with the $Li_6PS_5Cl_{0.5}Br_{0.5}$ electrolyte due to the huge steric hindrance of hexyl[38]. In another study, Lee et al. also used cosolvents consisting of xylene and isobutyl isobutyrate to prepare a 40 μm Li_6PS_5Cl-based solid electrolyte with a high ionic conductivity of 1.31 mS cm^{-1} at room temperature. Due to the good solubility of the acrylate-based binder, the Li_6PS_5Cl is able to disperse more uniformly in the slurry[54]. To further enhance the room-temperature ionic conductivity of the composite electrolyte film, future research should focus on the development of new polymer binders and the exploration of new solvent systems.

Infiltration method

During the above tape-casting process, sulfide electrolyte particles are typically encapsulated by polymer binders, which hinders the lithium ions conduction between the sulfide particles. To construct a continuous pathway for ion transport, the infiltration-cold (or hot) pressing method has emerged for obtaining composite electrolyte films. This method consists of two types: one involves infiltrating polymers into the three-dimensional sulfide framework, while the other entails infiltrating sulfides into the three-dimensional network formed by the polymer binders[55].

For the composite electrolyte film with sulfide as the skeleton and polymer binder as the fillers, the specific preparing process involves infiltrating polymer monomers into a three-dimensional sulfide framework, followed by in-situ polymerization to create a freestanding sulfide/polymer composite membrane (Fig. 4a)[56]. Due to the construction of a good three-dimensional network formed by sulfide electrolyte particles, lithium ions could not only fast diffuse through the sulfide ceramic phase but also along with the sulfide/polymer interface.

For example, Cui et al. utilized highly conductive Li_6PS_5Cl as a matrix and SeS_2 as a pore-forming agent to prepare a three-dimensional freestanding porous skeleton (denoted as p-LPSCl)[56]. Polyethylene glycol methyl ether acrylate (PEGMEA) as the monomer was infiltrated into the sulfide porous skeleton, followed by in situ polymerized to obtain a p-LPSCL/P(PEGMEA) composite electrolyte film. It has been revealed that both the sulfide ceramic phase and the p-LPSCl/P(PEGMEA) interfacial phase in this composite electrolyte provided fast ionic transport pathways, leading to an increase of the ionic conductivity from 0.0018 to 0.46 mS cm^{-1}. Moreover, the p-LPSCl/P(PEGMEA) exhibited good compatibility with the lithium metal anode. Based on the above film, the Li|3D composite|$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ ASSB was assembled. The cell delivered a reversible discharge capacity of 157 mAh g^{-1} with a high capacity retention of 84% after 90 cycles at a cut-off voltage of 4.5 V at 0.1 C. This work provides a highly effective strategy for designing solid electrolytes that meet the requirement of both high conductivity and excellent interfacial

Fig. 4 | Schematic illustration of the preparation of composite electrolyte films via different infiltration methods. a Composite electrolyte with sulfide as the skeleton and polymer binder as the fillers. The polymer is infiltrated into the sulfide framework. **b** Composite electrolytes with polymer obtained via electrospinning technology as skeleton and sulfides as the fillers. The sulfide suspension is dripped into the polymer skeleton. **c** Composite electrolytes with commercial nonwovens as skeleton and sulfides as fillers. The sulfide suspension is doctor-bladed on the polymer skeleton.
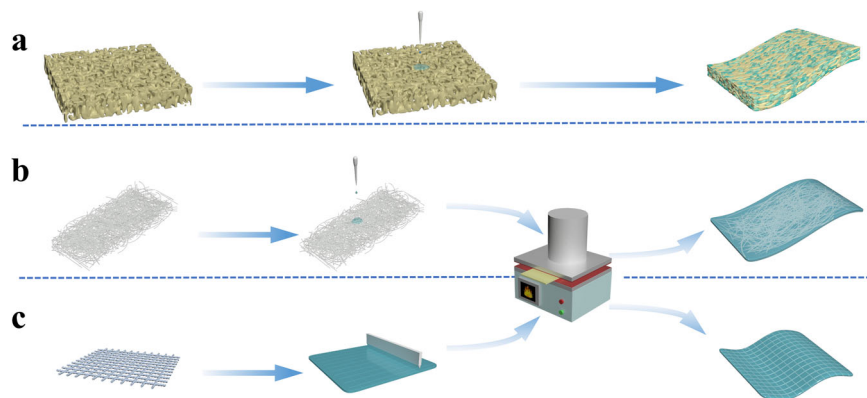
compatibility. However, the thickness of the composite membrane reaches 125 µm, which is still too thick to align with the demands of commercialization. Further reducing the thickness of the film is still necessary.

For the composite electrolyte film with polymer binder as the skeleton and sulfide as the fillers, this method involves infiltrating sulfide electrolyte suspension into the polymer skeleton, followed by either cold pressing or hot pressing to form a thin film (Fig. 4b, c). There are generally two options for the polymer binder skeleton, one is commercial nonwovens, and the other is the three-dimensional fiber network synthesized via electrospinning technology. For example, Xu et al. used Kevlar nonwovens as the scaffold to obtain a Li_3PS_4-based composite electrolyte film with a thickness of 100 µm and ionic conductivity of 0.3 mS cm^{-1} [57]. For another instance, Liu et al. prepared a poly(vinylidene fluoride-co-trifluoroethylene) three-dimensional framework by using electrospinning technology. Then the Li_6PS_5Cl suspension was infiltrated into the polymer skeleton to form a 30 µm film with an ionic conductivity of 1.2 mS cm^{-1} [58].

When it comes to the infiltration method, apart from directly dripping the sulfide electrolyte suspension into the polymer framework (Fig. 4b), doctor-blade is another facile way (Fig. 4c). For example, Liu et al. dripped the Li_6PS_5Cl–toluene suspension into the electrospinning polymer film[58], while Zhu et al. coated the Li_6PS_5Cl–chloroform suspension onto the cellulose skeleton with the doctor blade method[59]. To further improve the compactness and ionic conductivity of the film, hot pressing could be used in the final preparation process. By introducing a flexible polymer framework, the thickness of the solid electrolyte layer could be reduced, and both excellent mechanical performance and high room-temperature ionic conductivity could be achieved. In addition, the battery assembly challenges would be alleviated, and the production efficiency of ASSBs would be facilitated.

Dry process

In the liquid-phase synthesis process, the commonly used organic solvents are normally toxic, which will damage the environment. In addition, the sulfide electrolytes are easy to be wrapped by the binders, impeding the ionic transport between the sulfide particles, and resulting in low ionic conductivity of the composite electrolytes. In contrast, the dry method has garnered significant attention within the industry due to its lower energy consumption, minimal binder usage, and ability to maintain the high ionic conductivity of sulfides[60]. Currently, there are three kinds of dry methods for the fabrication of composite electrolyte films, including powder compression, powder spraying, and binder fibrillation. A brief overview of the operational steps and pros and cons of each specific method is as follows.

Powder compression

In laboratory-scale preparation of composite electrolyte films, powder compression is widely used because of its simplicity and cost-effectiveness. This method involves dry mixing polymer binders with sulfide electrolytes via ball milling, followed by cold (or hot) pressing to form composite

electrolyte films with thicknesses of 60–100 µm (Fig. 5a)[61–63]. However, this method has some drawbacks, including low elastic modulus, poor flexibility, susceptibility to cracking, and limitations in size due to the use of molds. Furthermore, polymer binders tend to agglomerate, hindering ionic transport and resulting in declined ionic conductivity. Therefore, the prepared composite electrolyte membrane typically exhibits low ionic conductivity of about 0.1 mS cm^{-1}. For example, Whiteley et al. mixed $77.5Li_2S·22.5P_2S_5$ solid electrolyte with polyimide by high-energy ball milling, and then the mixture was hot pressed at 100 °C and 228 MPa to obtain a sheet-like composite electrolyte film with an ionic conductivity of about 0.1 mS cm^{-1} and a thickness of 63.7 µm[62]. To further enhance the ionic conductivity of the composite electrolyte films, hot pressing could be used to densify the films, which requires the binder to possess good thermal stability and mechanical properties. For example, after the aramid fiber reinforced $(Li_2S)_{70}(P_2S_5)_{30}$ glass–ceramic composite electrolyte film being hot pressed at 240 °C and 200 MPa, the ionic conductivity of the composite film with 10 wt% aramid fiber increased to 2.48 mS cm^{-1} [61]. However, it should be pointed out that powder compression is not suitable for roll-to-roll production, limiting its application in large-scale film fabrication.

Powder spraying

Powder spraying is a widely commercial method used for preparing solid electrolyte films. The detailed preparation process is as follows[64]. Firstly, sulfide electrolyte and polymer binder powders are mixed homogeneously. Subsequently, electrostatic discharge occurs between needle electrodes and counter electrodes, as a result, the powders are charged and then deposited onto the counter electrode. Finally, the deposited powders are rolled to form a dense composite electrolyte film (Fig. 5b). Two common techniques for powder spraying are electrostatic spraying (PES) and electrostatic cylinder method (EDM)[60]. The composite electrolyte membrane prepared by PES is mainly affected by parameters such as charging voltage, gas pressure, and distance between the spraying gun electrode tip and current collector[60]. Currently, powder spraying is predominantly applied to composite electrode fabrication, with limited reported applications in the field of composite electrolyte films. One common challenge associated with powder spraying is the lack of an effective way to control the coating thickness. For the ASSB, the uneven thickness of the electrolyte membrane will have a severe impact on the specific capacity and cycling stability. In addition, a relatively large amount of binder (>5 wt%) is required for powder spraying. After melting, the binder will adhere to the surface of the sulfide particles, resulting in the formation of an insulating layer, which hinders ion conduction. Therefore, selecting a binder with a strong adhesive could help reduce the usage amount of binder and enhance the ionic conductivity of the composite electrolyte films.

Binder fibrillation

Binder fibrillation is a recently developed dry method. Detailed preparation process is as follows. First of all, the sulfide electrolyte is mixed with a

Fig. 5 | Schematic illustration of the preparation of composite electrolyte membrane by dry process. **a** The sulfides and polymer binder were dry mixed via ball milling followed by cold pressing. **b** The composite cathode mixture powder was sprayed, followed by hot rolling. **c** The composite cathode mixture was hot rolled to make the binder fibrillated.
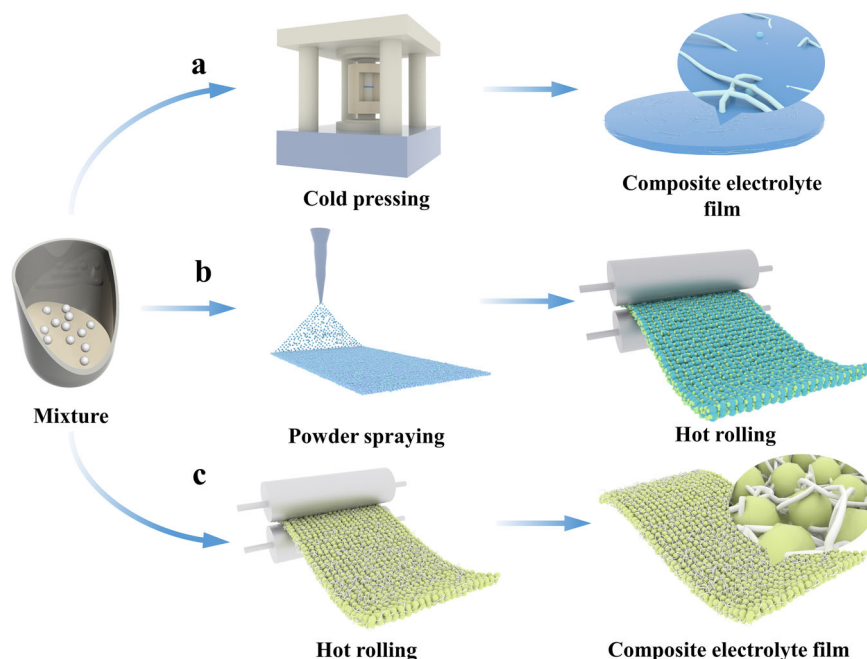
polymer binder. Then, additional shear force is applied to the mixture to induce polymer fibrillation. Finally, the polymer network is formed, which could serve as the support for the sulfide electrolytes (Fig. 5c). Binder fibrillation allows for the preparation of thin electrolyte films with a small amount of binder. Due to the uniform distribution of sulfide electrolytes within the fiber network, the reduction of ionic conductivity caused by binder agglomeration could be alleviated. In addition, hot rolling could be used to reduce the porosity and further enhance the ionic conductivity. For example, the $Li_{5.4}PS_{4.4}Cl_{1.6}$ sulfides and PTFE powder as starting materials were mixed in a weight ratio of 99.8:0.2 via ball milling, followed by hot rolling at 80 °C. During the rolling process, PTFE fibrillation occurred under shear force, resulting in a fibrous PTFE network and a denser film. Finally, a flexible ultra-thin (about 30 μm) composite electrolyte film with a remarkably high ionic conductivity of 8.4 mS cm^{-1} at 25 °C was obtained[65]. However, the current steps of binder fibrillation are mainly conducted manually, and further research is needed to reveal the underlying mechanisms. In 2019, Musk announced that Tesla planned to purchase Maxwell for $218 million[66]. After that, binder fibrillation has attracted worldwide attention. Subsequently, during Tesla Battery Day in 2020, Musk claimed that binder fibrillation could significantly reduce production cost[67]. This highlights that binder fibrillation shows great potential in the commercial production of composite electrolyte films and composite electrodes through roll-to-roll processes.

Performance of the composite electrolyte films
Ionic conductivity and thickness of the films
Table 1 shows the room-temperature ionic conductivity and thickness of sulfide-based composite electrolyte films prepared via various preparation methods. In order to highlight the recent advancements in sulfide-based composite films for ASSBs, a succinct timeline showcasing significant events in composite electrolyte films is depicted in Fig. 6. It could be observed that the composite electrolyte films prepared by the dry (or wet) mixing-cold pressing method is not flexible and typically thick (>60 μm) with low ionic conductivity (<2 mS cm^{-1}). Hence, this method is not suitable for large-scale applications. The ionic conductivity of composite films prepared by doctors blading the sulfide solution on the non-woven skeleton, or using the electrospinning-infiltration-hot pressing technique, will be relatively high (1–6 mS cm^{-1}). However, the thickness is still relatively thick (>30 μm) and needs to be further reduced. Compared with the wet process, the ionic

conductivity of the film via the dry process can reach up to 8.4 mS cm^{-1}. However, the thickness is difficult to be further reduced to <20 μm.

Tape casting method could be adopted to achieve the films with controllable thickness (8–70 μm) and ionic conductivity of ~1–2 mS cm^{-1}. Consequently, this method emerges as a highly promising approach for large-scale production of ultra-thin composite electrolyte films. In the future, more viscous binders could be used to reduce the amount of binder used. Additionally, using sulfide electrolytes with higher ionic conductivity (>10 mS cm^{-1}) and improving the mixing process could help further optimize the ionic conductivity of the composite electrolyte films.

Li symmetric battery performance
The stability and compatibility of pure sulfide electrolyte ceramics towards lithium metal anode are of significant importance for their practical applications. However, sulfide electrolytes typically react with lithium metal. For example, lithium argyrodite, such as $Li_{6-y}PS_{5-y}M_{1+y}$ ($0 \leq y \leq 1$, M = Cl, Br, I), will decompose to form a solid electrolyte interphase (SEI) layer containing Li_2S, Li_3P and LiCl when in contact with lithium metal. The SEI layer initially thickens and eventually stabilizes during resting, leading to an increase of interfacial resistance and polarization voltage[68]. Additionally, pores and cracks within the ceramics, inherent electronic conductivity, chemical environment, and surface roughness of the sulfides will lead to the formation and growth of lithium dendrites, ultimately resulting in short circuits of the cells, especially under high current density or large external pressure[69].

By compounding the sulfide ceramic matrix with polymer binders, the interfacial stability against lithium metal could be improved. For example, Wang et al. incorporated PVDF into the Li_6PS_5Cl matrix to reduce the porosity of the composite electrolyte membrane, resulting in a significant improvement in battery cycling life. The lithium symmetric cell assembled with Li_6PS_5Cl-based film containing 10 wt.% PVDF showed an extended lifespan from 1 hour to 67 hours, effectively suppressing lithium dendrite growth[28]. Similarly, Kim et al. prepared Li_6PS_5Cl-XNBR composite electrolyte films through wet mixing followed by rolling. Based on this film, the assembly lithium symmetric cell showed stable cycling for 500 h under the current density of 0.1 mA cm^{-2} and an areal capacity of 0.05 mAh cm^{-2} [52]. Furthermore, Liu et al. prepared Li_6PS_5Cl–P(VDF-TrFE) composite electrolyte membranes by electrospinning–infiltration–hot-pressing. The lithium symmetric cells assembled with this film exhibited stable cycling

Table 1 | Summary of typical sulfide-based composite electrolyte films prepared via various methods

Method	Sulfide solid electrolyte	Solvent	Binder	Binder content [wt%]	Ionic con-ductivity [mS cm^{-1}]	Thickness [μm]	Ref.
Wet process	Li_6PS_5Cl	Toluene-isobutyl isobutyrate	NBR	~5	1.12	50	[48]
	Li_6PS_5Cl	DBM	NBR-Li(G3)TFSI	50	3.3	70	[37]
	Li_3PS_4	Anisole	PPC	~6	0.11	~80	[73]
	Li_6PS_5Cl	Toluene	Ethyl cellulose	2	1.65	47	[45]
	$78Li_2S-22P_2S_5$	Ethyl acetate	PVDF-LiTFSI	3	0.707	~121	[74]
	Li_6PS_5Cl	ACN	PEO–SiO$_2$–LiClO$_4$	~5	0.283	65	[35]
	$Li_7P_2S_8I$	Heptane	PEP–MNB	3	1	70	[75]
	$Li_{9.88}GeP_{1.96}Sb_{0.04}S_{11.88}Cl_{0.12}$	Toluene	p(MMA/nBA)	3	1.9	8	[53]
	Li_6PS_5Cl	Xylene	BR	2	2.2	–	[76]
	Li_6PS_5Cl	Toluene	XNBR	5	0.38	47	[52]
	Li_6PS_5Cl	Toluene	P(VDF-TrFE)	21	1.2	30–40	[58]
	Li_6PS_5Cl	Chlorobenzene	Li_6PS_5Cl @polydopamine	–	0.2	35	[40]
	Li_6PS_5Cl	–	P(PEGMEA)	–	0.46	125	[56]
	Li_6PS_5Cl	Chloroform	CEL	–	6.3	60	[59]
	$Li_6PS_5Cl_{0.5}Br_{0.5}$	EtOH	PI	3.6–6.6	0.058	40	[72]
Dry process	$75Li_2S-25P_2S_5$	–	PFPE	23	0.1	150	[77]
	$70Li_2S-30P_2S_5$	–	Aramid fibers	10	2.4	100	[61]
	$70Li_2S-30P_2S_5$	–	1,4-butanediol	2	0.97	–	[78]
	$70Li_2S-30P_2S_5$	–	EG	2	0.11	–	[79]
	LGPS	–	PTFE	1	0.36	100	[80]
	$Li_{5.4}PS_{4.4}Cl_{1.6}$	–	PTFE	0.2	8.4	30	[65]
	Li_6PS_5Cl	–	PTFE	0.5	1.7	20	[81]

BR butadiene rubber, *DBM* dibromomethane, *PPC* poly(propylene carbonate), ACN is acetonitrile, *PEP-MNB* is poly (ethylene-co-propylene-co-5 methylene-2-morbornene), *NB* nitrile butadiene, *EG* ethylene glycol; p(MMA/nBA) is poly(methyl methacrylate)/n-butylacrylate; *PTFE* is polytetrafluoroethylene, *XNBR* carboxylated nitrile butadiene rubber, *P(PEGMEA)* poly(poly(ethylene glycol) methyl ether acrylate), *P(VDF-TrFE)* poly(vinylidene fluoride-co-trifluoroethylene).

for 200 h at a current density of 6.0 mA cm^{-2} and an areal capacity of 3.0 mAh cm^{-2}, despite a slight increase in overpotential from 0.6 to 1.08 V during the initial 30 cycles[58].

Although the composite electrolyte films prepared by dry process show relatively higher room-temperature ionic conductivity, the currently-used PTFE binder will react with the lithium metal anode and convert into carbene carbon, and finally into sp^2 carbon, thus greatly increasing the electronic conductivity of the films. To solve the above issues, it is necessary to add a buffer layer between the Li metal anode and the composite electrolyte film to suppress the side reactions[65]. For example, Zhang et al. added a layer of Al_2O_3 between the $Li_{5.4}PS_{4.4}Cl_{1.6}$–PTFE composite electrolyte film and the lithium metal anode, which greatly reduced the interfacial impedance and improved the adhesion to the interface. the assembled lithium symmetric cells showed an increased cycling life from 12 to 400 h under the testing conditions of 0.1 and 0.1 mAh cm^{-2} compared to those without Al_2O_3 coating[65]. Hence, for the dry film process in the future, it is necessary to find a binder that is stable against lithium anode and could be easily fibrillated.

Table 2 lists the lithium symmetric cell performance with sulfide-based composite electrolyte films. The addition of polymer binders could inhibit the lithium dendrite growth to a certain extent and improve the interfacial compatibility towards the lithium metal anode. However, the critical current density and areal capacity are still relatively low, and the cycle life is not long enough. While the addition of a polymer binder could enhance the density of sulfide ceramics, there are still some pores that promote lithium dendrite growth. Additionally, the polymer fails to completely wrap the sulfide electrolyte particles. Consequently, the sulfide electrolytes undergo reactions with the lithium-metal anode at the interface, resulting in an increase in interface impedance. Moreover, some binders would react with the lithium-metal anode, leading to an elevation of the electronic conductivity and further accelerating the lithium dendrite's nucleation and growth. Additionally, the mechanism of lithium dendrite growth in composite electrolyte films needs to be further elucidated. In the future, further optimization of binder selection and microstructure of the composite electrolyte film, and constructing artificial SEI will help to enhance the interface compatibility between the solid electrolyte film and lithium metal anode.

Application of composite electrolyte film in ASSB

Currently, most ASSBs with composite electrolyte films in the laboratory are assembled by Swagelok molds. Choosing bulky mold allows for the application of high external pressure on the cell, ensuring good interfacial contact among various components inside the composite cathode and stable cycling of ASSBs, especially when some conversion-type electrodes (e.g. sulfur, silicon, and lithium) with large volume change during the cycling are used. For example, Cao et al. prepared 47 μm Li_6PS_5Cl–ethyl cellulose film by vacuum filtration and then combined it with $LiCoO_2$–Li_3InCl_6 composite cathode and Li–In anode to assemble an ASSB. The cell delivered an initial discharge capacity of 160 mAh g^{-1} and exhibited a high capacity retention of 82% after 200 cycles. Considering the overall mass of the cathode–anode–electrolyte assembly, the ASSB exhibited a high specific energy of 175 Wh kg^{-1} [45]. In order to further improve the specific energy of SSBs, Cao et al. adopted a bipolar stacking structure based on the aforementioned composite electrolyte film, coupled with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NCM811) cathode and nano-Si anode. With this configuration, a high voltage of 8.2 V and a high specific energy of 204 Wh kg^{-1} were achieved[70]. Kang et al. coated Li_6PS_5Cl–NBR slurry
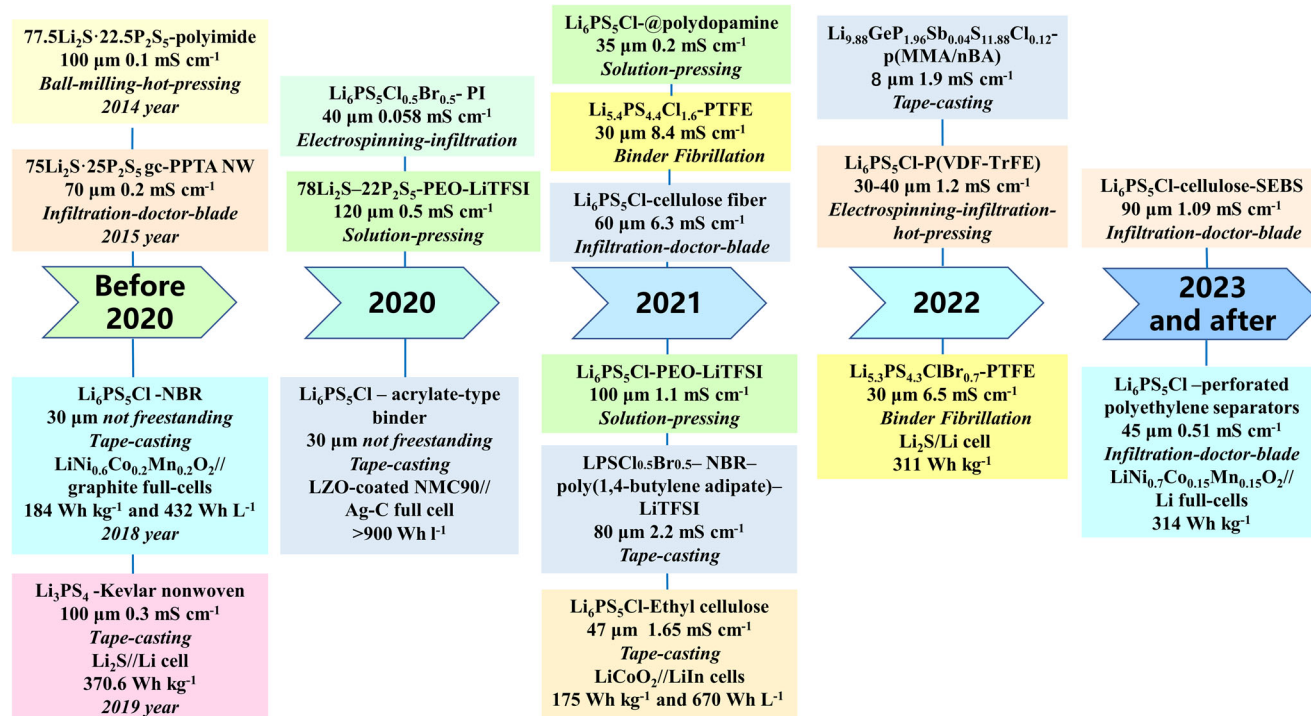
Fig. 6 | A brief chronology of the development of some important events in sulfide-based composite solid electrolyte films for ASSBs. The composite electrolyte films with the highest room-temperature ionic conductivity of 8.4 mS cm^{-1} were prepared by binder fibrillation[65]. The thinnest composite electrolyte membrane currently available is 8 μm, produced by tape casting[53]. The highest specific energy and energy density of all-solid-state batteries based on composite electrolyte films have been reported to be 370 Wh kg^{-1} [57] and 900 Wh L^{-1} [54], respectively.

Table 2 | Summary of the Li//Li symmetric cell performance based on sulfide-based composite electrolyte films

Composite electrolyte film	Plating current density [mA cm^{-2}]	Plating specific capacity [mAh cm^{-2}]	Cycling life [h]	Test temperature	Ref.
Li$_6$PS$_5$Cl–P(VDF–TrFE)	6	3	200	RT	58
Li$_6$PS$_5$Cl–P(PEGMEA)	0.25	0.25	>500	RT	56
Li$_3$PS$_4$–Kevlar	0.2	0.1	20	RT	57
Li$_6$PS$_5$Cl–NBR–LiTFSI	0.05	0.1	>30	70°C	38
Li$_6$PS$_5$Cl–XNBR	0.1	0.05	500	RT	52
Li$_7$P$_3$S$_{11}$–SEBS	0.11	1.1	2000	RT	51
Li$_6$PS$_5$Cl–PVDF	0.2	0.1	67	RT	28
Li$_{5.4}$PS$_{4.4}$Cl$_{1.6}$–PTFE@Al$_2$O$_3$	0.1	0.1	400	RT	65

on a nylon net template to obtain a 31 μm composite film with an ionic conductivity of 0.18 mS cm^{-1}. Based on the above film, the ASSB with LiCoO$_2$ as cathode and Li as anode displayed specific energy and energy density of 127.9 Wh kg^{-1} and 140.7 Wh L^{-1}, respectively[55]. Similarly, a 45 μm composite film with an ionic conductivity of 0.51 mS cm^{-1} was prepared via coating Li$_6$PS$_5$Cl–NBR slurry on a microporous PE separator. With the help of thin film, the Li ‖ LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ full cell delivered a high specific energy of 314 Wh kg^{-1} [42].

To further improve the energy density of the ASSBs, the concept of combining the conversion-type cathode with composite electrolyte film was proposed. For instance, an all-solid-state thin lithium–sulfur battery was assembled according to the following procedures. Firstly, the Kevlar fiber piece was placed on a stainless steel (SS) mesh-supported Li$_2$S–LiI cathode piece. Then the Li$_3$PS$_4$ suspension was dripped onto the assembly, and then dried overnight, followed by cold pressed together. Finally, a lithium foil was attached. The SS mesh served as a current collector, allowing high active material loading. The obtained ASSB with a high Li$_2$S loading of 7.64 mg cm^{-2} exhibited a high specific energy of 370.6 Wh kg^{-1}. It is worth noting that the energy density of the cell is not high if the weight of the SS

collector is considered, but this limitation could be effectively improved by using other conductive materials with lower density than the current collector[57].

The use of bulky Swagelok molds will greatly sacrifice the energy density of the whole cell. As a result, some research groups try to assemble coin cells based on the composite electrolyte films. Li et al. obtained a flexible Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$–PEO composite electrolyte film by hot pressing the mixture of Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ electrolyte powder (88 wt%), PEO–LiTFSI powder (12 wt%) and plasticizer. Based on the above electrolyte film, the coin-type ASSB with lithium metal as anode and the S-PAN as cathode were assembled. The full cell exhibited a high specific capacity of 588 mAh g^{-1} after 50 cycles at 0.1 C, and a high specific energy of 116 Wh kg^{-1} and energy density of 660 Wh L^{-1} were achieved[36].

In order to promote the commercialization of sulfide-based SSBs, the ultimate goal is to apply sulfide-based composite electrolyte films to the pouch cells. Zhao et al. adopted a tape casting method to successfully prepare a 20 μm Li$_{9.88}$GeP$_{1.96}$Sb$_{0.04}$S$_{11.88}$Cl$_{0.12}$–poly(methyl methacrylate)/n-butylacrylate composite electrolyte membrane with a high ionic conductivity of 1.9 mS cm^{-1}. Based on the above film, the Li|Li$_{9.88}$GeP$_{1.96}$Sb$_{0.04}$S$_{11.88}$Cl$_{0.12}$

film|LiCoO$_2$ solid-state pouch cell was fabricated, which delivered a capacity of 108 mAh g^{-1} after 250 cycles at 0.1 C at 60 °C[53]. Nam et al. prepared the graphite–NBR anode sheet and NCM622–carbon–NBR–Li$_6$PS$_5$Cl composite cathode sheet by tape casting, then the slurry of Li$_6$PS$_5$Cl–NBR was cast on the anode sheet to obtain a composite electrolyte film. Next, the composite cathode sheet was attached, and finally, these three layers were cold-pressed together to form a pouch cell. The battery delivered a high specific energy of 184 Wh kg^{-1} and an energy density of 432 Wh L^{-1} [71]. Lee et al. prepared a Li$_6$PS$_5$Cl-based composite electrolyte film with a thickness of 30 μm by wet process. The ASSB with high-nickel NCM as the cathode and an Ag–C nano-composite as the anode was assembled. In addition, the warm isostatic pressing technique was also applied to improve the interface contact between the electrode and the composite electrolyte film. The prototype pouch battery (0.6 Ah) exhibited a high energy density (>900 Wh L^{-1}), a high coulombic efficiency of more than 99.8%, and a long cycle life (1000 cycles)[54].

Recently, a new method similar to the liquid electrolyte injection in lithium-ion batteries emerged, where a sulfide electrolyte solution is injected into a pre-stacked cathode, anode, and a polyimide separator and then cured to obtain an ASSB. Due to the low room-temperature ionic conductivity of the sulfide electrolyte after dissolved into the ethanol, ASSB exhibited a low capacity of 109 mAh g^{-1} at 70 °C in the first cycle[72]. Therefore, this method still faces significant obstacles before it can be commercially applied.

Outlook

Firstly, we analyze the ionic transport mechanism in the sulfide/polymer composite electrolyte to provide a theoretical foundation for the design of composite electrolyte films with high room-temperature ionic conductivity. Subsequently, we systematically summarize the preparation methods of sulfide-based composite electrolyte films with polymer as a binder, including dry and wet methods. The wet methods encompass wet mixing—cold (or hot) pressing, tape casting, and infiltration, while the dry methods involve dry mixing—cold (or hot) pressing, spraying coating, and binder fibrillation. The advantages and disadvantages of these methods, as well as the obtained ionic conductivity and thickness of the films prepared via these methods, are discussed in detail. Finally, the application of these composite electrolyte films in ASSBs is briefly introduced.

The room-temperature ionic conductivity of the sulfide electrolyte is two orders of magnitude higher than that of the polymer-based electrolyte membrane. Although the ionic conductivity of the sulfide-based composite electrolyte could be further enhanced by using an ionically conductive polymer binder, according to the ionic transport mechanism of the composite electrolyte, the improvement is limited. Moreover, these polymer-based electrolytes require a large amount of expensive lithium salts or ionic liquids. Considering the trade-off between ionic conductivity improvement and cost, the development of ion-conductive binders is currently not cost-effective. Future development of sulfide/polymer composite electrolyte films should primarily focus on the development of new binders with favorable viscoelastic and low costs.

The composite electrolyte films obtained by the wet (or dry) mixing-cold pressing method are relatively brittle, and the thickness is difficult to reduce, making them less suitable for future commercial applications. Tape casting may be the most promising method for preparing large-scale composite electrolyte films. However, due to the decomposition of thiophosphate electrolytes in polar solvents, the ionic conductivity of sulfides decreases rapidly. Additionally, the binders used in commercial lithium-ion batteries, such as PVDF, are typically dissolved in polar solvents. Therefore, finding suitable binder-solvent pairs is crucial for achieving a composite electrolyte film with high room-temperature ionic conductivity. Future efforts could be made to develop new binders that offer improved viscoelasticity and solubility in non-polar solvents. Additionally, developing new sulfide electrolytes with good stability against polar solvents is also essential. Some strategies, such as doping some soft acid elements into the sulfide electrolyte or substituting soft alkali sulfur with hard alkali oxygen, could be adopted.

Dry-film technology is a new technique that has been applied to commercial electrodes. However, achieving a thinner composite electrolyte film by using the binder fibrillation method is challenging and requires substantial equipment improvements. Furthermore, the binder used in the dry process is mainly PTFE, which is unstable against lithium metal anode. Consequently, it is imperative to improve the existing dry-film technology equipment for better mixing and binder fibrillation. Moreover, developing new binders which is compatible with the lithium-metal anode. This is of utmost significance in the preparation of ultra-thin composite electrolyte films with good stability against lithium anode.

Improving the lifespan and critical current density of lithium symmetric batteries plays a vital role in the practical application of sulfide-based electrolyte films. Several strategies could be considered to achieve this goal, such as developing new binders compatible with the lithium anode, hot pressing of composite film to enhance density, lowering the electronic conductivity of sulfides, and constructing artificial SEI to alleviate the side-reaction between the composite film with lithium-metal anode.

The current researches about the composite electrolyte film mainly focus on reducing the thickness and enhancing ionic conductivity. As we know, the mechanical properties of the sulfide electrolyte will be improved by adding polymer binders. Therefore, in the future, it is essential to systematically evaluate the mechanical properties, flexibility, and thermal stability of the composite electrolyte films and the mechano-(electro)chemical effect at the composite electrodes/composite electrolyte interface. Furthermore, incorporating theoretical calculations, such as machine learning, phase field simulation, and finite element simulation, will help reveal the ionic transport mechanisms of the composite electrolyte membranes, which is of great significance for the future development of high-performance composite electrolyte films.

References

1. Wang, X. T. et al. Prospects for managing end-of-life lithium-ion batteries: present and future. *Interdiscip. Mater.* **1**, 417–433 (2022).
2. Huang, Y. The discovery of cathode materials for lithium-ion batteries from the view of interdisciplinarity. *Interdiscip. Mater.* **1**, 323–329 (2022).
3. Yan, J. et al. Recent progress on the modification of high nickel content NCM: coating, doping, and single crystallization. *Interdiscip. Mater.* **1**, 330–353 (2022).
4. Goodenough, J. B. & Kim, Y. Challenges for rechargeable Li batteries. *Chem. Mater.* **22**, 587–603 (2009).
5. Choi, N. S. et al. Challenges facing lithium batteries and electrical double-layer capacitors. *Angew. Chem. Int. Ed.* **51**, 9994–10024 (2012).
6. Yang, M. L. et al. High energy density sulfur-rich MoS$_6$-based nanocomposite for room temperature all-solid-state lithium metal batteries. *Adv. Energy Mater.* **13**, 2300962 (2023).
7. Randau, S. et al. Benchmarking the performance of all-solid-state lithium batteries. *Nat. Energy* **5**, 259–270 (2020).
8. Janek, J. & Zeier, W. G. Challenges in speeding up solid-state battery development. *Nat. Energy* **8**, 230–240 (2023).
9. Wang, S. et al. Interfacial challenges for all-solid-state batteries based on sulfide solid electrolytes. *J. Materiomics* **7**, 209–218 (2021).
10. Chen, S. J. et al. Sulfide solid electrolytes for all-solid-state lithium batteries: structure, conductivity, stability and application. *Energy Storage Mater.* **14**, 58–74 (2018).
11. Wu, J. et al. All-solid-state lithium batteries with sulfde electrolytes and oxide cathodes. *Electrochem. Energy Rev.* **4**, 101–135 (2021).
12. Jin, Y. M. et al. Fluorinated Li$_{10}$GeP$_2$S$_{12}$ enables stable all-solid-state lithium batteries. *Adv. Mater.* **35**, 2211047 (2023).

13. Zhao, Q., Stalin, S., Zhao, C.-Z. & Archer, L. A. Designing solid-state electrolytes for safe, energy-dense batteries. *Nat. Rev. Mater.* **5**, 229–252 (2020).

14. Xi, G. et al. Polymer-based solid electrolytes: material selection, design, and application. *Adv. Funct. Mater.* **31**, 2007598 (2020).

15. Wang, G. et al. Scalable, thin asymmetric composite solid electrolyte for high-performance all-solid-state lithium metal batteries. *Interdiscip. Mater.* **1**, 434–444 (2022).

16. Gao, Z. et al. Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries. *Adv. Mater.* **30**, 1705702 (2018).

17. Ren, Y. et al. Oxide-based solid-state batteries: a perspective on composite cathode architecture. *Adv. Energy Mater.* **13**, 2201939 (2022).

18. Li, X. et al. Progress and perspectives on halide lithium conductors for all-solid-state lithium batteries. *Energy Environ. Sci.* **13**, 1429–1461 (2020).

19. Zhou, L. et al. A new halospinel superionic conductor for high-voltage all solid state lithium batteries. *Energy Environ. Sci.* **13**, 2056–2063 (2020).

20. Wang, S. et al. High-conductivity argyrodite Li_6PS_5Cl solid electrolytes prepared via optimized sintering processes for all-solid-state lithium-sulfur batteries. *ACS Appl. Mater. Interfaces* **10**, 42279–42285 (2018).

21. Wang, S. et al. Effect of processing on structure and ionic conductivity of chlorine-rich lithium argyrodites. *Adv. Energy Sustain. Res*. 2200197 (2023).

22. Wang, S. et al. Facile synthesis of lithium argyrodite $Li_{5.5}PS_{4.5}Br_{1.5}$ with high ionic conductivity for all-solid-state batteries. *Front. Chem. Eng.* **4**, 883502 (2022).

23. Li, S. et al. High-entropy lithium argyrodite solid electrolytes enabling stable all-solid-state batteries. *Angew. Chem. Int. Ed*. **62**, e202314155 (2023).

24. Wang, S. et al. Lithium argyrodite as solid electrolyte and cathode precursor for solid-state batteries with long cycle life. *Adv. Energy Mater.* **11**, 2101370 (2021).

25. Wang, S. et al. Influence of crystallinity of lithium thiophosphate solid electrolytes on the performance of solid-state batteries. *Adv. Energy Mater.* **11**, 2100654 (2021).

26. Wu, J., Liu, S., Han, F., Yao, X. & Wang, C. Lithium/sulfide all-solid-state batteries using sulfide electrolytes. *Adv. Mater.* **33**, 2000751 (2021).

27. Wu, J. et al. Reducing the thickness of solid-state electrolyte membranes for high-energy lithium batteries. *Energy Environ. Sci.* **14**, 12–36 (2021).

28. Wang, S. et al. High-conductivity free-standing Li_6PS_5Cl/poly(vinylidene difluoride) composite solid electrolyte membranes for lithium-ion batteries. *J. Materiomics* **6**, 70–76 (2020). **This paper describes the sulfide-based composite electrolyte film produced by wet mixing–cold pressing method**.

29. Wang, C. et al. All-solid-state lithium batteries enabled by sulfide electrolytes: from fundamental research to practical engineering design. *Energy Environ. Sci.* **14**, 2577–2619 (2021).

30. Liu, Y. et al. Composition modulation and structure design of inorganic-in-polymer composite solid electrolytes for advanced lithium batteries. *Small* **16**, e1902813 (2020).

31. Liang, Y. H. et al. Challenges, interface engineering, and processing strategies toward practical sulfide-based all-solid-state lithium batteries. *InfoMat* **4**, e12292 (2022).

32. Fan, L.-Z., He, H. & Nan, C.-W. Tailoring inorganic–polymer composites for the mass production of solid-state batteries. *Nat. Rev. Mater.* **6**, 1003–1019 (2021).

33. Liu, H. et al. Priority and prospect of sulfide-based solid-electrolyte membrane. *Adv. Mater.* **35**, e2206013 (2022).

34. Fu, Z. H., Chen, X. & Zhang, Q. Review on the lithium transport mechanism in solid-state battery materials. *WIREs Comput. Mol. Sci.* **13**, e1621 (2023).

35. Luo, S. et al. A high energy and power all-solid-state lithium battery enabled by modified sulfide electrolyte film. *J. Power Sources* **485**, 229325 (2021).

36. Li, M. et al. Solid-state lithium–sulfur battery enabled by thio-LiSICON/polymer composite electrolyte and sulfurized polyacrylonitrile cathode. *Adv. Funct. Mater.* **30**, 1910123 (2020).

37. Oh, D. Y. et al. Slurry-fabricable Li^+-conductive polymeric binders for practical all-solid-state lithium-ion batteries enabled by solvate ionic liquids. *Adv. Energy Mater.* **9**, 1802927 (2019).

38. Kim, K. T. et al. Tailoring slurries using cosolvents and Li salt targeting practical all-solid-state batteries employing sulfide solid electrolytes. *Adv. Energy Mater.* **11**, 2003766 (2021).

39. Yi, J. G. et al. Enabling high-performance all-solid-state lithium batteries with high ionic conductive sulfide-based composite solid electrolyte and ex-situ artificial SEI film. *J. Energy Chem.* **58**, 17–24 (2021).

40. Liu, G. et al. Ultra-thin free-standing sulfide solid electrolyte film for cell-level high energy density all-solid-state lithium batteries. *Energy Storage Mater.* **38**, 249–254 (2021).

41. Choi, H. et al. Unexpected pressure effects on sulfide-based polymer-in-ceramic solid electrolytes for all-solid-state batteries. *Nano Energy* **102**, 107679 (2022).

42. Kim, D. et al. Thin, highly ionic conductive, and mechanically robust frame-based solid electrolyte membrane for all-solid-state Li batteries. *Adv. Energy Mater.* **14**, 2302596 (2023).

43. Lee, J., Lee, T., Char, K., Kim, K. J. & Choi, J. W. Issues and advances in scaling up sulfide-based all-solid-state batteries. *Acc. Chem. Res.* **54**, 3390–3402 (2021).

44. Liu, T. et al. Sulfide solid electrolyte thin film with high ionic conductive from slurry-casting strategy for all-solid-state lithium batteries. *J. Electroanal. Chem.* **928**, 117032 (2023).

45. Cao, D. et al. Amphipathic binder integrating ultrathin and highly ion-conductive sulfide membrane for cell-level high-energy-density all-solid-state batteries. *Adv. Mater.* **33**, 2105505 (2021).

46. Oh, D. Y. et al. Excellent compatibility of solvate ionic liquids with sulfide solid electrolytes: toward favorable ionic contacts in bulk-type all-solid-state lithium-ion batteries. *Adv. Energy Mater.* **5**, 1500865 (2015).

47. Nam, Y. J. et al. Bendable and thin sulfide solid electrolyte film: a new electrolyte opportunity for free-standing and stackable high-energy all-solid-state lithium-ion batteries. *Nano Lett.* **15**, 3317–3323 (2015).

48. Emley, B. et al. On the quality of tape-cast thin films of sulfide electrolytes for solid-state batteries. *Mater. Today Phys.* **18**, 100397 (2021).

49. Inada, T. Fabrications and properties of composite solid-state electrolytes. *Solid State Ion.* **158**, 275–280 (2003).

50. Ito, S. et al. A rocking chair type all-solid-state lithium ion battery adopting $Li_2O–ZrO_2$ coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and a sulfide-based electrolyte. *J. Power Sources* **248**, 943–950 (2014).

51. Tan, D. H. S. et al. Enabling thin and flexible solid-state composite electrolytes by the scalable solution process. *ACS Appl. Energy Mater.* **2**, 6542–6550 (2019).

52. Kim, S., Chart, Y. A., Narayanan, S. & Pasta, M. Thin solid electrolyte separators for solid-state lithium–sulfur batteries. *Nano Lett.* **22**, 10176–10183 (2022).

53. Zhao, X. et al. Toluene tolerated $Li_{9.88}GeP_{1.96}Sb_{0.04}S_{11.88}Cl_{0.12}$ solid electrolyte toward ultrathin membranes for all-solid-state lithium batteries. *Nano Lett.* **23**, 227–234 (2023). **This paper describes the thinnest sulfide-based composite electrolyte film produced by tape casting**.

54. Lee, Y.-G. et al. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. *Nat. Energy* **5**, 299–308 (2020).

55. Kang, S. H. et al. Mechanically robust ultrathin solid electrolyte membranes using a porous net template for all-solid-state batteries. *ACS Appl. Mater. Interfaces* **15**, 28064–28072 (2023).

56. Wang, Y. et al. Facile design of sulfide-based all solid-state lithium metal battery: In situ polymerization within self-supported porous argyrodite skeleton. *Adv. Funct. Mater.* **31**, 2101523 (2021).

57. Xu, R. C. et al. Cathode-supported all-solid-state lithium-sulfur batteries with high cell-level energy density. *ACS Energy Lett.* **4**, 1073–1079 (2019).

58. Liu, S. et al. Super long-cycling all-solid-state battery with thin Li_6PS_5Cl-based electrolyte. *Adv. Energy Mater.* **12**, 2200660 (2022). **This paper describes the sulfide-based composite electrolyte film produced by electrospinning-infiltration-hot pressing method**.

59. Zhu, G. L. et al. A self-limited free-standing sulfide electrolyte thin film for all-solid-state lithium metal batteries. *Adv. Funct. Mater.* **31**, 2101985 (2021).

60. Li, Y. et al. Progress in solvent-free dry-film technology for batteries and supercapacitors. *Mater. Today* **55**, 92–109 (2022).

61. Yersak, T., Salvador, J. R., Schmidt, R. D. & Cai, M. Hot pressed, fiber-reinforced $(Li_2S)_{70}(P_2S_5)_{30}$ solid-state electrolyte separators for Li metal batteries. *ACS Appl. Energy Mater.* **2**, 3523–3531 (2019).

62. Whiteley, J. M., Taynton, P., Zhang, W. & Lee, S. H. Ultra-thin solid-state Li-ion electrolyte membrane facilitated by a self-healing polymer matrix. *Adv. Mater.* **27**, 6922–6927 (2015). **This paper describes the sulfide-based composite electrolyte film produced by ball-milling followed by cold pressing**.

63. Chometon, R. et al. Targeting the right metrics for an efficient solvent-free formulation of $PEO:LiTFSI:Li_6PS_5Cl$ hybrid solid electrolyte. *ACS Appl. Mater. Interfaces* **15**, 58794–58805 (2023).

64. Jiang, Z. et al. A facile path from fast synthesis of Li-argyrodite conductor to dry forming ultrathin electrolyte membrane for high-energy-density all-solid-state lithium batteries. *J. Energy Chem.* **74**, 309–316 (2022).

65. Zhang, Z. H., Wu, L. P., Zhou, D., Weng, W. & Yao, X. Y. Flexible sulfide electrolyte thin membrane with ultrahigh ionic conductivity for all-solid-state lithium batteries. *Nano Lett.* **21**, 5233–5239 (2021). **This paper describes the sulfide-based composite electrolyte film with highest ionic conductivity produced by binder fibrillation**.

66. Tesla. *Tesla Completes Acquisition of Maxwell Technologies* https://ir.tesla.com/press-release/tesla-completes-acquisition-maxwell-technologies (2019).

67. Tesla. *In 2020 Annual Meeting of Stockholders and Battery Day* https://ir.tesla.com/press-release/tesla-announces-updates-2020-annual-meeting-stockholders-and (2020).

68. Wenzel, S., Sedlmaier, S. J., Dietrich, C., Zeier, W. G. & Janek, J. Interfacial reactivity and interphase growth of argyrodite solid electrolytes at lithium metal electrodes. *Solid State Ion.* **318**, 102–112 (2018).

69. Kasemchainan, J. et al. Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells. *Nat. Mater.* **18**, 1105–1111 (2019).

70. Cao, D. X., Sun, X., Wang, Y. & Zhu, H. L. Bipolar stackings high voltage and high cell level energy density sulfide based all-solid-state batteries. *Energy Storage Mater.* **48**, 458–465 (2022).

71. Nam, Y. J., Oh, D. Y., Jung, S. H. & Jung, Y. S. Toward practical all-solid-state lithium-ion batteries with high energy density and safety: comparative study for electrodes fabricated by dry- and slurry-mixing processes. *J. Power Sources* **375**, 93–101 (2018).

72. Kim, D. H. et al. Thin and flexible solid electrolyte membranes with ultrahigh thermal stability derived from solution-processable Li argyrodites for all-solid-state Li-ion batteries. *ACS Energy Lett.* **5**, 718–727 (2020).

73. Hatz, A. K. et al. Chemical stability and ionic conductivity of LGPS-Type solid electrolyte Tetra-Li_7SiPS_8 after solvent treatment. *ACS Appl. Energy Mater.* **4**, 9932–9943 (2021).

74. Zhang, Y. B. et al. Free-standing sulfide/polymer composite solid electrolyte membranes with high conductance for all-solid-state lithium batteries. *Energy Storage Mater.* **25**, 145–153 (2020).

75. Choi, S. J. et al. Synthesis and electrochemical characterization of a glass–ceramic $Li_7P_2S_8I$ solid electrolyte for all-solid-state Li-ion batteries. *J. Electrochem. Soc.* **165**, A957–A962 (2018).

76. Kim, H. J. et al. Controlled prelithiation of silicon monoxide for high performance lithium-ion rechargeable full cells. *Nano Lett.* **16**, 282–288 (2015).

77. Villaluenga, I. et al. Compliant glass–polymer hybrid single ion-conducting electrolytes for lithium batteries. *Proc. Natl Acad. Sci. USA* **113**, 52–57 (2015).

78. Hayashi, A., Harayama, T., Mizuno, F. & Tatsumisago, M. Mechanochemical synthesis of hybrid electrolytes from the $Li_2S–P_2S_5$ glasses and polyethers. *J. Power Sources* **163**, 289–293 (2006).

79. Hayashi, A., Harayama, T., Mizuno, F. & Tatsumisago, M. Characterization of hybrid electrolytes prepared from the $Li_2S–P_2S_5$ glasses and alkanediols. *Solid State Ion.* **192**, 130–133 (2011).

80. Jiang, T., He, P., Liang, Y. & Fan, L.-Z. All-dry synthesis of self-supporting thin $Li_{10}GeP_2S_{12}$ membrane and interface engineering for solid state lithium metal batteries. *Chem. Eng. J.* **421**, 129965 (2021).

81. Wang, C. H. et al. Solvent-free approach for interweaving freestanding and ultrathin inorganic solid electrolyte membranes. *ACS Energy Lett.* **7**, 410–416 (2022).

Acknowledgements

Author contributions

S.W. proposed the idea. S.L., Z.Y., S.-B.W. and M.Y. equally contributed to this work, drew the figures, and wrote the draft. H.H. contributed to the discussion of content. C.-W.N., S.W. and X.Z. supervised the projects, reviewed, and edited the manuscript.

Competing interests

Hongcai He is employed by Qingtao Energy Development Inc. The remaining authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s43246-024-00482-8.

Correspondence and requests for materials should be addressed to Xin Zhang or Shuo Wang.

Peer review information *Communications Materials* thanks the anonymous reviewers for their contribution to the peer review of this work. Primary Handling Editors: Jet-Sing Lee. A peer review file is available.

Reprints and permissions information is available at http://www.nature.com/reprints

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.