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Recent Progress in Quasi/All-Solid-State Electrolytes for Lithium–Sulfur Batteries

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Lithium–sulfur batteries have received increasing research interest due to their superior theoretical capacity, cost-effectiveness, and eco-friendliness. However, the commercial realization of lithium–sulfur batteries faces critical obstacles, such as the significant volume change of sulfur cathodes over the de/lithiation processes, uncontrollable shuttle effects of polysulfides, and the lithium dendrite issue. On this basis, the lithium–sulfur battery based on solid-state electrolytes was developed to alleviate the previously mentioned problems. This article aims to provide an overview of the recent progress of solid-state lithium–sulfur batteries related to various kinds of solid-state electrolytes, which mainly include three aspects: the fundamentals and current status of lithium–sulfur solid-state batteries and several adopted solid-state electrolytes involving polymer electrolyte, inorganic solid electrolyte, and hybrid electrolyte. Furthermore, the future perspective for lithium–sulfur solid-state batteries is presented. Finally, this article proposed an initiation for new and practical research activities and paved the way for the design of usable lithium–sulfur solid-state batteries.

Keywords: solid-state lithium-sulfur batteries, solid-state electrolyte, shuttle effect, lithium dendrites, interface

1 INTRODUCTION

With the growing demands for global energy, high-energy-density and long-cycling batteries are broadly developed and play a growing role in the global energy system (Wu et al., 2021). A rechargeable Li battery based on the Li chemistry is considered a promising candidate for battery systems and related functions. Typically, lithium–sulfur batteries (LSBs) are selected as ideal choices for energy storage systems due to their high theoretical-specific capacity (1,672 mA h/g) and theoretical-specific energy density (2,600 W h/kg), which is five times higher than traditional lithium-ion batteries (LIBs) (Dai et al., 2021; Zhou et al., 2021; Zhu et al., 2022). Meanwhile, compared to the lithium-ion battery, elemental sulfur, the main active material in LSBs, has the advantages of being abundantly stored, low-cost, simple to prepare, and environmentally friendly (Li et al., 2019; Gong and Wang, 2020; Liu X.-Z. et al., 2021; Pang et al., 2021). Therefore, significant research effort into LSB has potential advantages for future energy storage (Wang H. et al., 2017; Fan et al., 2021; Zheng et al., 2021; Phuc et al., 2022).

However, several issues still inhibit the development of Li-S batteries, such as the shuttle effect that dissolution and unwanted crossover between the anode and cathode of long-chain polysulfide, undesirably causing a capacity loss and a reduced roundtrip efficiency (Bonnick et al., 2019). The

continued growth of lithium dendrites can easily lead to internal short-circuit and even thermal runaway failure (Wei et al., 2019; Zhang R. et al., 2022). To alleviate the aforementioned issues, numerous strategies have been applied, such as using host matrices (Wang M. et al., 2017) and electrolyte additives (Ding et al., 2020). Researchers (Gong et al., 2022) demonstrated that by modulating the multiple interactions between the functional groups through copolymerization the binder was able to coordinate the LiPSs with higher binding energy for shuttle effect alleviation and cycling performance improvement. Significant advances were achieved by designing sulfur cathodes with nanostructure (Li et al., 2021) and developing polysulfide-affinitive metal catalysts (De Luna et al., 2021; Liu X.-M. et al., 2021). Lei et al. (2018) reviewed the recent research progress of solid-state Li-S batteries, mainly including gel, solid-state polymer, ceramic, and composite electrolytes, and strategies for overcoming the deficiencies of solid-state electrolytes such as low room-temperature ionic conductivity and high interfacial resistance.

Recently, solid-state electrolytes (SSEs) have received much attention from academics in the energy field due to many advantages of being applied to LSBs. SSE could function as a physical barrier to block or hinder polysulfide migration (Yang S. et al., 2020). The mechanically robust solid electrolyte could also withstand the puncture of Li dendrites, thereby lowering the risk of internal short-circuiting and thermal runaway of batteries caused by dendrites (Cheng et al., 2019; Ding et al., 2022). Moreover, diverse SSEs and combinations can be exploited with lithium-sulfur chemistries, conveying various lithium-sulfur solid-state batteries (Miura et al., 2019; Bi et al., 2022). However, its practical applications are restricted by the sluggish electrochemical activities due to the high interfacial resistance and limited utilization of actives (Li et al., 2019; Chen Y. et al., 2021). The problem can be improved by modifying the solid electrolyte with various additives and preparing different types of SSEs. Generally, lithium-sulfur SSEs can be divided into polymer electrolytes, inorganic solid electrolytes, and hybrid electrolytes. A polymer electrolyte involves solid polymer electrolytes and gel electrolytes. Solid Polymer electrolytes attract more research attention due to their excellent processability, but this kind of electrolyte faces three critical issues: 1) insufficient ionic conductivity at an ambient temperature; 2) soft nature that can barely survive in the penetration of dendrites; and 3) dissolution of polysulfides in electrolytes. Gel electrolytes feature the advantages of the liquid electrolyte, such as high ionic conductivity of above 1.0 mS/cm and good interfacial compatibility to electrodes. Shuttle effects of polymer sulfides and dendrites are two significant issues challenging their applications. In contrast to gel electrolytes, inorganic solid electrolytes possess better mechanical strength and electrochemical/chemical stability. However, the apparent resistance of this electrolyte is exceptionally high due to the resistance of involved grain boundaries. Poor processability and shapeability of inorganic electrolytes limit the tangible applications of this inorganic electrolyte. For example, sulfide-based electrolytes possess a high bulky ionic conductivity of 10 mS/cm. Fabricating this electrolyte into a battery-usable

membrane requires the addition of organic polymers. This approach inevitably sacrificed the ionic conductivity. In comparison, hybrid electrolytes combine the advantages of various components of electrolyte and alleviate the aforementioned issues. This article comprehensively reviewed the lithium-sulfur SSE current development status and proposed the future development direction. It aimed to provide guidance to the lithium-sulfur SSE design.

This review is organized as follows: the details of lithium-sulfur solid-state batteries (SSBs) are presented in **Section 2**. Lithium-Sulfur SSB working principle, charging/discharging curves, ion conduction mechanism, and current challenges are given in **Sections 2.1–2.4**. Designing electrolyte material strategies are reviewed in **Section 3**. Polymer electrolyte application for the lithium-sulfur SSB is provided in **Section 4**. Inorganic solid electrolytes and hybrid electrolytes are discussed separately in **Section 5** and **Section 6**, respectively. Finally, the conclusions and future perspectives are provided in Section 7.

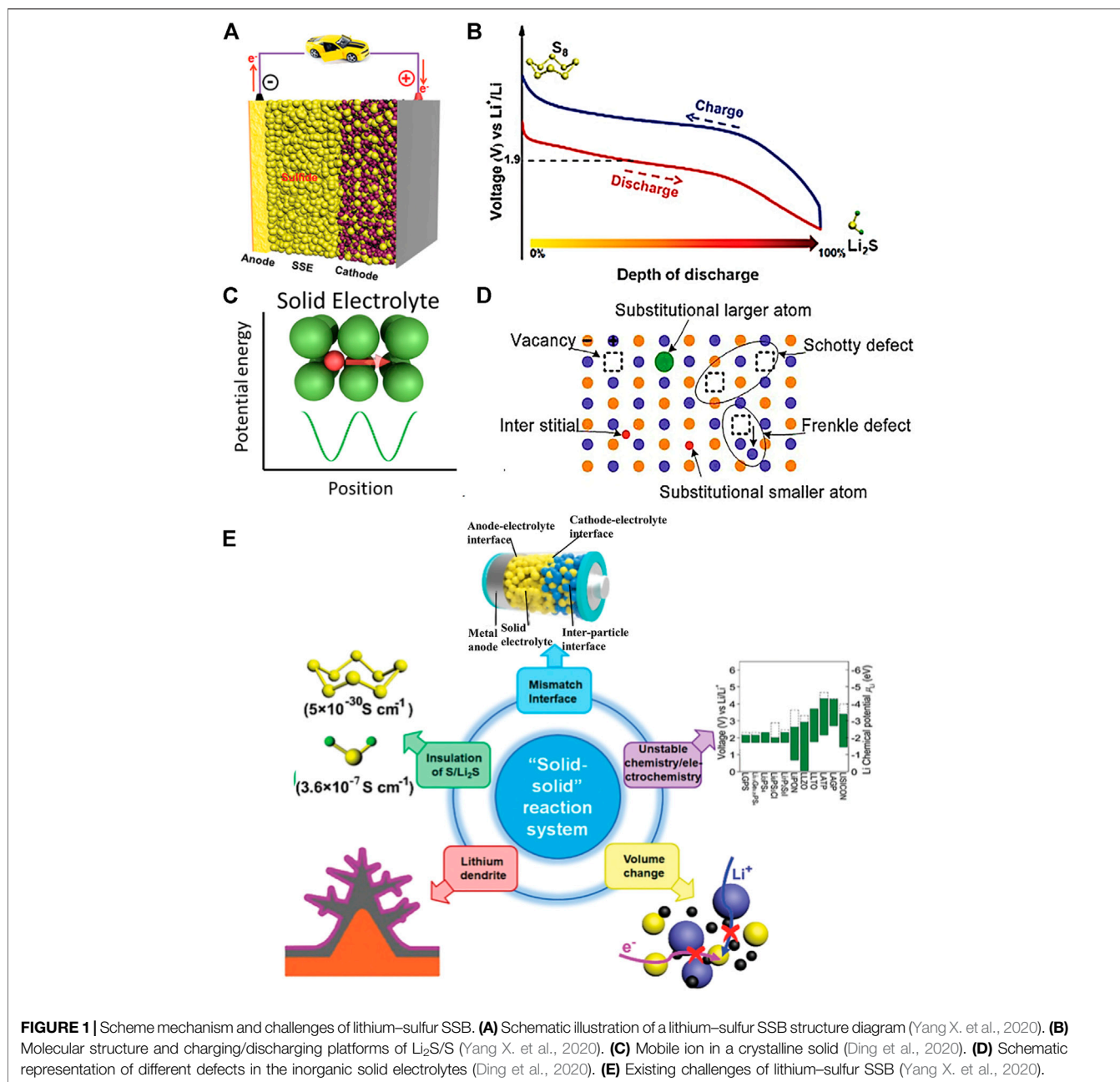
2 SOLID-STATE LITHIUM-SULFUR BATTERY

2.1 Working Principle

A lithium-sulfur SSB usually included the Li metal anode, SSE, and sulfur-based cathode. **Figure 1A** presents the typical lithium-sulfur configurations (Yang X. et al., 2020). In terms of the anode, the metallic Li is a suitable material choice because of its outstanding theoretical capacity ($3,860 \text{ mA h g}^{-1}$) and lowest negative electrochemical potential (-3.040 V) (Cheng et al., 2017). Yet, lithium-sulfur SSB faces Li dendrite growth issues during the battery charging/discharging cycle due to the existing Li metal anode/unstable SSE interface. To alleviate the Li dendrite issues, the Li-M alloys ($M = \text{In, Sn, or Ge}$) and metal are usually conducted as anodes to solve the problems (Hikima et al., 2020; Zhang et al., 2021).

2.2 Charge/Discharge Curves

When LiPSs are not dissolved into the solvent, lithium-sulfur SSBs follow a solid-solid reaction process. Wherein, there is direct interconversion between S and LiS, with no intermediate LiPSs. This reaction is common in sulfide-based SSE systems, as shown in **Figure 1B**. The discharge process is known as a one-step discharge process (Yang X. et al., 2020), which is likely attributed to the sluggish electrochemical kinetics of solid sulfur electrodes. High output energy could be achieved in this system. The theoretical discharge capacities of sulfur and lithium metal are 1,675 and 3,860 mAh g^{-1} , respectively (Guo and Zheng, 2020). However, liquid carbonate-based LSB with bonded S or an intact coating on the sulfur cathode can effectively suppress LiPS dissolution and be observed to exhibit a single discharge plateau at around 2.0V during the reaction (Luo et al., 2020). Sometimes, in polymer electrolytes, where a small amount of liquid or polymer electrolyte is present in a mixed SSE, the solid-liquid and solid-solid reactions occur simultaneously, so that the mixed discharge profile exhibits multiple discharge



plateaus. The reaction process is known as a quasi-solid phase reaction process (Li et al., 2018).

2.3 Ion Conduction Mechanism

As shown in **Figure 1C**, ions are transported through a periodic barrier (Goodenough, 2003), the energy barrier in a crystalline solid in a lithium-sulfur SSB. In amorphous polymers, the transport of lithium ions can generally be described by a hopping transport model. As shown in **Figure 1D**, lithium ions travel along the polymer chain, jumping from one coordination site to another or migrating from one coordination site to another (Sing et al., 2014). In some cases, the crystalline polymer phase’s ionic conductivity in the SSE may

be higher than that in the non-crystalline phase. This is because the polymer chains in the crystalline phase can form a cylindrical tunnel in which the lithium ions can be transported rapidly without the aid of segmental movement of the polymer chains. However, most studies have not shown a clear correlation between structure and properties of solid polymer electrolytes, so the ion transport mechanism is still not clear (Ding et al., 2020). The ion transport mechanism of inorganic solid-state electrolytes is achieved by employing various defects in the crystal structure (Zhou et al., 2020). As shown in **Figure 1D**, different defects determine the type and concentration of carriers, such as point defects (i.e., Schottky defects and Frenkel defects), thus directly impacting the ion conductivity of inorganic SSEs

(Varzi et al., 2016). In addition, the spatial distribution, composition, and structure of the fixed framework within the inorganic SSE and its interaction with Li-ions can affect the energy barriers and thus should be overcome during Li-ion transport. (Motavalli, 2015).

2.4 Current Challenges

Despite the significant advantages and advances in developing lithium–sulfur SSBs, there are still fundamental challenges to the current state of research. As shown in **Figure 1E**, these challenges are currently the ones that need to be overcome to improve the electrochemical performance and ultimately bring lithium–sulfur solid-state batteries into practical applications. In solid-phase reaction systems, the main issues are interfacial problems (Zhong et al., 2021) and chemical/electrochemical instabilities (Han et al., 2015). In contrast, shuttle effects (Liu et al., 2010) and gas emissions (Yang et al., 2016) (in systems containing liquids) remain the main drawbacks of solid–liquid dual-phase reaction systems. Problems such as insulating properties of S/Li₂S, Li dendrite growth, and volume changes during cycling are common to both solid and liquid LSBs (Wang D. et al., 2017). In future research, the optimal design of lithium–sulfur LSBs should be carried out to address the aforementioned issues and to make an essential contribution to promoting the commercialization of lithium–sulfur SSBs.

3 GENERAL STRATEGIES FOR DESIGNING ELECTROLYTE MATERIALS

Lithium–sulfur SSEs are important to achieve high performance of lithium–sulfur SSBs. Generally, lithium–sulfur SSEs can be classified into polymer electrolytes, inorganic solid electrolytes, and hybrid electrolytes. Therein, polymer electrolytes include solid polymer electrolytes and gel electrolytes. The content will be comprehensively reviewed in the next section. In some cases, it greatly declined the lithium–sulfur SSB performance due to the shuttling effect of polysulfides. Therefore, different types of cathode-bonded S in polymers have been developed to alleviate the problem of shuttle effects. For instance, polyacrylonitrile (PAN)-s (Peng et al., 2017), 1,3-diisopropenylbenzene (DIB)-s, and trithiocyanuric acid (TTCA)-s (Kim et al., 2015) by polymerizing the sulfur chains into the scaffold of polymers can suppress the LiPS dissolution and shuttling effects.

Quasi/solid polymer electrolytes are among the promising SSEs and being received extensive attention due to their excellent flexibility and diversity (Huo et al., 2019; Lu et al., 2020). Critical issues restrict their applications with lithium–sulfur chemistries, such as shuttle effects, dendrite problems, and liquid leakage in some specific quasi-solid electrolytes (Pan et al., 2020). As polymer electrolytes are soft materials with thermal instability, temperature variation within polymer electrolytes can lead to uneven ionic conductivity. This is very favorable for the local overcharge and the formation of Li-dendrites (Yin et al., 2020). Regarding the quasi-solid electrolyte, suitable matrices are highly required, which should meet the

following requirements: first, high porosity and good wettability so that it can quickly impregnate enough liquid electrolytes to obtain high ionic conductivity; then, high Li transfer number to achieve homogenous Li-ion migration and reduce ion concentration gradient; additionally, influential functional groups to limit the shuttle of polysulfide and obtain excellent long-term cycling stability (Chen S. et al., 2021; You et al., 2022); moreover, good mechanical properties to inhibit dendrite growth; finally, high thermal stability (Han et al., 2019).

At present, polyvinylidene fluoride (PVDF) and polyethylene oxide (PEO), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), and polypropylene cyanide (PAN) have been demonstrated as polymeric matrices to fabricate quasi-solid electrolytes (Qiu et al., 2019). However, an SEI layer would form in the systems using quasi-solid electrolytes. Although this may result in the loss of some active substances, it can effectively inhibit the shuttle effect, ensuring the high utilization rate of active substances. Additionally, incorporating an organic redox mediator within a quasi-solid electrolyte facilitates the redox kinetics of sulfur, mitigates the dissolution of sulfur, and promotes battery power (Zhao et al., 2021). Although it is challenging to design an utterly insoluble electrolyte for polysulfides, the negative impact caused by the dissolution of multi-lithium sulfide on the battery can be minimized.

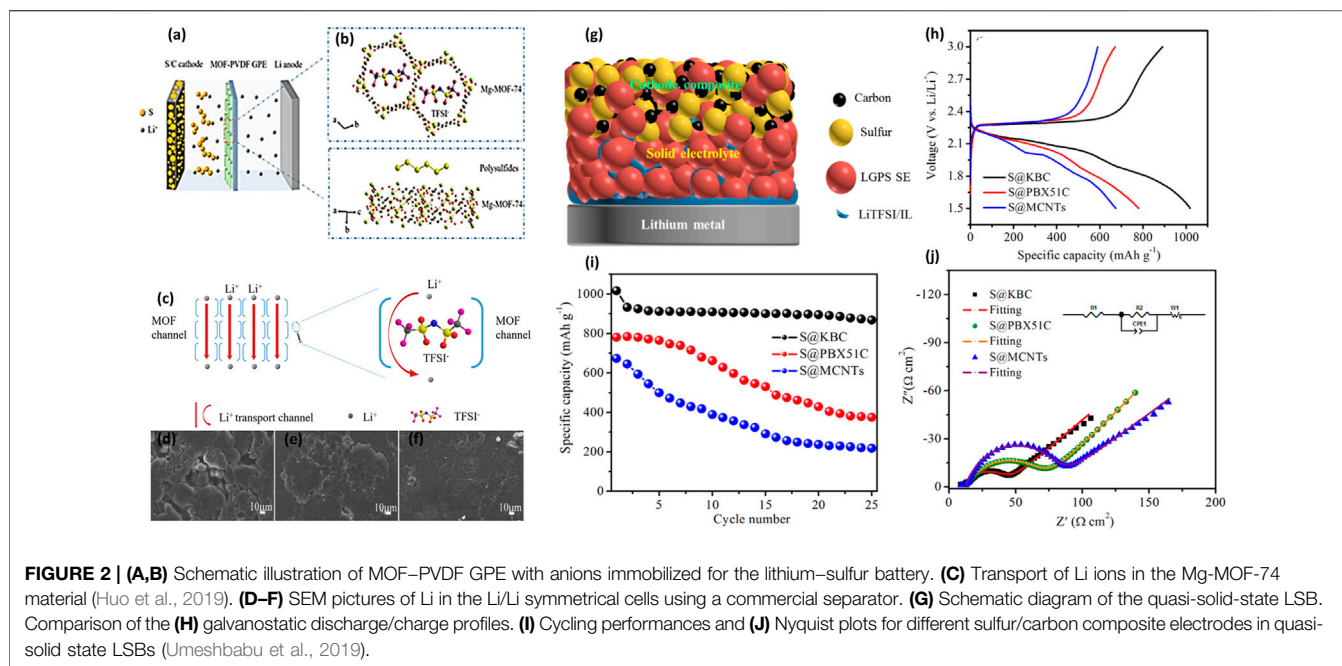
Among inorganic solid electrolytes, solid sulfide electrolytes are the critical material of lithium–sulfur all-solid-state batteries (Miura et al., 2019; Deng et al., 2021) because of its high ion conductivity and deformability. LSBs are not sufficient to completely break down Li₂S (Wang et al., 2020). Employing this SSE could effectively alleviate the shuttle effects and mitigate the dendrite issue. Some strategies are applied to improve the performance of lithium–sulfur SSBs such as surface modification to improve the ionic conductivity, defect engineering, incorporating liquid with solid, and enhancing the stability of SEI (Chen P. et al., 2021). However, the application of inorganic solid electrolytes introduces new challenges, such as increased interfacial resistance. The significant volume expansion of about 76% in solid cells will result in mechanical degradation and poor contact between electrodes and electrolytes (Wang et al., 2020). A proper design of the inorganic materials is also required.

4 POLYMER ELECTROLYTE APPLICATION FOR THE LITHIUM–SULFUR SSB

4.1 Gel/Quasi-Solid Polymer Electrolyte

4.1.1 Metal–Organic Framework-Modified Gel Polymer Electrolyte

A MOF-based gel polymer electrolyte (GPE) has been used for LSBs to stabilize the lithium anode (Ren et al., 2020). Due to abundant micropores in the MOF skeleton, the as-prepared GPE can block the large-sized polysulfide ions in the MOF skeleton and immobilize the relatively large anions. This unique property significantly enables a uniform transport of Li-ions and achieves a homogenous lithium stripping/plating (Gao et al., 2021). In addition to the size-exclusion of MOF matrices, the impregnated liquid electrolyte would help to form a dense SEI



passive layer, which further improves the cycling performance of batteries. As shown in **Figures 2A,B**, Gao et al. proposed a novel GPE with immobilized anions is applied in LSBs, stabilizing the lithium anode. Wherein, Mg–MOF–74 material is used to modify the PVDF-based GPE to attain a MOF-modified GPE. The MOF material has a suitable pore size of 10.2 Å and abundant Lewis acidic sites. Additionally, the Li-ion transportation by the skeleton of Mg–MOF–74 material is shown in **Figure 2C**. The experimental result presented that the MOF–PVDF electrolyte has the highest by comparing Celgard and PVDF GPE. It indicated that the MOF–PVDF has excellent ionic diffusivity. Meanwhile, as shown in **Figures 2D–F**, scanning electron microscopy (SEM) analysis found that the Mg–MOF–74-based PVDF electrolyte has a smooth lithium surface, which indicates that the Mg–MOF–74 material has an even lithium plating/stripping process (Huo et al., 2019).

4.1.2 Ionic Liquid Interface-Modified Gel Polymer Electrolyte

A straightforward approach to stabilize the interface stability is employing electro-chemically stable ionic liquid. As a typical example, lithium-based ionic liquid, i.e., 1 M LiTFSI/PYR₁₃TFSI was exploited as a surface modifier between the Li₁₀GeP₂S₁₂ (LGPS) solid electrolyte and lithium metal anode. As depicted in **Figure 2G**, due to ionic-liquid-modified LGPS being considered the quasi-solid or gel electrolyte, the resulting battery featured a considerably decreased interfacial resistance of 142 Ω cm² (**Figure 2J**). Paired with the sulfur-based cathode within S@KBC in this case, the battery delivered a high discharge capacity of 1,017 mAh g⁻¹ (**Figure 2H**). The researchers explored a facile and straightforward approach to enhance the interface stability between the lithium superionic-conducting Li₁₀GeP₂S₁₂ solid electrolyte and Li metal (Umeshbabu et al., 2019).

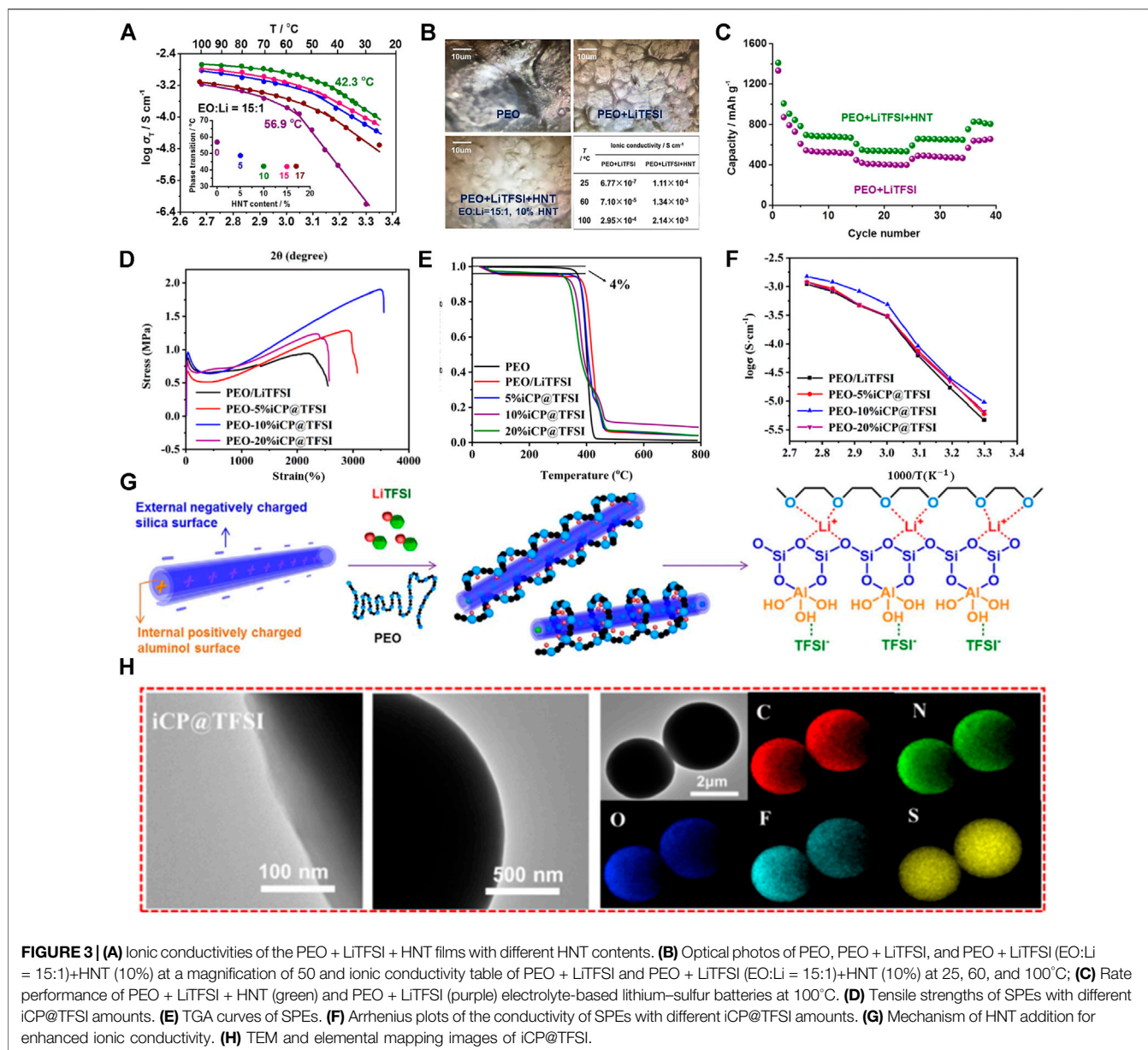
4.1.3 Polymer Matrix-Based Quasi-Solid/Gel Electrolyte

PVDF–HFP is a proper polymer matrix, demonstrated as a functional host in quasi-solid electrolytes (Yubuchi et al., 2019). For example, propylene polycarbonate was blended with PVDF–HFP to fabricate a flexible membrane separator *via* a solution casting method (Bi et al., 2021; Wang et al., 2022). The as-prepared gel polymer electrolyte features a high ionic conductivity of 1.18×10^{-3} S cm⁻¹ and a wide electrochemical window of 4.8 V vs. Li/Li + at an ambient temperature. The increased ionic conductivity could be attributed to the matrix's lower polymer crystalline and excellent ion conduction of impregnated propylene polycarbonate. With flexible polymer chains in PVDF–HFP, this polymer possesses good chain mobility and could potentially achieve an excellent ionic conductivity (Chen et al., 2019; Xiao et al., 2021). However, the PVDF–HFP electrolyte membrane has low mechanical strength, which can hardly hinder the dendrite growth and withstand the puncture of dendrites. Meanwhile, there are no influential functional groups within the structure of PVDF–HFP. Post-modification or tuning its functional structure to achieve negatively charged constituents might be a promising approach to prevent the shuttle effect of polysulfides. Donnan-exclusion will be introduced to repulse the negatively charged polysulfides.

4.2 Solid Polymer Electrolyte

4.2.1 Solid Polymer Electrolyte-Based Natural Halloysite Nano-Tube

A new type of a solid polymer electrolyte (SPE) membrane was prepared using a natural halloysite nano-tube (HNT), and it is applied to the flexible solid electrolyte membrane of the HNT lithium–sulfur SSB for the first time. Wherein, the lithium–sulfur



SSB can work in a broad temperature range of 25–100°C with the HNT electrolyte. The Gamry electrochemical instrument measured the electrochemical properties of the PEO/LiTFSI/HNT electrolyte. The experimental data indicated that the highest ionic conductivity was attained with the presence of 10% HNT and an EO: Li molar ratio of 15:1 (Figure 3A). As shown in Figure 3B, at 100°C, the highest ionic conductivity is $2.14 \times 10^{-3} \text{ S cm}^{-1}$, whereas the ionic conductivity of SPE at room temperature is in a range from 10^{-8} to $10^{-4} \text{ S cm}^{-1}$. Therefore, the PEO/LiTFSI/HNT electrolyte presents excellent ion conduction ability. The reason for the electrolyte improving the ionic conductivity was further studied. It is found that the Lewis acid–base interaction between HNT, LiTFSI, and PEO arranges lithium ions into 3D channels (Figure 3G). These interactions will curtail the free Li^+ ion transfer distance,

reduce ionic coupling, interfere with PEO crystallinity, and provide a high-speed channel for lithium-ion transmission. They also make SPE film electrolytes more even and have better mechanical strength. Additionally, the rate characteristics of the LSB with the PEO/LiTFSI electrolyte containing HNT were compared with those without HNT at 100°C, and the results are illustrated in Figure 3C. A battery based on PEO/LiTFSI/HNT indicated a higher capacity than batteries without HNT (Lin et al., 2017).

4.2.2 Polymer Electrolyte Based on PEO

PEO/LiTFSI polymer electrolytes with different (5%–20%) cyclopropenium cationic-based covalent organic polymers (iCP@TFSI) have been prepared. The effect of iCP@TFSI on the electrochemical performance of polymer LSBs was

TABLE 1 | Ionic conductivity, advantages, and disadvantages of inorganic SSEs.

Classification	Material	Conductivity	Advantage	Disadvantage	Ref
Perovskite	$\text{Li}_{0.34}\text{Nd}_{0.55}\text{TiO}_3$	8.00×10^{-8}	High mechanical strength	High grain boundary resistance	Zhang et al. (2017)
	$\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$	7.00×10^{-5}	High oxidation voltage	Unstable with Li metal	Ladenstein et al. (2020)
NASICON	$\text{LiTi}_2(\text{PO}_4)_3$	2.00×10^{-6}	High oxidation voltage	Unstable with Li/Na metal	Lang et al. (2015)
	$\text{Li}_{1.2}\text{Al}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$	5.00×10^{-3}	Air/water stable	Frangibility	de Klerk and Wagemaker, (2018)
	$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$	4.0×10^{-4}	Low processing cost	High cost of Ge	Mariappan et al. (2011)
	$\text{LiZr}_2(\text{PO}_4)_3$	3.80×10^{-5}	High ionic conductivity	[-]	Yutao et al. (2016)
Garnet	$\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$	1.00×10^{-5}	Thermal stable	High interfacial resistance	Inaguma et al. (1997)
	$\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$	1.54×10^{-6}	Stable with Li metal	Expensive for large-scale application	Lustosa et al. (2021)
	$\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$	4.00×10^{-5}	Air stable	Moisture-sensitive	Kokal et al. (2012)
Thio-LISICON	$\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$	1.31×10^{-7}	Thermal stable	Air/water-sensitive	Westover et al. (2020)
	Li_7SiPS_8	6.40×10^{-4}	Water stable	[-]	Harm et al. (2019)
	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.20×10^{-2}	High ionic conductivity	[-]	Mo et al. (2012)
Argyrodite	$\text{Li}_6\text{PS}_5\text{Cl}$	4.60×10^{-3}	High ionic conductivity	Air/water-sensitive	Yubuchi et al. (2015)
	$\text{Li}_6\text{PO}_5\text{Cl}$	1.00×10^{-9}	High oxidation voltage	[-]	Xu et al. (2019)

investigated. The iCP@TFSI-incorporated PEO/LiTFSI matrix has a positive influence on ionic conductivity, and the mechanical capacity of SPEs, additionally, increases the stability of lithium metal anode. As shown in **Figure 3D**, the ultimate tensile strength of PEO-10%iCP@TFSI electrolyte can reach 1.9 MPa, and the elongation at break augments to 3,557.15%. Additionally, LSBs with PEO-10%iCP@TFSI electrolyte have the high Coulombic efficiency, excellent cycling stability, and low capacity fade of 0.032% per cycle after 500 cycles at 1°C (Wang et al., 2021). As shown in **Figure 3E**, the PEO/iCP@TFSI electrolyte shows high thermal stability at above 300°C, and it meets the basic requirements of energy storage. Meanwhile, it is also found that the PEO-10% iCP@TFSI electrolyte has a higher ion on conductivity, as shown in **Figure 3F**. The ionic conductivity of PEO-10%iCP@TFSI at a room temperature of 80°C is up to $1.2 \times 10^{-3} \text{ Scm}^{-1}$. However, the PEO-20%iCP@TFSI polymer electrolyte presents lower ion conductivity, possibly due to the uneven distribution of iCP@TFSI in the PEO matrix. The surplus iCP@TFSI may lead to aggregation, phase separation, and bubbles and finally decrease the ionic conductivity of SPEs. In addition to the discussion mentioned earlier, SPE membranes' capacity to resist high stress and high strain is vital for realizing the stable cycling of lithium-sulfur SSB. As shown in **Figure 3H**, the transmission electron microscope (TEM) combined with (energy dispersion spectrometer) EDS elemental mapping was employed to obtain the element distribution of iCP@TFSI. The EDS spectra proved that the TFSI-ions are evenly dispersed in the polymer without aggregation, which is essential for improving the ionic conductivity of the PEO/iCP@TFSI electrolyte.

5 INORGANIC SOLID-STATE ELECTROLYTES

In contrast to polymer-based electrolytes, inorganic solid electrolytes exhibit better thermal stability and mechanical

strength. Moreover, inorganic solid electrolytes feature a wide electrochemical window and insolubility to polysulfides. Ideally, they are the best separator to realize the lithium-sulfur SSBs with a good electrochemical performance. Currently, inorganic solid electrolytes include two widely studied families, oxide-based SSEs and sulfide-based SSEs. Sulfide-based SSEs include glass and glass-ceramic ionic conductors. Oxide-based SSEs include LISICON, NASICON, thio-LISICON, perovskite, and garnet-type solid electrolytes. The ionic conductivity, advantages, and disadvantages of inorganic SSEs are summarized in **Table 1**. However, all these electrolytes generally have a high contact resistance to electrodes due to the rigid contact of solids. The grain boundaries involved in these electrolytes also increase the interfacial resistance and reduce the overall ionic conductivity. In lithium-sulfur SSBs, sparse inorganic electrolytes were explored.

5.1 Sulfide Solid-State Electrolytes

5.1.1 Mixed Electrolyte of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$

Recently, Yao et al. (2017) reported double-layer $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) 24%/75% $\text{Li}_2\text{P}_2\text{S}_5$ 1% P_2O_5 as the electrolyte and cathode for RGO-modified S of all-solid-state LSB. As shown in **Figure 4**, the reduction of graphene oxide (rGO) nano S layer on the interface between the cathode and the electrolyte resistance decreased significantly, as proved by the atomic force microscope (AFM) results. The resultant lithium-sulfur SSB exhibited an initial discharge capacity of 1,629 mAh g^{-1} and good rate ability (0.05–5°C). The remarkable output capacity is attributed to the restricted shuttle effects and limited volume change of sulfur in de/lithiation. Later, a nanocomposite S@CNTs cathode was prepared and investigated in lithium-sulfur SSBs. This battery demonstrated a high-rate performance (60°C) and long cycle life. In addition, CNTs@S conveyed a stable capacity of 660.3 mAh g^{-1} at 1°C over 400 cycles. The electron-conductive nano-tubes could effectively accommodate sulfur and tolerate its volume change over electrochemical processes (Wu J. et al., 2020).

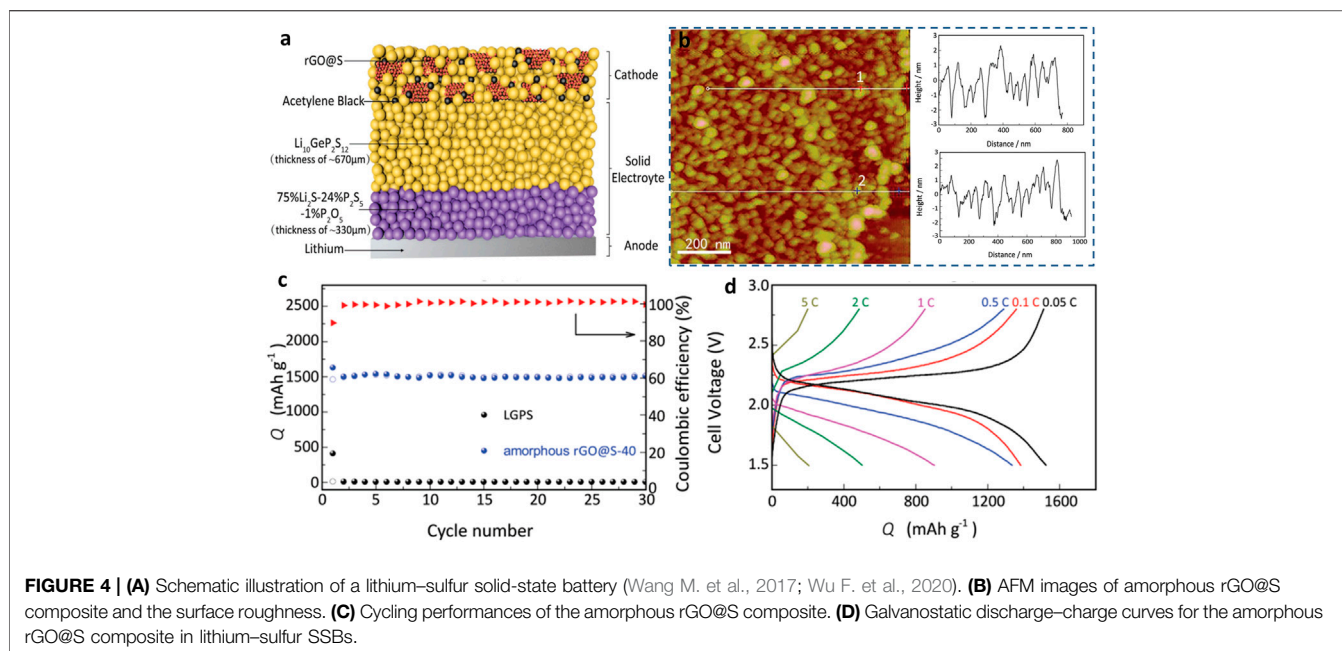


FIGURE 4 | (A) Schematic illustration of a lithium-sulfur solid-state battery (Wang M. et al., 2017; Wu F. et al., 2020). **(B)** AFM images of amorphous rGO@S composite and the surface roughness. **(C)** Cycling performances of the amorphous rGO@S composite. **(D)** Galvanostatic discharge-charge curves for the amorphous rGO@S composite in lithium-sulfur SSBs.

5.1.2 High-Conductivity Argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ Solid Electrolytes

Argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ was regarded as a promising electrolyte with high ionic conductivity in the range of 10^{-3} – 10^{-2} S cm^{-1} at room temperature (Deiseroth et al., 2008). The typical preparation method for $\text{Li}_6\text{PS}_5\text{Cl}$ SSEs is ball milling. Wang S. et al. (2018) prepared highly Li-ion-conductive $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolytes (SSEs) by sintering at 550°C for 10 min, which was more efficient compared with other reported methods to synthesize $\text{Li}_6\text{PS}_5\text{Cl}$ SSEs. All-solid-state lithium sulfur batteries (ASSLSBs) with $\text{Li}_6\text{PS}_5\text{Cl}$ SSE were assembled using nano-sulfur/multiwall carbon nano-tube composite materials and combined with $\text{Li}_6\text{PS}_5\text{Cl}$ as the cathode and Li-In alloy as the anode. The cell delivered a high discharge capacity of $1,850 \text{ mAh g}^{-1}$ at room temperature for the first full cycle at 0.176 mA cm^{-2} . In addition, the Coulombic efficiency remained nearly 100% during galvanostatic cycling. The experiment results indicated that $\text{Li}_6\text{PS}_5\text{Cl}$ was a good candidate for SSE used in ASSLSBs.

5.2 Oxide Solid-State Electrolytes

Oxide-SSEs, another major inorganic SSEs, have recently received extensive attention from researchers due to their high electrical conductivity properties compared to polymer-SSEs. Developed oxide-based SSEs primarily involve LISICON, NASICON, thio-LISICON, perovskite, and garnet-type solid electrolytes. The perovskite-type $\text{Li}_{3-x}\text{La}_{(2/3)-x}\text{Ti}_{(1/3)-2x}\text{TiO}_3$ (LLTO), which has RT ionic conductivities of over 10^{-4} S cm^{-1} (Kwon et al., 2017; Yang D. et al., 2021). Li et al. (2016) have first developed NASICON-structured $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as the cathode material for Zn-ion batteries. With $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ as a cathode, Zn metal as both counter and reference electrodes, and 0.5 mol L^{-1} $\text{Zn}(\text{CH}_3\text{COO})_2$ solution as an electrolyte, the aqueous Zn-ion battery delivers a reversible capacity of 97 mA h g^{-1} at 0.5°C and

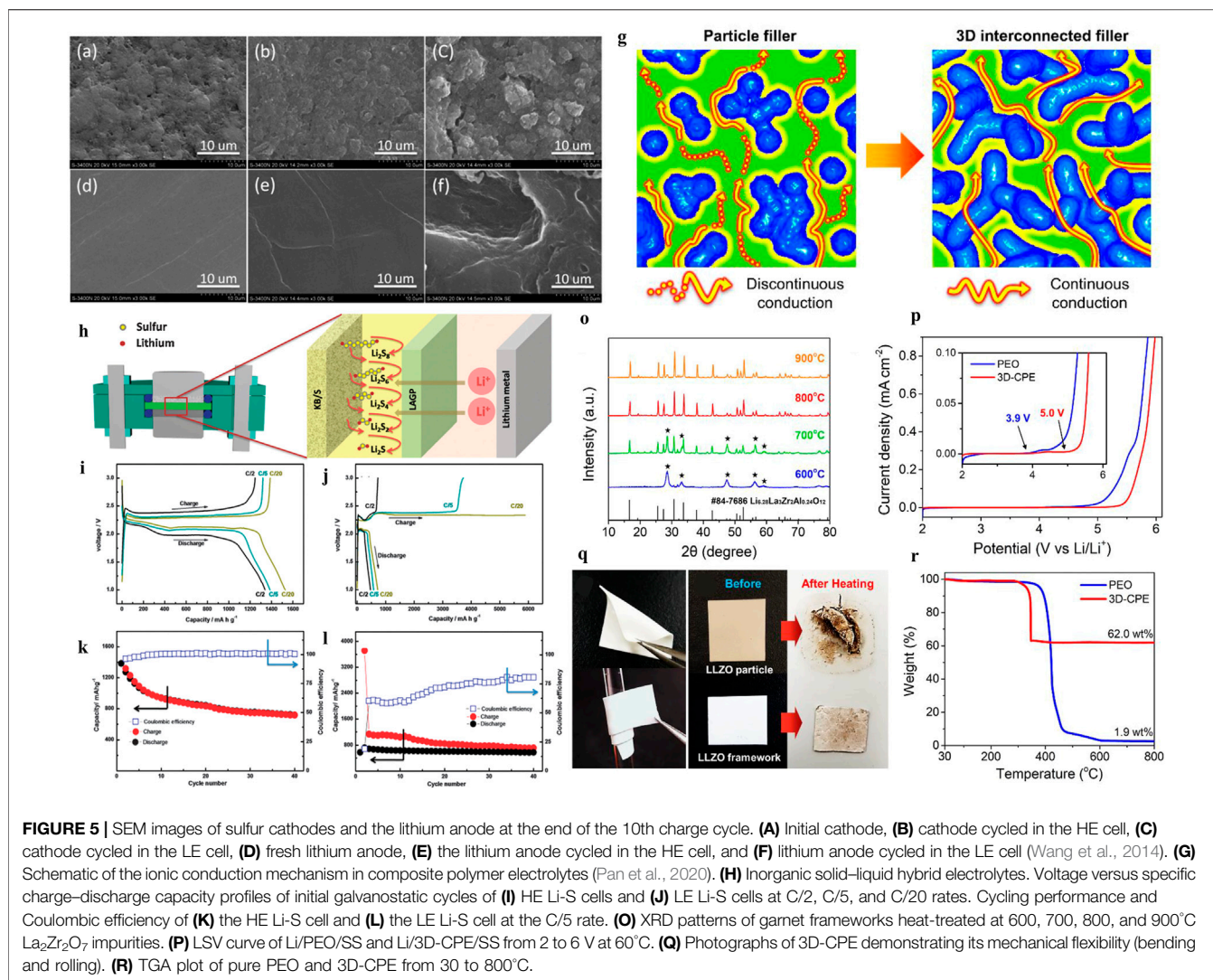
retains 74% capacity after 100 cycles. Usually, oxide-based SSEs are coupled with polymer-based SSEs, liquid electrolytes, or ionic liquids to reduce the interfacial resistance. These classic hybrid SSEs will be discussed in **Section 6**.

6 HYBRID ELECTROLYTES

Though inorganic solid electrolytes have relatively high ionic conductivity, they endure instability with high interfacial resistance and instability of the surrounding atmosphere (Pan et al., 2020). To alleviate the shortcomings of single-component SSEs, in recent years, hybrid electrolytes have drawn increasing research interest due to their advantages, such as ionic conductivity and easy processability (Ding et al., 2020). Hybrid electrolytes (inorganic-organic composite electrolytes (IOCEs) and inorganic solid-liquid composite electrolytes (ISLCEs)) containing two or more components have been considered potential electrolytes for LSBs (Wang L. et al., 2018). Hybrid electrolytes are expected to combine each component's advantages to improve the electrochemical performance of the LSBs. However, the disadvantages between the components cannot be completely avoided. This section mainly discusses the effect of hybrid electrolytes on improving the electrochemical performance of LSBs.

6.1 Inorganic-Organic Composite Electrolytes

Composite polymer electrolytes (CPEs) with solid-state fillers are widely researched to improve the Li-ion conductivity of SPEs. There are two kinds of fillers in the polymer matrix (Pan et al., 2020), which involve nonionically conductive fillers, such as TiO_2 , Al_2O_3 , and ceramic nanowires (Liu et al., 2017) and Li

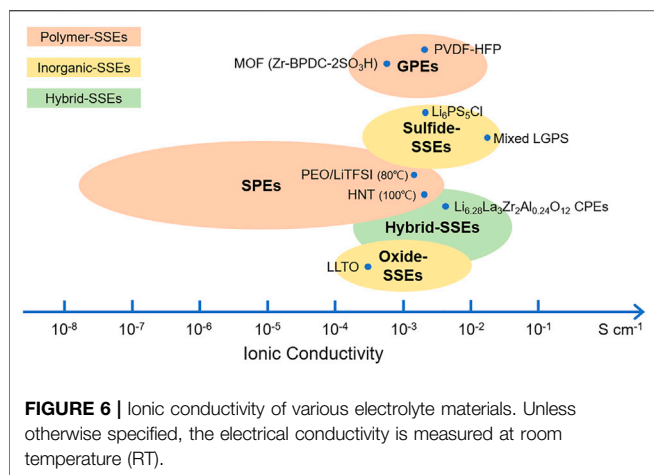


ionically conductive fillers (such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$). For nonionically conductive fillers, the use of alumina nanoparticles can improve the mechanical properties and electrochemical stability of CEPs due to the formation of a more stable SEI. Nevertheless, it is not suitable to apply Al_2O_3 -CPEs directly in Li-S cells, as Judez et al. (2017) show that the discharge capacity of LSB with Al_2O_3 -CPEs is only 300 mAh g^{-1} . In addition to oxides, the Li ionically conductive fillers are another strategy to ameliorate Li-ion conductivity for SPEs. A novel three-dimensional nanostructured $\text{Li}_{6.28}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{12}$ framework as a filler in the PEO matrix was developed in (Bae et al., 2018) to study the effect of Li-ion conductivity. As illustrated in Figures 5G–R, the three-dimensional garnet frame provides a continuous Li-ion conduction path, and the simulation results showed that the ionic conductivity was improved up to $\sim 10^{-3} \text{ S cm}^{-1}$ at 60°C (Bae et al., 2018).

6.2 Inorganic Solid-Liquid Electrolytes

As illustrated in Figures 5A–F, X-ray photoelectron spectroscopy (XPS) and EDS spectra analysis indicated side reactions between

lithium metal and polysulfides for LSBs with the solid-liquid electrolyte. The polysulfide shuttling effects can be suppressed by applying the solid-liquid hybrid electrolyte (Wang et al., 2014). To address the shuttle effect of the Li_2S_x problem and interface contact problem (Liu G. et al., 2021), as shown in Figure 5H, Wang and co-workers proposed a room temperature hybrid electrolyte-based Li-s battery, which combined solid and liquid electrolytes. In this work, $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) as a separator to hinder the soluble polysulfides for a hybrid electrolyte (HE) Li-S battery was proposed. The NASICON-type structured LAGP electrolyte is a choice due to its favorable chemical stability against lithium and wide electrochemical window up to 6V. Meanwhile, the electrode and solid electrolyte are connected by 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the 1,3-dioxolane and 1,2-dimethoxyethane (1:1, v/v) (LiTFSI/DOL/DME) liquid electrolyte. As shown in Figures 5I–L, the discharge-specific capacity reached $1,386 \text{ mAh g}^{-1}$ and $1,341 \text{ mAh g}^{-1}$ at C/20 and C/5, respectively, while the initial discharge-specific capacity was $1,528 \text{ mAh g}^{-1}$. Additionally, the reversible specific capacity remains at



720 mAh g⁻¹ after 40 cycles at the C/5 rate, indicating an outstanding coulombic efficiency.

7 CONCLUSION AND OUTLOOK

In this review, we have systematically reviewed the recent progress of lithium–sulfur SSBs. The structure and principle of the lithium–sulfur SSBs, electrolyte material design, and specific work are summarized, and **Figure 6** gives a summary of the conductivity of various electrolytes. The electrolytes of lithium–sulfur SSBs can generally be divided into three types: polymers, inorganics, and hybrid SSEs. GPEs are able to trap a large fraction of liquids (organic or ionic liquids), and the conductivity could almost reach that of the free solvent, which is up to almost 10⁻² S cm⁻¹ at room temperature. In addition, gels together with dry polymers could tether negative charge to the backbone, which results in transference numbers close to unity. Eliminating liquid electrolytes for safety consideration, SPEs are attractive alternatives but limited by their low ionic conductivities (typically 10⁻⁸–10⁻⁶ S cm⁻¹ at RT). Inorganics (ceramics) are often considered the ultimate solution to address the weaknesses of the liquid electrolyte systems. However, sintering processes cannot prepare solid electrolytes with thicknesses below 30 μm, and a high temperature is required for garnet electrolytes. The composite materials prepared by the deposition techniques that involve a vacuum process are normally expensive and have low production efficiency. In this respect, sulfide-based electrolytes are considered a promising candidate because they can be easily pressed and shaped in a low-cost manner. The interfacial contact is often established by the insertion of a layer of polymer/gel or liquid. Hybrid SSEs intend to balance the merits and drawbacks of each component. The most common hybrid SSEs are composed of a soft component and rigid inorganic SSEs, in which the inorganic SSEs contribute to high ionic conductivity/mechanical strength and the flexible component ensures a good interface.

Despite the tremendous efforts to promote performances of the lithium–sulfur SSBs, the following aspects remain challenging:

- 1) As the ultimate solution of a lithium metal battery, SSB could tackle the shuttle effect and the pulverization of lithium metal at its root, which could manipulate the irreversible capacity loss and low coulomb efficiency. Nevertheless, the SSE may debase the advantage of high specific energy because of the low ion and electron conductivity. Moreover, because the electrochemical reaction of SSB generates on the tri-phase-boundary, the crucial element of the stability and the regulation between each boundary is urgent for research.
- 2) The flexible electrode will also be a critical challenge to the lithium–sulfur SSBs. Initially, the flexible sulfur cathode has the characteristics of synergistic effort of both chemical and physical adsorptions, which could excellently restrain the shuttle effect. Moreover, the flexible design could buffer the volume expansion of the sulfur cathode. All the aforementioned methods can significantly improve the electrochemical performances of lithium–sulfur SSBs. Unfortunately, as another crucial role, the flexible lithium metal anode is facing more challenges but less studied than the flexible sulfur cathode. Developing flexible lithium metal anode is worthy of further research.
- 3) Big data is a promising solution to the full-lifespan management of lithium–sulfur SSBs, including material synthesis, manufacturing of batteries, operating process, battery recycling (Hu et al., 2016), and cascade utilization. Our group proposed a cyber hierarchy and interaction network (CHAIN) to solve this problem (Yang S. et al., 2020). A series of multi-scale models, the “digital twin” technology, and the “digital thread” technology can be applied to virtual out a battery completely from a multi-dimension containing molecular scale, morphology scale, electrode and electrolyte scale, and battery and system scale, which could provide guidance for the design and optimization process of the batteries (Yang S. et al., 2021; Zhang L.-S. et al., 2022). With related data shared and stored in the cloud, we could attain an optimized control strategy *via* data processing and artificial intelligence to enhance the full-lifespan management of lithium–sulfur SSBs.

In general, the future work of the lithium–sulfur SSBs will be focused not only on the material development and battery electrochemical performances but also on how to realize full-lifespan management.

AUTHOR CONTRIBUTIONS

SY: conceptualization, methodology, and writing—original draft. ZZ: methodology, software, and visualization. JL: investigation and validation. LZ: data curation. LW: supervision and visualization. SC: supervision and writing—review and editing. CZ: supervision. XL: supervision.

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