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REVIEW

All-solid lithium-sulfur batteries: present situation and future progress

Yannis De Luna[1] · **Mohanad Abdullah**[1] · **Sarra N. Dimassi**[1] · **Nasr Bensalah**[1]

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Abstract

Lithium-sulfur (Li–S) batteries are among the most promising next-generation energy storage technologies due to their ability to provide up to three times greater energy density than conventional lithium-ion batteries. The implementation of Li–S battery is still facing a series of major challenges including (i) low electronic conductivity of both reactants (sulfur) and products (polysulfides) that limits the rate capability of the battery; (ii) high solubility of the polysulfide products into the electrolyte that affects the cycle life; and (iii) the reactivity of the lithium metal anode that induces serious safety hazards. Replacing hazardous organic electrolytes with solid-state electrolytes (SSEs) can prevent lithium polysulfides crossover and Li dendrite growth. SSEs with high ionic conductivity and good electrochemical stability can boost Li–S technology by improving electrochemical performance and cycling stability. All-solid lithium-sulfur batteries (SLSBs), comprising of sulfur cathode, solid electrolyte, and Li metal anode, are much safer than liquid-based electrochemical batteries such as conventional lithium batteries. They possess longer cycle life and require less effort in terms of packaging and monitoring circuits. SLSBs have the powerful ability to transfer the converted stored chemical energy into electrical energy with high efficiency and without the release of harmful gasses. This review focuses on the types of SSEs, their advantages and drawbacks in conjunction with Li–S batteries, and the challenges that hinder the practical application of SLSBs.

Keywords Lithium-sulfur · Safety · Cycle life · All solid-state batteries · Solid electrolytes

Introduction

Combatting global warming urgently requires, among other actions, an effective usage of other prospective energy sources and the substitution of gasoline- and diesel-powered car engines with non-emitting electric motors, such as plug-in hybrid vehicles (PHEVs) or, ideally, full electric vehicles (EVs). All CO_2-free energy sources, such as solar, wind, and geothermal, would benefit from energy storage devices that could offer a solution for time and space limitations to allow continuous energy production. The most attractive are portable electrochemical batteries, in particular lithium batteries, due to their exceptional capability to deliver stored chemical energy as electrical energy with remarkable conversion proficiency, high energy density, and without any kind of gaseous exhaust. Moreover, lithium batteries are the most promising, if not the sole players, to power efficiently PHEVs and EVs. However, the present lithium battery technology is not adequate for boosting PHEVs or EVs and fails to satisfy the high energy requirement that allows for an acceptable driving distance. With the present lithium technology (150 Wh/kg), over 150 kg of batteries would be needed to provide a driving range of 250 km with a single charge of an average consumer car, which is an unacceptable weight load. Hence, advanced lithium batteries with higher energy density than that of the conventional ones are urgently needed. Among these, lithium-sulfur (Li–S) battery system is attracting a worldwide interest since it offers 3,500 Wh/kg of energy density versus 380 Wh/kg from the present lithium-ion batteries (see Fig. 1). In addition, there is an added advantage of a significant cost reduction as sulfur is much cheaper than the cobalt-based cathodes used today. Furthermore, this battery is of strategic interest where sulfur is largely available as by-product in gas processing plants.

Although its concept dates back several decades ago, the Li–S battery has been silent until very recently when the appearance of a series of papers [1–8] has consistently renewed interest in this high-energy system. However,

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✉ Nasr Bensalah
nasr.bensalah@qu.edu.qa

[1] Chemistry Program, Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, PO Box 2713, Doha, Qatar

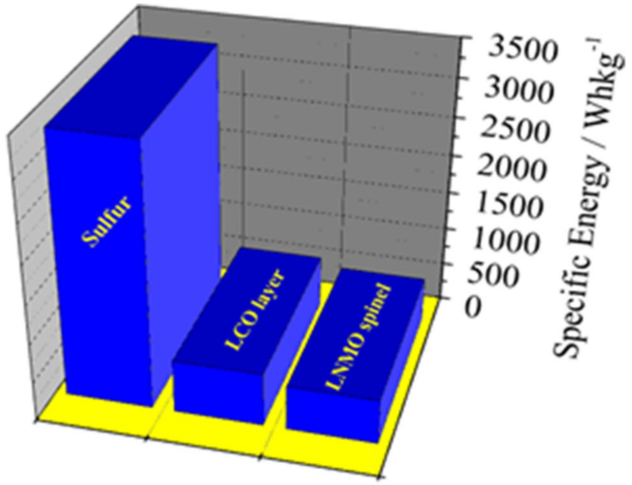

Fig. 1 Comparison of the theoretical energy density of a lithium-sulfur battery versus that of conventional lithium-ion batteries

despite these mostly academic successes, the implementation of the battery is still restrained by a series of unresolved issues. These are mainly: (i) low electronic conductivity of both reactants (sulfur) and products (polysulfides) that limits the rate capability of the battery; (ii) high solubility of the polysulfide products into the electrolyte that affects the cycle life; and (iii) the reactivity of the lithium metal anode that produces serious safety hazards. Lithium-sulfur batteries are among the potential next-generation energy storage technologies since they have much greater energy density by 2 to 3 times than other lithium-ion batteries [9]. In addition, SLSBs are attracting more attention and interest than other electrochemical batteries since they have longer cycle life, better safety, and fewer efforts in monitoring circuits compared to conventional liquid lithium-ion batteries (LIBs) [10]. Beside the high energy density, which can reach 2600 Wh kg^{-1}, Li–S batteries have an extremely high specific capacity of 1675 mA h g^{-1} [11]. Moreover, Li–S batteries are lower in cost and the cathode material is highly abundant, which makes them extremely attractive as an energy storage technology. In addition, the manufacturing of Li–S batteries could be fabricated with the same configurations and identical factors as lithium-ion batteries. Furthermore, electrode reactions work spontaneously, and their kinetics are fast, enabling Li–S batteries to work well by achieving good rates of charging and discharging without any external intervention of a catalyst or any thermal source [12]. Li–S batteries are extremely attractive since they have the ability to effectively deliver the converted stored chemical energy into electrical energy with high energy density and in environmentally friendly way without any harmful gas exhaust. This encourages researchers to devote stronger efforts to improve the performance of these batteries by implementing several technologies and enhancements that could boost lithium-based batteries in general, while keeping the same features. However, in spite of all their successful improvements, Li–S batteries are still hindered by many issues. One of the most significant problems is scaling up the sulfur loading. Moreover, the low conductivity (sulfur and lithium polysulfides) limits the capacity of Li–S batteries. The relatively high solubility of lithium polysulfides in the electrolyte has a negative impact on the cycle life. Finally, the relatively high reactivity of the anode (lithium metal) raises some concern over safety hazards by the formation of Li dendrites [13].

Solid-state electrolytes have many advantages in improving the long-term cycling performance by having high ionic conductivity and a good electrochemical stability. In addition, they prevent lithium polysulfides crossover and growth of Li dendrites. There are many cathode materials used in SLSBs including elemental sulfur, lithium sulfides, metal sulfides, lithium thiophosphates, and lithium polysulfidophosphates, while using a Li/Li-M alloys as anode materials. Moreover, all SLSBs exhibit high energy densities with an excellent safety due to the interfacial modifications of cathode and anode materials by the side reactions of carbon additives and solid-electrolyte interface (SEI) coatings.

In this review, the progress in the development of various types of solid electrolytes and remaining challenges in the practical application of SLSBs will be discussed. Solid electrolytes used in SLSBs can be classified into several categories including inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), glass–ceramic electrolytes (GCEs), and gel polymer electrolytes (GPEs). All of these electrolyte types and their combinations will be discussed further.

Fundamentals and principles of lithium-sulfur batteries

The basic Li–S cell is composed of a sulfur cathode, a lithium metal as anode, and the necessary ether-based electrolyte. The sulfur exists as octatomic ring-like molecules (S_8), which will be reduced to the final discharge product, which is Li_2S, and it will be reversibly oxidized to sulfur while charging the battery. The cell operation starts by the discharge process. The full reaction could be represented as shown in Eq. 1.

$$S_8 + 16Li \rightarrow 8Li_2S \quad (1)$$

However, the most common electrochemical reaction for Li–S batteries in the processes of discharge/charge is extremely complex and includes many side reactions that lead to the formation of various polysulfides, as shown in Fig. 2 [9, 14, 15]. The order of product formation during the discharge process is highlighted in Eq. 2.

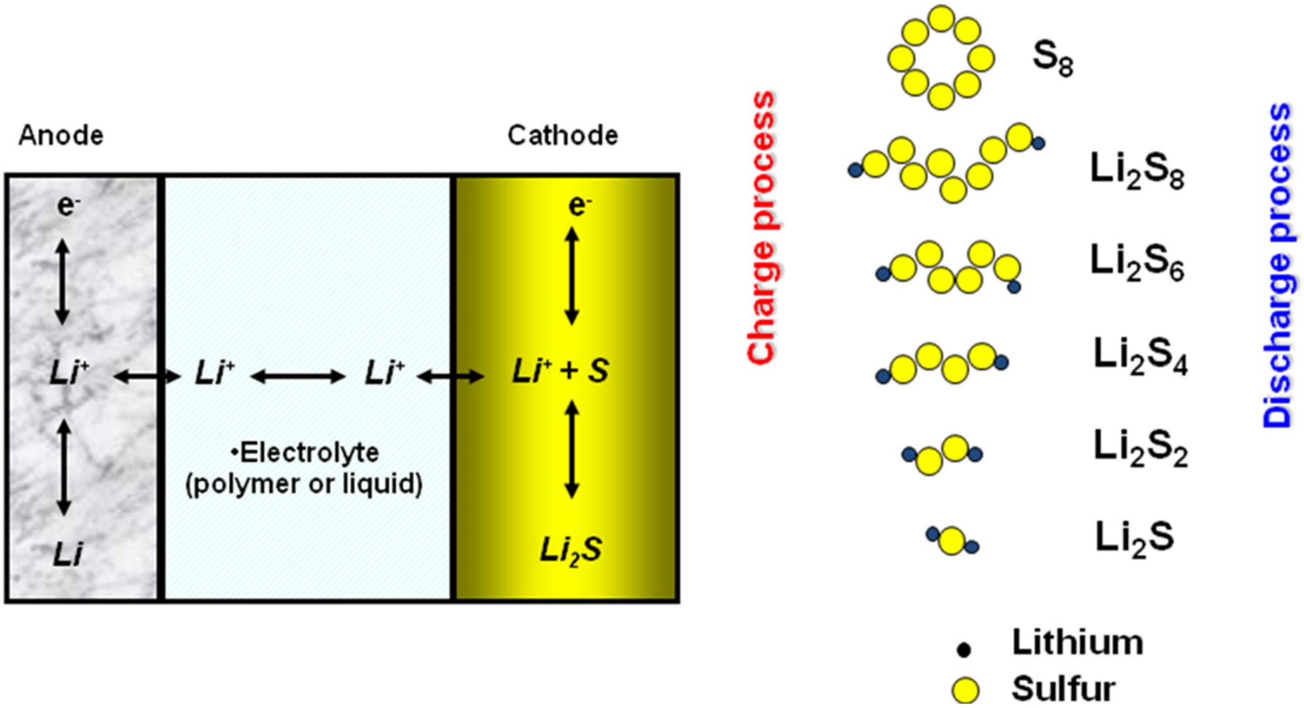

Fig. 2 Scheme of the lithium-sulfur battery and its charge–discharge process

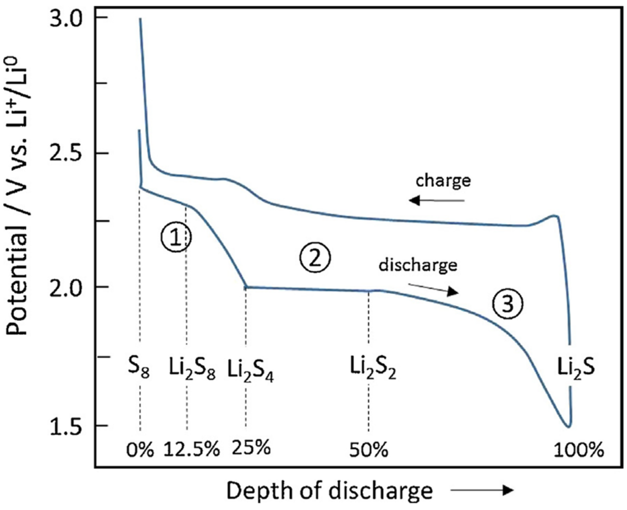

Fig. 3 Discharge/charge profiles of a lithium-sulfur cell, showing 3 stages: (I) solid sulfur converted to soluble polysulfides; (II) polysulfides converted to solid Li_2S_2; (III) solid Li_2S_2 converted to solid Li_2S [17]

$$Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_2 \rightarrow Li_2S \tag{2}$$

The working mechanism of Li–S batteries of charge and discharge processes is done in stages as the discharge process splits into two or three stages of reduction [16], depending on the electrolyte and its composition (see Fig. 3).

Discharge–charge process is an electrochemical reaction, which occurs approximately in three stages, as shown in Fig. 3. The first region is the reversible conversion of sulfur to polysulfides which are soluble through a reduction reaction $S^0 \rightarrow S_4^{2-}$. The kinetics of this reaction is fast due to the solubility of the polysulfides. The second region represents the conversion of polysulfides S_4^{2-} to Li_2S_2 ($S^{0.5} \rightarrow S^-$), which is more complicated than the previous reaction due to the energy required to nucleate the solid phase. The third and final stage is the conversion of the last product (solid Li_2S_2) to solid Li_2S. This step is the most challenging step due to the very slow diffusion of the solid lithium [17].

Challenges with conventional Li–S batteries

Formation of polysulfides

The overall electrochemical process (Eq. 1) involves a series of steps involving the sequential formation of polysulfides. The initial, highly ordered Li_2S_x polysulfides ($4 < x < 8$) are very soluble in typical electrolytes used in Li-ion batteries, such as $LiPF_6$ EC-DMC (LP30) organic solution. This allows the polysulfides to diffuse by a shuttle mechanism to the lithium metal anode to form lower ordered polysulfides ($2 < x < 4$), which tend to be less soluble and may precipitate on the anode itself (see Fig. 4). All of these result in a loss

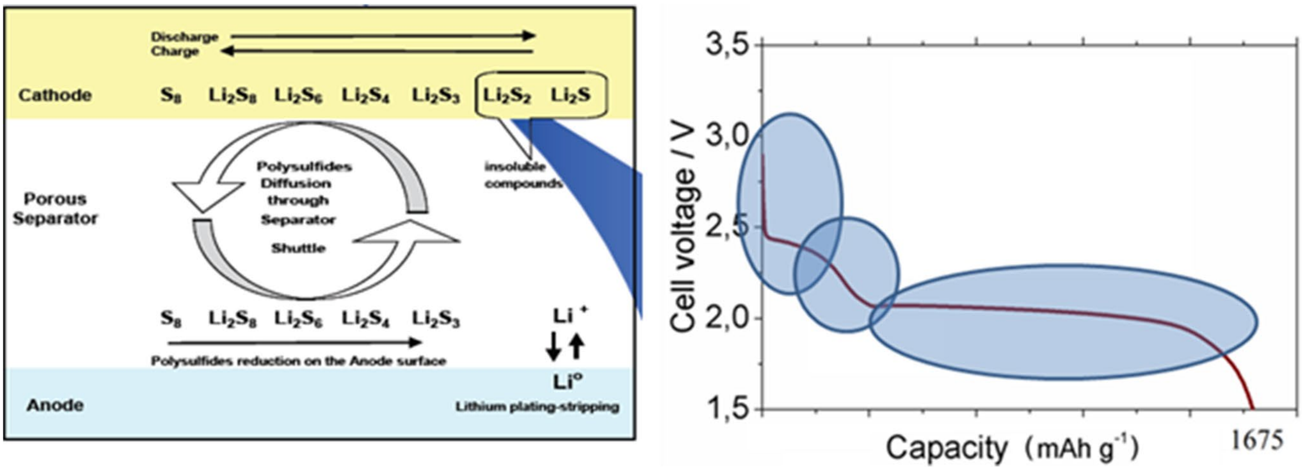

Fig. 4 Scheme of the issues affecting the lithium-sulfur battery and voltage profile of its discharge. The dash blue regions identify the zones of stability of the various polysulfides

of active mass with associated severe capacity fading upon cycling.

Another developed safe electrolyte based on ε-caprolactam/acetamide can dissolve all sulfide and polysulfide species, and therefore, major issues associated with Li_2S/Li_2S_2, such as volume expansion, uncontrollable deposition, and voltage polarization, can be minimized [18]..

Another aspect of concern is in the low resistivity ($\sim 5 \times 10^{-30}$ S/cm at 25 °C, almost insulator) of both reactant (S_8) and product (Li_2S_8), and in their large volume variation upon cycling, giving rise to serious problems in terms of low kinetics and of mechanical stresses at the cathode side. Most of the works so far performed on the Li–S battery have been addressed to the optimization of the sulfur electrode morphology, with the aim of keeping the mechanical and electrical integrity of the sulfur cathode by constraining sulfur (charge) and lithium polysulfide within the electrode framework using various types of host materials, including mesoporous carbons, carbon nanotubes and spheres [19]. These consistent findings participated in upgrading the technology of the Li–S battery; however, some obstacles still retard the complete effective utilization of this high-energy battery system.

Electrolyte

The majority of the recent works still rely on classical liquid organic carbonate solutions as the suitable electrolyte. Although sulfur and/or lithium sulfides are protected by the previously described carbon matrices, this essentially prevents contact with the electrolyte. In addition, it has not been fully determined whether the addition of carbon matrices inhibits the dissolution of the polysulfides. Therefore, finding alternative electrolytes capable of preventing the polysulfide dissolution will have a great significance for the evolution of the Li–S battery technology.

In terms of safety, the utilization of organic liquid electrolytes in batteries causes serious hazards such as fires and explosions. The majority of liquid electrolyte organic solvents possess low boiling point (generally below 300 °C) and a flash point below 150 °C. The safety issues for batteries that use organic liquid electrolytes such as Li-ion batteries (LIBs) were for several reasons which are the flammability, thermal instability, and volatility of the organic liquid electrolytes [20, 21].

Anode

Another serious issue, often ignored, is the use of lithium metal as the anode material. As well known, lithium metal may cause significant safety hazards due to the irregular dendrites deposited upon charge, which may grow and reach the positive electrode leading to a battery short circuit and subsequently, explosions or fire (see Fig. 5). Due to this safety threat, battery manufacturers are generally very reluctant to use lithium metal as electrode. Hence, the replacement of the reactive lithium metal with a more reliable anode would be

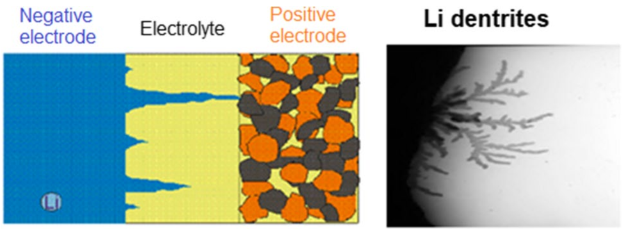

Fig. 5 Scheme and view of dendrites growing through a cell using lithium metal electrode

a step forward for promoting the practical implementation of the Li–S battery.

Eligibility of solid-state electrolytes for Li–S batteries

Electrolytes play a huge role in transporting ions in Li–S batteries. Some liquid electrolytes could achieve fast kinetics, but it also creates many concerns about safety and life cycle of the battery. The electrolytes which are used nowadays are composed mainly of organic electrolytes such as ethers or carbonates. These electrolytes have very low thermal stability and can leak out, which causes serious safety concerns. However, ionic liquids are considerably safe and nonflammable, but they are critical in terms of environmental hazards, high in cost, and inadequate for large-scale application in batteries. In addition, there are no solutions yet that prevent the issues of consumptive side relations and the formation of Li dendrites, which happens in the cells wherein liquid electrolytes are used [22–25]. The substitution of these liquid electrolytes with solid-state electrolytes (SSEs) would be a great way to solve the safety issues associated with organic liquid electrolytes since SSEs are non-flammable and thermally stable. In the 2000s, plenty of research that aimed the implementation of SSEs were done in several kinds of lithium-based batteries which include LIBs [20, 26], Li–S batteries [27, 28], and Li-air batteries [29, 30]. However, until now there is no developed individual SSE that covers all the functionalities. Various SSEs have several challenges that prevent their practical applications, which will be discussed further in their respective sections in this review. Recently, a considerable progress has been made for all solid-state lithium batteries by experiments that develop and optimize the solid electrolytes [31, 32]. During the previous four decades, many promising Li–S batteries, which use conducting solid electrolytes, have been introduced due to their potency to enhance the safety and energy density of Li–S batteries simultaneously [33, 34]. There are numerous solid electrolytes available today, which differ in properties and compositions. Solid electrolytes for Li–S batteries, including inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs) [33, 34], and composite polymer electrolytes (CPEs) that are obtained by the addition of fillers, are attracting more attention nowadays (see Fig. 6). Generally, a good solid electrolyte should have a high ion conductivity, great electrical insulation, wide electrochemical window, and chemically stable with electrode materials.

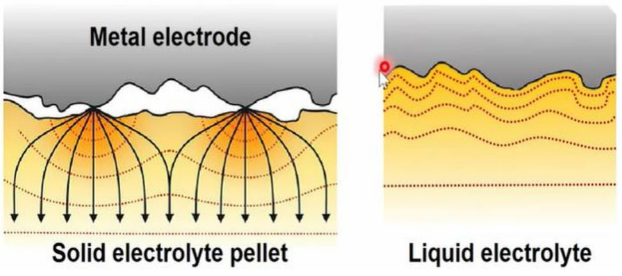

Fig. 7 The contact area at the electrolyte/electrode of solid and liquid electrolytes and the difference between them [39]

However, there are many remaining problems for the lithium metal solid electrolyte interface [36]. In all-solid-state Li-based batteries, which operate with inorganic solid electrolytes, the most crucial problem is the tendency to make a solid–solid interface between the electrode and the solid electrolyte. Recent studies show that the probed contact between the solid/solid is too small to be detected for short-term experiments. However, some reports have shown that $Li_7La_3Zr_2O_{12}$ (LLZO) is so far the only solid electrolyte which has a sufficient speed that illustrates an adequate stability in contact with Li metal [37, 38]. Figure 7 shows the difference between solid and liquid electrolytes in terms of

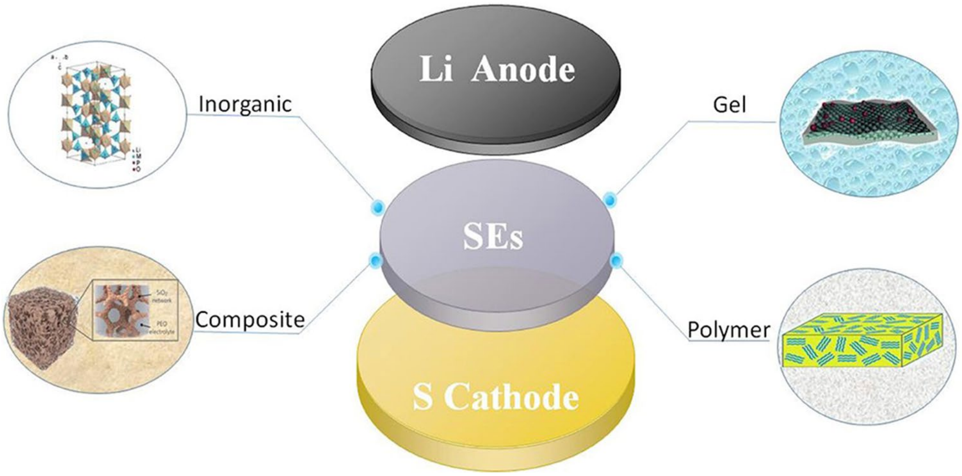

Fig. 6 Li–S battery diagram based on different electrolytes [35]

contact area at the electrolyte and electrode. In order to prevent the shuttle effect of the polysulfides, which are formed during the charge and discharge process, new electrolytes should be studied to ensure the high lithium ion conductivity. Thus, the cycle life of Li–S batteries and the utilization of active sulfur species will be improved.

Traditional liquid electrolyte-based Li–S batteries, shown in Fig. 8a, face some challenges; these challenges mainly come from four undesirable phenomena: (1) the insulating properties of elemental sulfur (ca. 10^{-30} S cm^{-1} at 25 °C) and discharged product Li_2S (ca. 10^{-13} S cm^{-1} at 25 °C), although the interface between the charged and discharged product may be more conductive; (2) the formation, dissolution, and shuttling of Li polysulfide (LiPS) intermediates in the liquid electrolyte; (3) the significant volumetric expansion of sulfur during lithiation; and (4) the poorly controlled and rather unstable Li/electrolyte interface. To mitigate these issues, various strategies have been applied, such as using "host" materials, "interlayer" materials, various "core–shell" particle architectures, concentrated electrolytes, and various electrolyte additives, among many others. However, so far the above approaches could not fully address the existing challenges, particularly for high areal capacity loading battery electrodes (4–10 mAh cm^2), where the fraction of inactive materials (such as foils and separator membranes) is small and which are currently required for attaining lower fabrication cost and higher energy characteristics. In addition, the safety hazards associated with the poor stability of liquid electrolyte in contact with Li metal and the resulting Li metal pulverization, expansion, and dendrite growth-induced thermal runaway remain very serious drawbacks [40, 41].

A potential solution is replacing a liquid electrolyte with a solid-state electrolyte to construct solid-state Li–S batteries. Compared with liquid electrolyte-based Li–S batteries, solid-state Li–S batteries may offer several advantages: (1) the improved cycling ability and increased energy efficiency due to the elimination of LiPS formation and shuttling; (2) the enhanced stability of Li stripping/plating; and (3) greatly improved safety by using the nonflammable solid-state electrolytes that do not evaporate upon thermal runaway and thus do not amplify undesirable fire hazard. In recent years, the trend of developing both quasi-solid-state Li–S batteries (Fig. 8b) and all-solid-state Li–S batteries (Fig. 8c) is increasing rapidly within a research community due to their high energy density and safety showing great potentials for mobile and stationary energy storage systems [41].

Generally, solid electrolytes such as solid polymer electrolytes (SPEs) are single-ion conductors, unlike liquid electrolytes which have the ability to include at least two types of mobile species. The mobile ionic species' concentration in electrolytes is 1 mol/L or greater for energy storage and conversion applications. At these concentrations, the ionic interactions play a significant role by leading to dynamic correlations in the movement of ions, as shown in Fig. 9.

In particular, the ions do not move randomly, but they perform correlated movements which could affect the charge and mass transport properties. The ion movement depends on the ion interactions, which means ions could prefer to move in the same or opposite direction. Moreover, correlated ion movements are mostly relevant to the highly concentrated liquid electrolytes like ionic liquids, solvate ionic liquids, and solvent in salt electrolytes [43–48]. The higher the diffusion coefficient, the higher the ionic conductivity due to the increase in the concentration of mobile ions, which leads to the increase of the conductivity. Yet, the influence of ionic correlations on the conductivity depends strongly on the type of electrolyte whether it is a solid or a liquid electrolyte, also on the concentration of the ionic species. For example in Fig. 9, lithium transference numbers in solid electrolytes are much higher than in liquid electrolytes, which means that the dynamic ion correlations in the bulk are simpler. All of these advantages make SSEs much preferred than liquid electrolytes.

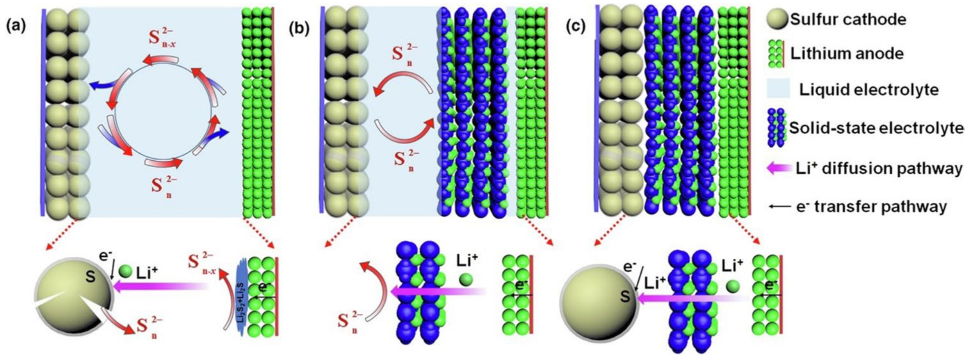

Fig. 8 Schematic illustrations of **a** liquid electrolyte-based Li–S battery, **b** quasi-solid-state Li–S battery, and **c** ALSS Li–S battery [41]

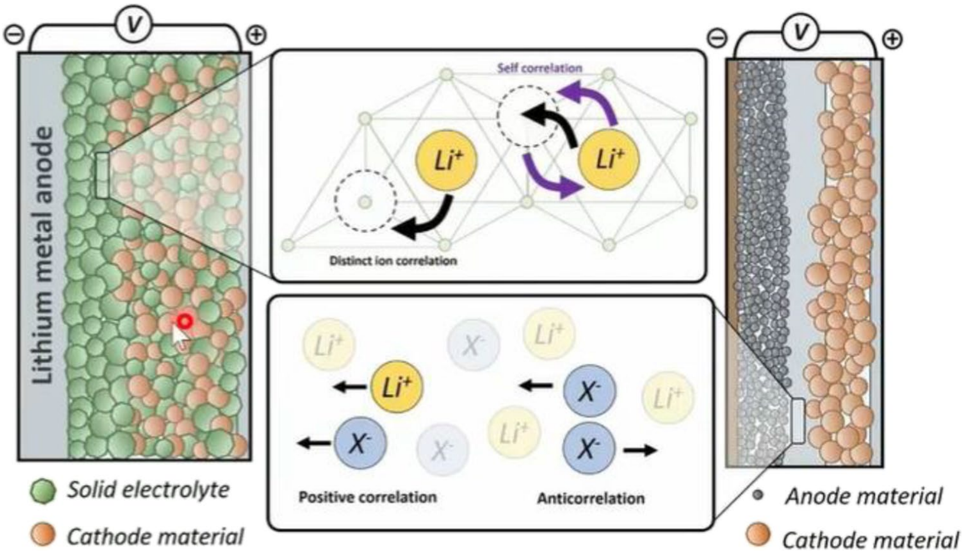

Fig. 9 Graphical representation of all-solid-state batteries SSBs (left side) and of LIBs which contains a liquid electrolyte (right side). The middle part represents the zoomed-in regions which describes the possible ion movements in the electrolyte [42]

Types of SSEs for Li–S batteries

Inorganic solid electrolytes

Inorganic solid electrolytes (ISEs) which are used in Li–S batteries are chemically diverse and even larger than their organic polymer analogs. Most ISEs are sulfide- or phosphate-based with crystalline structures [49], while a smaller selection are of non-crystalline nature (glass–ceramics) including LiPON [50]. The various types of SSEs and their recent developments are summarized in Table 1. Some of these inorganic solid electrolytes were applied in Li–S batteries such as Li_3PS_4 [51], $LiBH_4$-LiCl [52], and Li_2S-P_2S_5 [53]. In addition, some of these ISEs demonstrate higher ionic conductivity compared to liquid electrolytes even at room temperature, such as Li_6PS_5Br [54] and $Li_{10}GeP_2S_{12}$ [55]. Although ISEs have many advantages, they are still restricted by some challenges due to high interfacial resistance, which could lower the overall

Table 1 Comparison between solid-state electrolytes for Li–S batteries in terms of composition and properties

Type of electrolyte	Components	Ionic conductivity ($S{\cdot}cm^{-1}$) at 25 °C	Advantages	Challenges/disadvantages	Ref
Inorganic solid electrolyte (ISE)	Inorganic material and lithium salt	10^{-5} to 10^{-4}	- High ionic conductivity - Outstanding thermal stability	- High interfacial resistance - Low ionic conductivity	[59]
Glass–ceramic electrolyte (GCE)	Inorganic material, lithium salt, and additive	$1-3\times10^{-6}$ (LiPON) 10^{-3} ($Li_7P_3S_{11}$-based)	- Chemically stable - Wide range of electrochemical window - Low interfacial resistance	- Low ionic conductivity (LiPON)	[60–62]
Solid polymer electrolyte (SPE)	Polymer, lithium salt, and additive	$<10^{-5}$	- Low interfacial resistance - Great thermal stability - Safe and flexible	- Low ionic conductivity - Low mechanical strength	[59, 63]
PEO-based solid electrolyte	Polymer-PEO (polyethylene oxide) LiTFSI/polyethylene oxide	6.35×10^{-7}	- Very low mass densities, high flexibility, and suitability with large-scale roll-to-roll manufacturing - High stability of the mechanical properties at the reasonable potentials of charging in the Li–S cell	- Semi-crystalline substances and ion transport take place in amorphous material - Low ionic conductivity at room temperature	[64]

electrode reaction kinetics. Moreover, plenty of the most attractive ISEs are chemically unstable when they come in contact with the Li anode. Researchers have found that the implementation of LiIn [54] and LiAl [56] as anode reduced the interfacial resistance between the anode and SSE. Furthermore, the insertion of an electrolyte layer that is compatible with Li (i.e., unreactive) can prevent physical contact between the SSE and Li anode, which ultimately prevents any reaction between the two interfaces and preserves the integrity of the SSE. For instance, an electrolyte layer composed of Li_2S-P_2S_5-P_2O_5 was added between a $Li_{10}GeP_2S_{12}$ electrolyte and Li anode, resulting in a favorable performance [57, 58].

Crystalline solid electrolytes

A recent study reported the development of a new structure of solid-state Li–S batteries wherein reduced graphene oxide and sulfur nanocomposites are mixed with $Li_{10}GeP_2S_{10}$-acetylene black at the cathode side. This process was done in order to preserve the high ionic conductivity and to lower the stress and strain during the charge/discharge process [55]. Ionic conductivity, being one of the most important criteria in the development of SLSBs, has been extensively researched in the hopes of further enhancing these values. The incorporation of carbon in other various forms in SLSBs has been widely reported to improve ionic conductivity, including Li_2S-carbon nanotubes composite with $Li_{10}GeP_2S_{10}$ [65], Li_3PS_7-mesoporous carbon cathode composite [66], carbonized cotton fiber with $Li_7P_3S_{11}$ coating [67], and low-melting $Li_3I_3(HPN)_2$ with sulfur-3D graphene foam [68]. However, another issue that might arise from this is creating a homogenized composite with sulfur, carbon, and SSE to achieve greater electrochemical performance. As a solution, Alzahrani et al. [69] prepared a sulfur-carbon composite via sulfur vapor deposition and created a "three-component sulfur-carbon-solid electrolyte composite" with Li_3PS_4. The composite as a cathode material for SLSBs achieved higher discharge specific capacity due to greater homogeneity and deeper confinement of sulfur in the composite, compared to the more common preparation methods (sulfur liquid deposition and sulfur solid deposition). On the contrary, the inclusion of carbon in SSE-cathode composites has been observed to result in low Coulombic efficiency (CE) due to SSE oxidative degradation upon contact between carbon and SSE during charge [70, 71]. A solution for this issue is to utilize a sulfur host material such as transition metal sulfides [72–74]. More recently, Xu et al. [74] investigated the electrochemical performance of sulfur/VS_2/Li_3PS_4 composite as cathode for SLSBs. Electrochemical findings have shown that it has achieved 96% CE during the initial cycle and remained at almost 100% throughout cycling, which is an improvement from the CE values from other SLSBs [75–77].

As another strategy to increase the conductivity of crystal ISEs, elemental substitution technique could be effective. For instance, it was corroborated that the conductivity of Li_3PS_4 crystal could be boosted by the incorporation of phosphorus and germanium into the crystal. As a result, $Li_{3.25}P_{0.75}Ge_{0.25}S_4$ crystal shows a high conductivity that reaches 2.2×10^{-3} S cm^{-1} at room temperature condition [78]. To sum up, this solid-state electrolyte has plenty of valuable features in terms of fabrication, electrochemical properties, and safety. Lithium-stuffed garnet-type oxide $Li_7La_3Zr_2O_{12}$ (LLZO) has been largely studied due to its high conductivity (above 10^{-4} S cm^{-1} at room temperature), outstanding thermal performance, and great stability against Li metal anode [38]. LLZO has cubic and tetragonal crystal phases [79–81]. Its cubic crystal structure is shown in Fig. 10A. Figure 10B illustrates the variation of ionic conductivity for the Ba- and Ta-substituted LLZO samples as function of 1000/T. Ba-substitution levels affect both the ionic conductivity and the activation energy. The lattice size of LLBZOT at $x \leq 0.10$ keeps reducing with the increase of

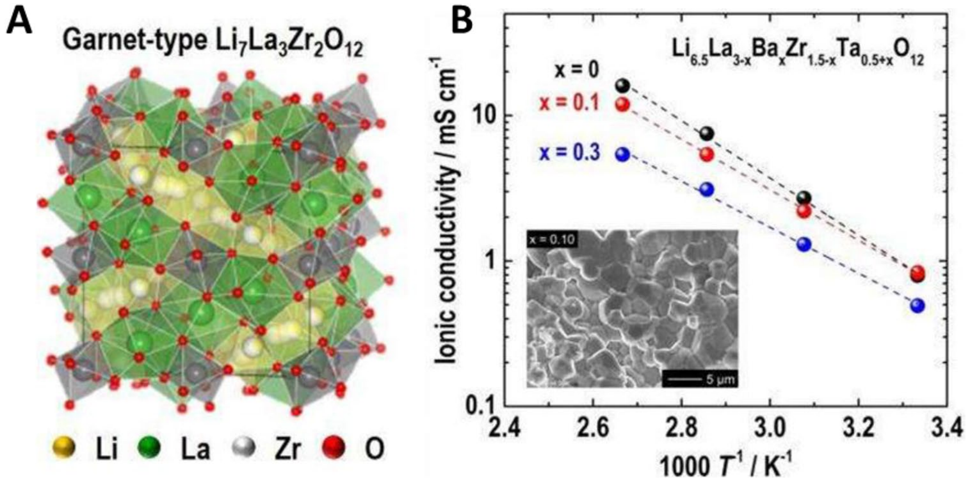

Fig. 10 **A** Schematic representation of the crystal structure of cubic garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) and **B** represents the temperature dependence of ionic conductivity for Ba- and Ta-substituted LLZO with several compositions [82]

x, while the ionic conductivity is slightly increasing at room temperature. Furthermore, the lattice size of Ba- and Ta-substituted LLZO continues to increase with *x*, while ionic conductivity is reduced when *x* is increasing from 0.1 to 0.3.

For Li–S batteries, in order to reduce the interfacial resistance between S and the ion/electron conductive matrix due to the poor ionic/electronic conductivities of S and Li_2S, LLZO nanoparticle-decorated carbon foam (LLZO@C) was synthesized by the one-step facile Pechini sol–gel method. Figure 11 shows that S is uniformly dispersed in the porous carbon matrix. The LLZO-PEO-$LiClO_4$ electrolyte is casted onto the composite cathode directly. Meanwhile, the cathode and electrolyte have very close components, which is beneficial to reduce the interface resistance between the solid-state electrolyte and the cathode electrode. The S cathode constructed from the LLZO@C (Fig. 11) shows remarkable cyclability and can work at the normal human body temperature of 37 °C. Compared to using polymer composites of PEO with ZrO_2 for Li–S batteries operated at 70 °C, and using PEO polymer with LiTNFSI for Li–S battery at 60 °C, LLZO@C work represents a step forward toward lower temperature operation due to the improved ionic and electronic conductivity [83].

Non-crystalline solid electrolytes: glass–ceramics

Glass–ceramic electrolytes (GCEs), which are of amorphous nature, were first introduced and reported in 1992 at Oak Ridge National Laboratory with a thin film material called lithium phosphorous oxynitride (LiPON) as an electrolyte [50]. The material was deposited using radio frequency (RF) magnetron sputtering from Li_3PO_4 target in pure nitrogen gas atmosphere. It was suggested by Fu et al. [84] that thin films of LiPON could be high-temperature materials. Furthermore, it is chemically stable with the lithium metallic anode with a wide electrochemical potential range of 0 to 5.5 V (vs. Li/Li$^+$). All these advantages make it a competitive electrolyte material [85]. However, the bulk-type batteries based on that electrolyte material have insufficient mechanical stability. In addition, LiPON possesses a low Li ionic conductivity of $1-3\times10^{-6}$ S cm^{-1} at 25 °C, which could restrain the further development of batteries with thick LiPON membranes [60]. Recently, there were many studies done on optimizing LiPON electrolyte layer, especially on enhancing the lithium ionic conductivity and investigating the deposition condition [86, 87]. In addition to the thickness optimization [88], the results of these investigations show that the quality of LiPON thin film is extremely sensitive on sputtering power, pressure, nitrogen (N_2) gas atmosphere, and the deposition rate [89]. Crystalline LiPON structures have been synthesized throughout the years but they fail to match the ionic conductivities of amorphous LiPON, even at elevated temperatures [90–92].

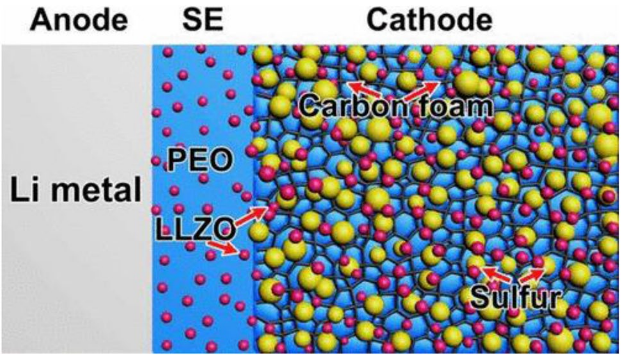

Fig. 11 Schematic illustration of an all solid-state Li–S battery based on LLZO nanostructures. The blue background indicates the PEOLiClO_4 solid polymer electrolyte. The pink and yellow spheres correspond to the LLZO and S particles, respectively [83]

Figures 12a and b represent the 2D and 3D atomic force microscope (AFM) images of lithium-LiPON thin film, respectively. The largest height of surface undulation is 1.6 nm on the Li-LiPON thin film. In those LiPON thin films, the element ratio was studied by executing the inductively coupled plasma (ICP) tests in order to analyze the lithium content in LiPON electrolyte layer. The electrical response of the samples, shown in Fig. 12c, is represented by an equivalent circuit. For example, the resistance R1 is representing the resistance of the Cu current collectors, and CPE1 is representing the constant phase element of the top and bottom Cu-LiPON junctions. The bulk LiPON response is symbolized by the CPE2 element, which is in parallel with R2. The lithium ionic conductivity (σ) of each electrolyte was determined by the evaluation of the high frequency part of the Nyquist diagram $\sigma = d/(R2\times A)$, where d is the thickness of the film, A is the surface area of the metal contact, and R2 is the electrolyte resistance determined from the fitting to equivalent circuit. The electrochemical impedance spectra (EIS) results for N-LiPON electrolyte layer illustrate an increase of ionic conductivity when the working pressure is decreased from 0.5 to 0.2 Pa. It also shows the largest ionic conductivity at 2.4×10^{-6} S cm^{-1} under pressure of 0.2 Pa. Yet when the working pressure is decreasing to 0.08 Pa, the ionic conductivity decreased dramatically. In addition, the fitted results of N-LiPON and Li-LiPON electrolyte layers are showed in Fig. 12c which are measured under pressure of 0.2 Pa. All results confirmed that combining Li in LiPON electrolyte could improve the Li ionic conductivity [93]. Furthermore, Fig. 12d represents the cycle dependence on the discharge capacities of thin film lithium batteries (TFLBs) at specified rates. All solid-state TFLBs are a promising candidate for micro-power implementations [94]. It could be widely used in smart cards, radio frequency identification, portable electronic devices, and other micro-electromechanical systems. TFLBs are

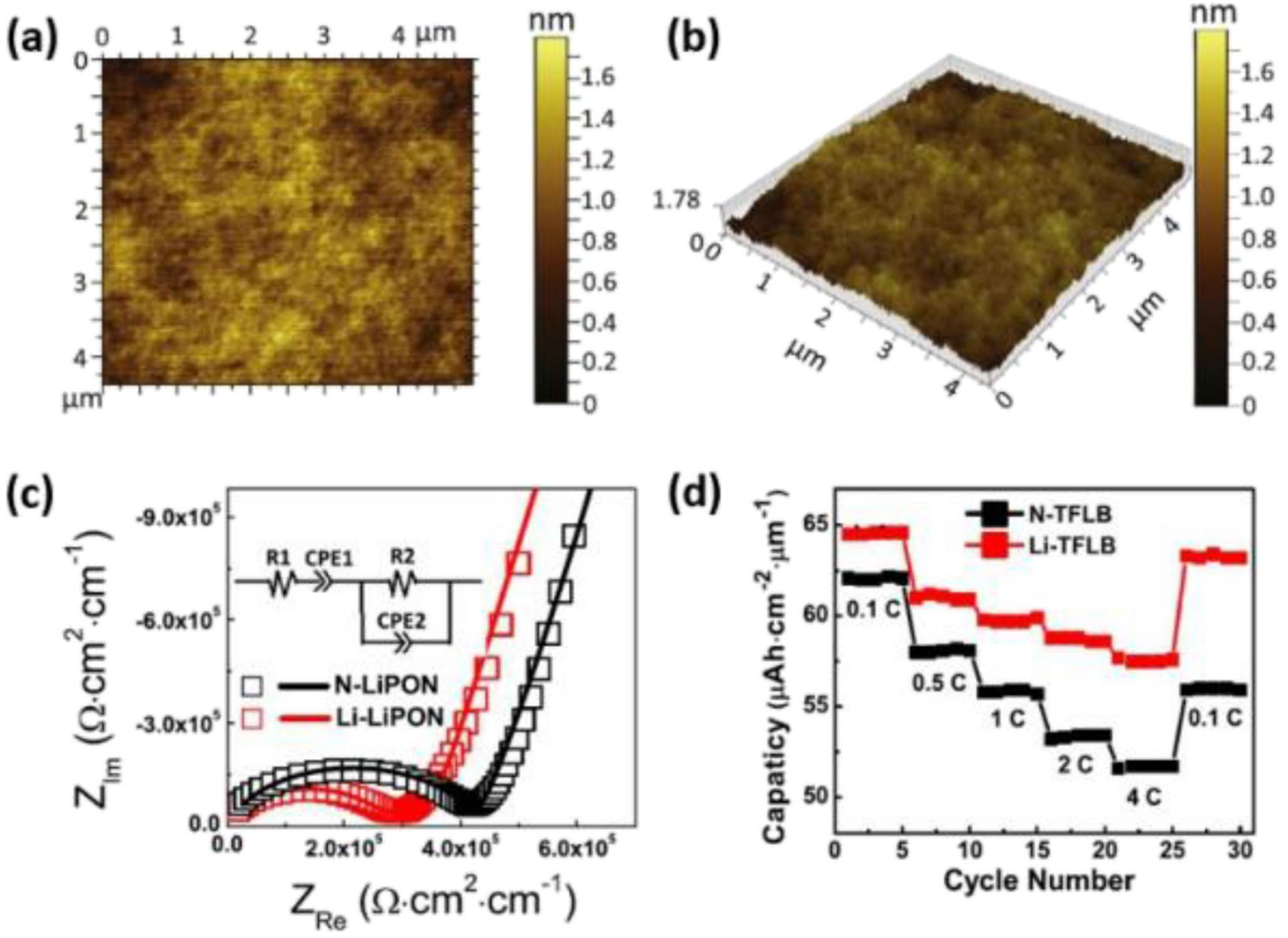

Fig. 12 **a** and **b** represents the 2D and 3D atomic force microscope (AFM) images of Li-LiPON electrolyte thin film, respectively. **c** The electrochemical impedance spectra of electrolyte layers and **d** cycle dependence on the discharge capacities for thin film lithium batteries (TFLBs) at specific rates [95]

comprised of a cathode layer, an electrolyte layer, and an anode layer. The discharge capacity for N-TFLB decreased from 62.1 $\mu Ah\cdot cm^{-2}\cdot \mu m^{-1}$ at 0.1 C to 51.7 $\mu Ah\ cm^{-2}\cdot \mu m^{-1}$ at 4 C. However, the degradation of Li-TFLB is noticeably slighter than N-TFLB.

For Li–S batteries, the LiPON coating serves as an electrochemically stable, mechanically robust, and highly ionic conductive interfacial layer for Li metal anodes. The coating has the ability to minimize the corrosive reactions with dissolved sulfur, soluble lithium polysulfides or organic electrolytes, and resisting the incursion of Li dendrites at the Li/LiPON interface. As such, LiPON-coated Li metal cells exhibited a very stable and dendrite-free cycling for over 900 cycles at a high current density of 3 mA cm^{-2}. In addition, using the LiPON-coated Li as anode, the Li–S cells demonstrated a large capacity and a significantly enhanced cycle performance, even in high-energy–density pouch cells (Fig. 13). This facile and effective approach opens a new route for stabilizing the Li metal anode and could lead to the practical application in the field of rechargeable Li metal batteries [96].

Glass–ceramic electrolytes in general have many various advantages as they possess isotropic properties, which eases the ion migration and facilitates the control of properties by changing the chemical compositions [97]. On the other hand, GCEs also face some challenges as they are extremely sensitive to humidity and air [33]. A recent study developed a superionic conductor glass–ceramic electrolyte ($Li_7Sb_{0.05}P_{2.95}S_{10.5}I_{0.5}$) that is stable in air, highly conductive at room temperature (2.55 mS cm^{-1}), and has a stable electrochemical window of up to 7 V vs. Li^+/Li [61]. Another study doped a sulfide-based SSE ($Li_7P_3S_{11}$) with Nb and O as a way of enhancing electrochemical and chemical performance, forming $Li_{6.988}P_{2.994}Nb_{0.2}S_{10.934}O_{0.6}$ glass–ceramic electrolyte [62]. Results have shown that this novel GCE is also stable in air, has excellent stability against Li, and higher ionic conductivity at room temperature (2.82 mS cm^{-1}), compared to $Li_7P_3S_{11}$. In addition, the newly

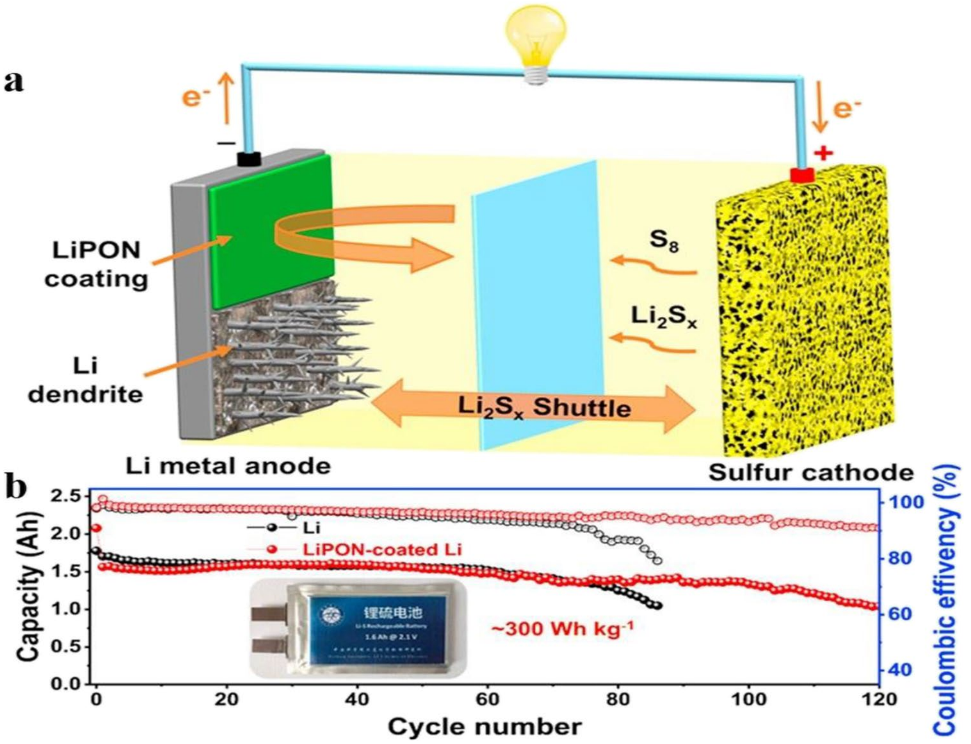

Fig. 13 **a** The performance of a LiPON-coated Li metal anode in Li–S battery configurations; **b** galvanostatic cycling performance of Li–S pouch cells at 0.79 mA cm^{-2} [96]

synthesized GCE exhibited lower interfacial resistance compared to $Li_7P_3S_{11}$, which has resulted in high discharge capacity and ≈100% Coulombic efficiency.

Oxidative stability of ISEs

In order to determine the kinetic stability limit of the electrolytes against oxidation (using carbon C65), cyclic voltammetry was conducted. Dewald et al. reported a model case investigation by comparing with solid-state batteries while excluding the reactions with active materials. The stability limits against oxidation are illustrated in Fig. 14 [98], in addition to the theoretical predictions of the stability windows [36]. Figure 15 shows the stability of thiophosphate solid electrolytes, the practical stability window, and the redox of decomposition products. The results obtained show that the oxidative stability of these electrolytes is higher than the predicted values. Moreover, the materials are partially unstable against the typical cathode materials, which may be solved by the use of coatings.

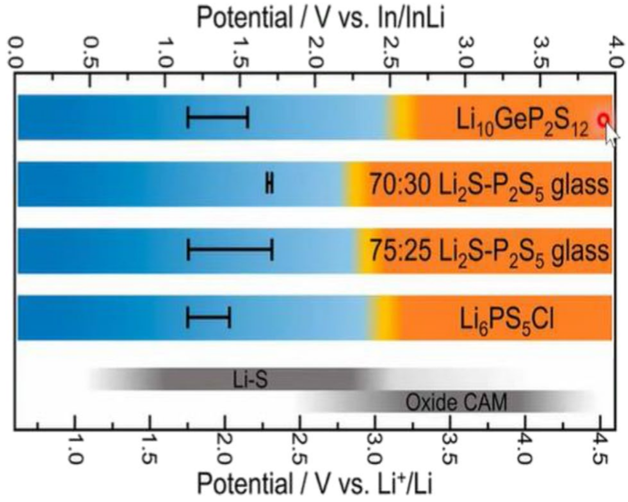

Fig. 14 The practical oxidative stability limit of thiophosphate-based solid electrolytes ($Li_{10}GeP_2S_{12}$, 70:30 Li_2S-P_2S_5 glass, and Li_6PS_5Cl) vs. a carbon composite electrode which is indium metal counter electrode. The stability region of each electrolyte is illustrated in blue and the oxidative decomposition is represented in orange [98]

Round-robin approach was performed using several lithium argyrodites which exhibits different orders of magnitude with various ionic conductivities as reference materials. Nowadays, rapid ionic conductors such as lithium and sodium thiophosphates are deeply investigated for their implementation in all-solid-state batteries [40, 100]. Recent studies show that there is several Li$^+$- and Na$^+$-based materials, such as the thiophosphates $Li_{10+x}M_{1-x}P_{2+x}S_{12}$ {M = Si, Ge, Sn} [78, 101–105], Li_2S-P_2S_5 glasses [106–112], and Li_6PS_5X {X = Cl, Br, I} [113–118]. All of these materials can offer an ionic conductivity which is higher than 1 mS cm^{-1}, making them applicable for solid-state battery implementations. The stepwise cyclic voltammetry and X-ray photoemission illustrate the oxidative decomposition of the tested electrolytes which are $Li_{10}GeP_2S_{12}$, 70:30 Li_2S-P_2S_5 glass, and Li_6PS_5Cl electrolytes. Most of the electrolytes

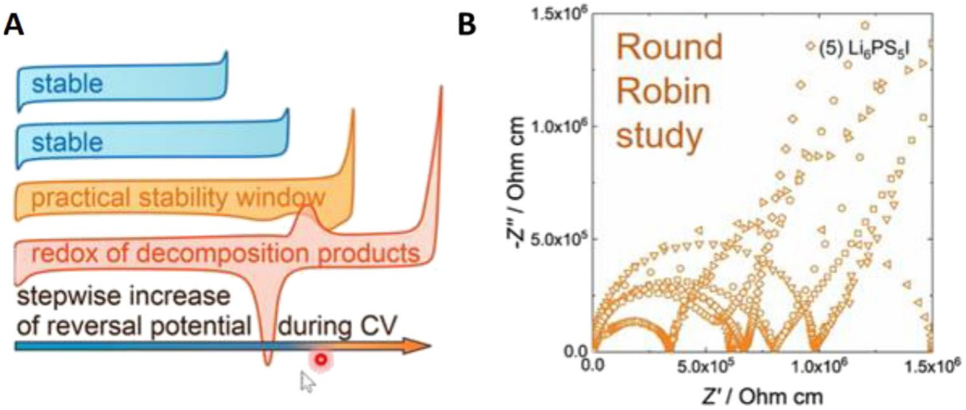

Fig. 15 **A** Schematic representation that shows the stability of thiophosphate solid electrolytes [98], **B** round-robin study [99]

exhibit a high oxidative stability limit (between 2.3 and 2.6 V vs. In/InLi, which corresponds to 2.9 V and 3.2 V vs. Li + /Li) when measured against an electrode which is composed of carbon unlike the theoretical calculations. In addition, the results illustrate that the practical oxidative stability limits are much higher than the theoretical values. Furthermore, in order to provide higher electrode stability with the active cathode materials, coating could be included. Finally, by increasing the electrolyte stability, long-time cycling stability of SSBs could be increased.

Solid polymer electrolytes

Solid polymer electrolytes (SPEs) are safer and have better flexibility compared to other SSEs and liquid electrolytes. These advantages make SPEs one of the promising electrolyte candidates for all kinds of solid-state Li batteries including Li-ion, Li-air, and Li–S batteries [119].

SSLSB typically use lithium metal as the anode to achieve high energy density. The cathode is usually a mixture of sulfur/carbon/electrolyte composite. This is because of the insulating nature of sulfur and Li_2S. Carbon materials serve as electron conductors and solid electrolytes serve as Li-ion conductors. Sulfur should be in good contact with both electron conductor and Li-ion conductor to ensure high sulfur utilization. Some examples of polymer electrolytes for Li–S batteries are polyethylene oxide-based electrolytes and composite polymer electrolytes [120].

PEO-based solid electrolytes

Studies on SPEs initiated from the discovery of polyethylene oxide (PEO) complexes by Wright and his colleagues in 1973 [121]. PEO could easily convert to crystalline form at room temperature which prevents the Li-ion migration. Lithium ion migration depends on the movement of polymer chains and usually takes place in amorphous phases [122, 123]. Therefore, PEO-based batteries usually work at temperature higher than the melting temperature of the PEO itself, generally over 80 °C. Yet, PEO homopolymer is a liquid with high viscosity under these conditions, which makes it mechanically very weak to reduce the growth of Li metal dendrites while cycling [124, 125]. This has led to the exploration of PEO combined with lithium salts, in which lithium salts could be dissolved by the polymer solvent in order to form the cations and anions in the solid polymer electrolyte system [63, 126]. In particular, Li^+ cations are solvated by the polymer, making it more dynamic when moving through the polymer chains (see Fig. 16). However, the free Li^+ cations have the ability to move significantly through the chain, which could affect the Li^+ transportability in the SPE system, and ultimately affect the performance of the batteries.

Many studies were done in order to enhance the ionic conductivity and mechanical properties of PEO-based SPEs. In addition, these were conducted to gain more understanding of the conductivity mechanisms since the movement of Li^+ ions in SPEs at room temperature is much less than in liquid electrolytes, even less than ISEs. Some strategies to improve ionic conductivity include the utilization of nanosized fillers and nanostructured block/grafted copolymers, which help in promoting the formation of localized amorphous regions [128, 129]. The addition of fillers to SPEs gives rise to a new type of SSE: composite polymer electrolytes (CPEs). Figure 17 shows that the addition of nanosized inorganic fillers or the modification with block polymers has the ability to interrupt the structural order of the polymer matrix and boost the content of amorphous phase, resulting in the transfer of Li^+ ions [130–133].

Since the discovery of the ionic conductivity of PEO complexes combined with alkali metal salts almost 40 years ago, PEOs combined with oligoether constitutes (-CH2-CH2-O-)n were studied in an extensive way [135]. In general, polymers such as PEO are able to enhance the ion pair dissociation by coordinating with the Li^+ cation in the salt. This kind of electrolytes could be synthesized easily and has very low mass densities, high flexibility, and suitability with large-scale roll-to-roll manufacturing, which makes them attractive. However, PEO-based

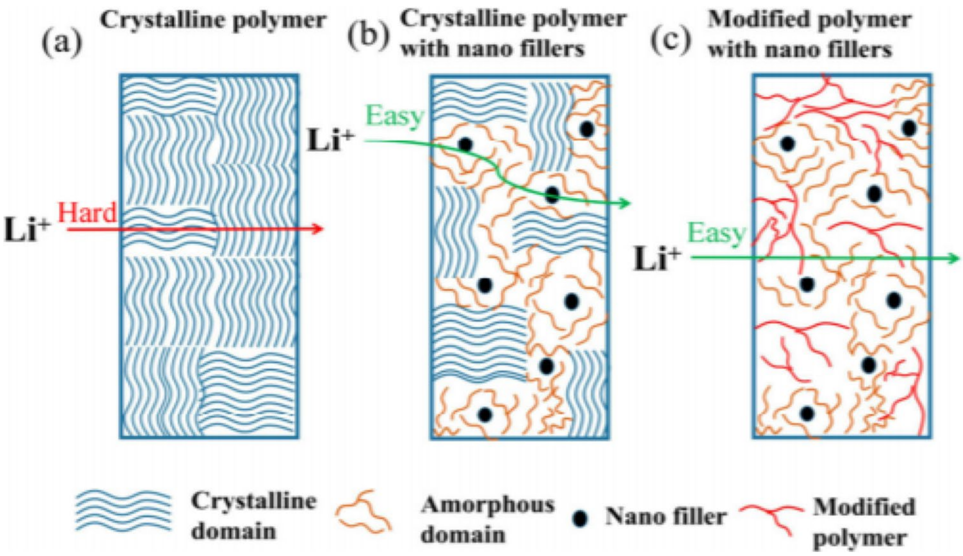

Fig. 16 Schematic representation of Li-ion transfer across three different kinds of polymers: **a** a crystalline polymer, **b** crystalline polymer with nanofillers, and **c** a modified polymer with nanofillers [127]

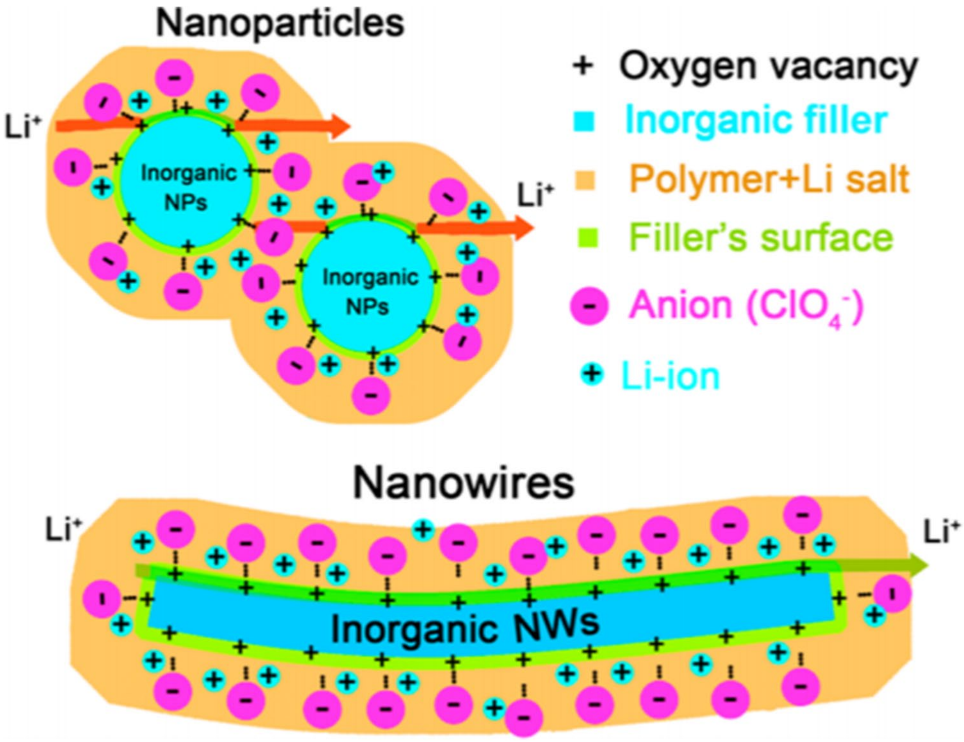

Fig. 17 Schematic representation for lithium-ion transport in the composite polymer (with nanoparticles and nanowires) [134]

electrolytes face some challenges since these polymers are semi-crystalline substances, and ion transport generally takes place in amorphous phase. Furthermore, SPEs often require a high temperature (> 60 °C) to achieve high ionic conductivity [136–138], which restricts their applications to SLSBs that function at room temperature. Moreover, elevated temperatures will ultimately diminish the ability of SPEs to suppress the shuttle effect [35, 139] and Li dendritic growth [140]. Low ionic conductivity of 6.35×10^{-7} S cm^{-1} at temperature of 25 °C has been reported for PEO-based polymer (PEO/LiTFSI) (Fig. 18) [141]. More recent developments in CPEs include PEO-$LiBH_4$ composite electrolyte with SiO_2 nanofillers [142], cyclopropenium cationic-based covalent organic polymer as fillers [143], and cathode-supported-electrolyte [144]. The latter provides better contact between SSE and electrode than the conventional lamination method; therefore, reduced interfacial resistance and enhanced electrochemical performance were observed [144]. However, it is worth noting that these reported developments still require elevated temperatures due to PEO's low ionic conductivity at room temperature.

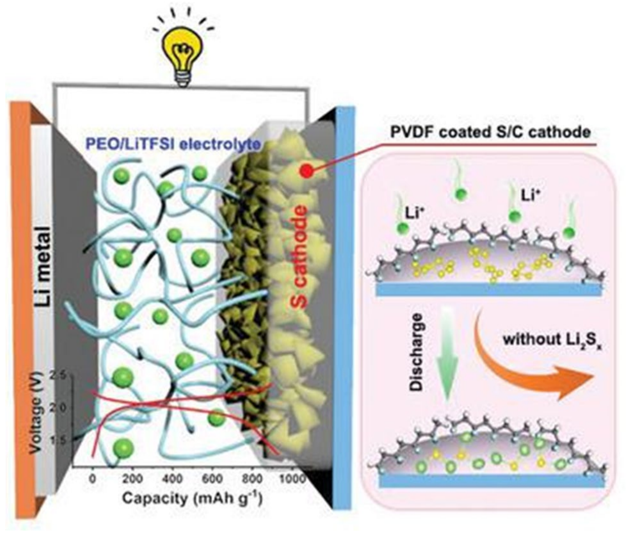

Fig. 18 Schematic illustration of solid-state lithium-sulfur battery that used PEO/LiTFSI electrolyte and a polyvinylidene fluoride (PVDF)-coated cathode [145]

Many studies have been performed in order to develop new strategies and technologies to improve this type of electrolytes and boost their ionic conductivity. It was found that the strong interaction of nanosized fillers with the polymer or salt causes disruption in the crystallization of PEO, resulting in an amorphous phase with higher conductivity at room temperature [64]. Furthermore, the dispersion of nanofillers including ZrO_2 [146], montmorillonite clays [147]. SiO_2 [148], and cornstarch [149] in PEO can enhance ionic conductivity of PEO at room temperature. Moreover, some fillers can form thinner and more compacted layer with increased conductivity in all solid-state Li–S batteries, such as LiN_3 [150]. The same effect was observed with the addition of P_2S_5 into PEO-based SPE, as well as increased interfacial stability between SSE and electrodes and suppression of Li dendritic growth and shuttle effect of polysulfides. In addition, improved cycling performance and high Coulombic efficiency were achieved in the solid-state Li–S cell [151]. Other strategies involve the use of a bilayer electrolyte (layer of Li^+-intercalating material with SPE) [152] and the inclusion of a conductive carbon nanotubes interlayer [153], with operating temperatures of 25 and 35 °C, respectively.

Polyvinylidene fluoride (PVDF) coating was used as a binder in the sulfur cathode, as shown in Fig. 18. As a result, the cycling performance of PEO-based Li–S cells has considerably improved by inhibiting the formation of polysulfides with the PVDF polymer. The long chains of polysulfide intermediates were not produced in the PVDF-coated S-cathode during cycling, which shows a direct transformation of sulfur to solid Li_2S_2/Li_2S. Therefore, the solid Li–S cells preserve the reversible discharge capacity of 630 mAh g^{-1} after 60 cycles (at 0.05 mA cm^{-2} and 55 °C). In addition, the implementation of the solid–solid step reaction in PEO-based SSLBs provides an additional path for the development of high-energy Li–S batteries which are characterized by a long cycle stability [145]. In a similar manner, Garbayo et al. [154] investigated the effect of alumina nanofilm coating on the PEO-based membrane (cathode-electrolyte interface). Despite having a lower initial discharge capacity than its uncoated counterpart, the coated membrane achieved considerably longer cycling (120 cycles) with almost 100% Coulombic efficiency.

As mentioned previously, many approaches were done to improve the ionic conductivity and mechanical properties of PEO-based SPEs. This includes the utilization of nanosized fillers to provide a higher surface area that (i) allows efficient contact with electrolytes, (ii) improves the cell capacity, (iii) shortens the lithium diffusion pathways, and (iv) facilitates the lithium insertion-extraction reaction compared to their traditional bulk counterparts. Furthermore, adding nanoparticles such as SiO_2, Al_2O_3, and TiO_2 could prevent the local reorganization of chains in the polymer and reduce polymer crystallization, which makes the lithium ion transport higher. Meanwhile, copious studies showed that the Lewis acid–base model interactions could support the increase in ionic conductivity, which make it an interesting approach to enhance the electrochemical performance of composite polymer electrolytes [155].

Composite polymer electrolytes

It is known that Lewis acid sites inserted on the filler surfaces could strongly interact with anions of salt, release the positively charged lithium ions, and enhance the ionic conductivity of the composite polymer [128, 156–161]. Oxygen-ion conducting ceramics, which are improved for solid oxide fuel cells and sensors, are capable of achieving these effects due to high ionic conductivity and high stability (chemically, thermodynamically, and mechanically) over a large temperature and oxygen partial pressure ranges. Y_2O_3-doped ZrO_2 (YSZ) is an example of the most credible oxide-ion conductors at very high temperatures [162–167]. The oxygen vacancies located in YSZ have a positive charge and can act as Lewis acid sites in the composite polymer electrolyte, as illustrated in Fig. 15. The oxygen-ion conducting YSZ nanowires can improve the ionic conductivity of PAN-$LiClO_4$ polymer electrolyte in an efficient way. In addition, Liu et al. [168] utilized nanowires instead of nanoparticles as results from their previous study revealed that nanowires allowed higher continuous ion conducting across longer distance, as well as the creation of an effective percolation network, unlike nanoparticles which are isolated as shown in Fig. 17.

Another example of composite polymer for Li–S battery uses an electrolyte membranes fabricated by the incorporation of $Li_{10}SnP_2S_{12}$ into the poly(ethylene oxide) (PEO) matrix using a solution-casting method. The incorporation of $Li_{10}SnP_2S_{12}$ plays a positive role on Li-ionic conductivity, mechanical property, and interfacial stability of the composite electrolyte and thus significantly enhances the electrochemical performance of the solid-state Li–S battery compared to the pure PEO/LiTFSI electrolyte (Fig. 19) [169].

Challenges that face the implementation of solid lithium-sulfur batteries

The implementation of the Li–S technology has been hindered by plenty of practical problems and challenges with the materials of choice or the system itself. The solid-state electrolyte may be a better option than liquid electrolytes due to their efficiency in reducing the dissolution and shuttle of polysulfides. However, the low ionic conductivity and poor interfacial stability, which are associated with the majority of SSEs, could cause more issues when they are used in SLSBs. Despite of the rapidly growing interest in SLSBs, numerous challenges still need to be overcome in both the manufacturing and fundamental understanding of the technology. There are many challenges that face the implementation of solid lithium-sulfur batteries. However, there are two main challenges which must be addressed before the practical application of M lithium to be commercialized in batteries which are the lithium dendrite growth and the low Coulombic efficiency after the long-term charging/discharging processes. Li dendrites are the main issue, which cause internal short circuits, thermal runaway, and may even lead to a significant failure. With traditional liquid electrolytes, the growth of lithium dendrites could be partially prevented by inserting some additives. However, it does not completely solve the issue, especially the safety problems that face the Li metal batteries [22, 170]. Therefore, the best strategy to overcome those issues is by replacing the conventional liquid electrolytes with the SSEs due to their considerable advantages, such as the lack of leakage or flammability in SSEs and the ability to suppress Li dendritic growth through various strategies. However, SSEs still have some disadvantages and challenges that hinder the practical application of all SLSBs in general, such as the complex manufacturing process, extremely poor mechanical strength, and huge interfacial impedance. In addition, the further increase in energy and power density could cause additional issues for SLSBs. Moreover, SSEs tend to have insufficient ionic conductivities, as the ionic conductivity (IC) in ceramic conductors is found to be within the range of 10^{-5} to 10^{-3} S cm^{-1}, which is lower than the IC of organic liquid electrolytes (LEs) (usually 10^{-2} S cm^{-1}). Furthermore, there is poor interfacial compatibility between electrode and SSE. Generally, the high solid–solid interfacial resistances are produced after the first charging process because of the high strain and stress produced at the interface. Also, the suitable interfaces between the Li metal anode and SSEs are very difficult to be formed due to the existence of grain boundaries, which are on the surface of SSEs in bulk SSBs. Another challenge which could prevent the implementation of SLSBs is the insufficient knowledge of the interfacial process after charge and discharge, and the movement of Li ions and the interfacial evolution, which are very crucial for SLSBs [171]. The major challenges in developing solid-state batteries are represented in Fig. 20. The formed SEI between the Li anode and the SSE is represented by $R_{SE/SEI}$. Also, the grains and grain boundaries of SSE are represented by R_{SE} and $R_{SE,gb}$. Mostly, SSEs react with active cathodes which needs to be protected them by coating the active material, as shown in Fig. 20. The red line shows the drop of the electric

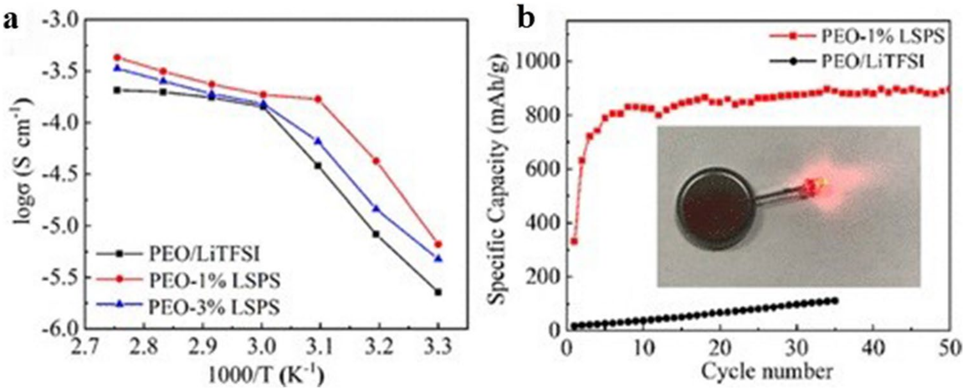

Fig. 19 Pure PEO/LiTFSI, PEO-1%$Li_{10}SnP_2S_{12}$, and PEO-3%$Li_{10}SnP_2S_{12}$ electrolytes for Li–S batteries comparison in terms of **a** temperature dependence of the ionic conductivity of the three polymer electrolytes and **b** cycling performance of the Li–S cells with the PEO-1%LSPS electrolyte and the PEO/LiTFSI electrolyte with a photograph of the solid-state polymer Li–S battery with PEO-1%LSPS lighting a red LED device is inserted in [169]

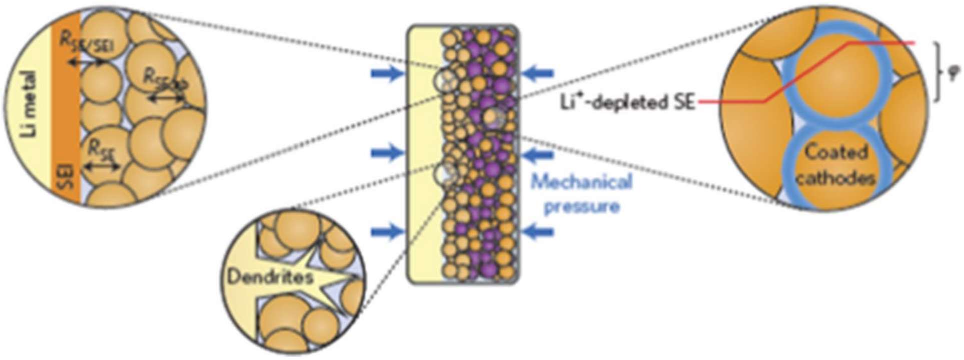

Fig. 20 The major challenges in developing solid-state batteries (SSBs) [40]

potential across the space, while the blue arrows illustrate the mechanical pressure.

The inorganic solid-state electrolytes, such as LLZO and Li_3PS_4, are still suffering from the Li dendrite formation issue [172–174]. The reason behind this could be that Li dendrites grow around the grain boundary of the SSEs. The challenges and the solutions for SSE/electrode interface are illustrated in Table 2

Strategies to overcome challenges with SSEs

As already pointed out, the strategy to upgrade the Li–S battery involves addressing the issues with the electrolyte and anode used. The attention was first focused on the research of suitable electrolytes to replace the common carbonate organic solutions with the goal of addressing the polysulfide solubility issue. In this respect, polymer-like membranes or solvent-free polymer membranes appeared as very promising systems. A valid example of the former is the so-called gel polymer electrolytes (GPEs). One may simply describe GPEs as hybrids consisting of liquid-polymer blends with the liquid component constrained within the polymer matrix (see scheme of Fig. 21). It is proposed that the polymer shell plays the role of a protective layer to prevent contact between the polysulfide cathode products and the inner liquid solutions.

GPEs have many advantages as it combines the advantages of liquid and solid electrolytes, while sharing more similarities with liquid electrolytes [189]. In fact, gel polymer electrolytes are more practical than solid polymer electrolytes, which has led to its earlier commercialization than SPEs. These electrolytes are extremely attractive due to their very low volatility, high thermal stability, and safety [190]. One of the most used polymers in GPEs is polyvinylidene fluoride (PVDF) since it has a strong electron-withdrawing functional group (–F). Polymers based on PVDF could possess an extremely high anodic stability. The high dielectric constant increases the ionization of lithium salts by providing a high concentration of charge carriers [191].

Table 2 Challenges and proposed solutions for PEO- and LLZO-based solid-state electrolyte for Li–S batteries

Solid-state electrolyte (SSE)	Interface challenges toward Li anode	Solutions for SSE/Li anode interface	Interface challenges toward cathode	Solutions for SSE/cathode interface
Solid polymer electrolyte polyethylene oxide (PEO-SPE)	Li dendrite formation [175]	Inorganic fillers to improve the mechanical strength and interface stability [176] Rigid support to enhance the mechanical strength [177, 178] Cross-linked polymer to improve the mechanical strength [179]	Electrochemical oxidation of PEO at very low voltage less than 3.8 V [180]	Interface adjustment with metal oxide and polymer materials [181, 182] Modifying SPE with a high voltage stable polymer electrolyte [183]
LLZO	Poor wettability [175] High interfacial resistance	Interface engineering to obtain the lithiophilic LLZO/Li interface [175]	Poor interface contact [184] High interfacial resistance Side reactions [185]	Co-sintering with low melting point SSE [186] Coat the interface to avoid side reaction [187] Enlargement of SSE/electrode materials contact by porous SSE [188]

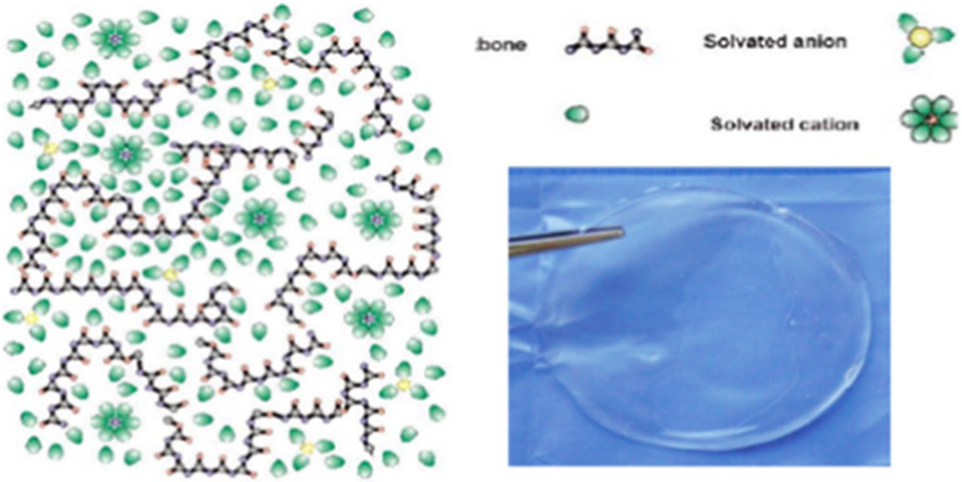

Fig. 21 Scheme and appearance of a gel-type membrane that may be described as formed by a liquid component contained within a polymer network

A more efficient way to stop the dissolution of the reaction products is foreseen to be offered by applying solvent-free, solid-state, lithium conducting membranes, usually called "polymer electrolytes" (PEs). Well-known examples are complexes formed by poly(ethylene oxide) (PEO) and lithium salts complexes, added by small-sized ceramic powders, in order to form the so-called composite polymer electrolytes (CPEs), as shown in Fig. 22. The polymer chains fold around the lithium ions separating them from the corresponding anions. The lithium ion transport occurs via an inter-chain hopping mechanism. Accordingly, fast ion transport requires high chain flexibility, a condition that is only attained between 70 and 90 °C. These membranes demonstrated their effectiveness as separators for Li–S cells with quite interesting results, showing that indeed full cell capacity can be acquired by solid-state, PEO-based polymer Li–S batteries (see Fig. 23).

Evidently, these polymer electrolyte batteries have shown a better performance due to enhanced conductivity between 70 and 90 °C. However, this will not be considered a drawback, especially if the battery is designed for applications and devices that withstand high temperature operation, such as in the electric vehicle sector. In addition, since it is totally liquid-free, these membranes are the only electrolytes that can be safely used in conjunction with a lithium metal anode. Therefore, PEO-based Li–S batteries can also provide a high degree of safety. However, in the cases where the high temperature of operation may be an issue, more conventional liquid electrolytes must be used, which brings back the risk associated with the reactivity of the metallic lithium anode. Consequently, an important step forward in the Li–S battery technology is the replacement of lithium with a more stable and reliable anode. On the other hand, this operation requires adapting the structure of the cell such as to provide the source of lithium ions necessary to drive the electrochemical process. Alternatively, an artificial SEI can be integrated to block contact between Li anode and SSE. This was previously done with Li_3N, which has exhibited increased capacity retention but has failed to inhibit Li dendrite growth over long-term cycling [192]. The latest material to be used

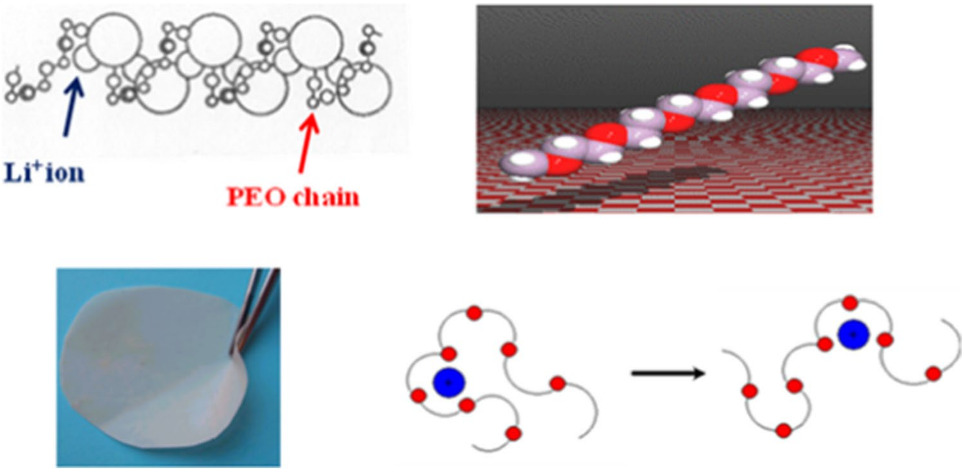

Fig. 22 The poly(ethylene oxide) PEO-lithium salt membrane. Structure, appearance, and conductivity mechanism

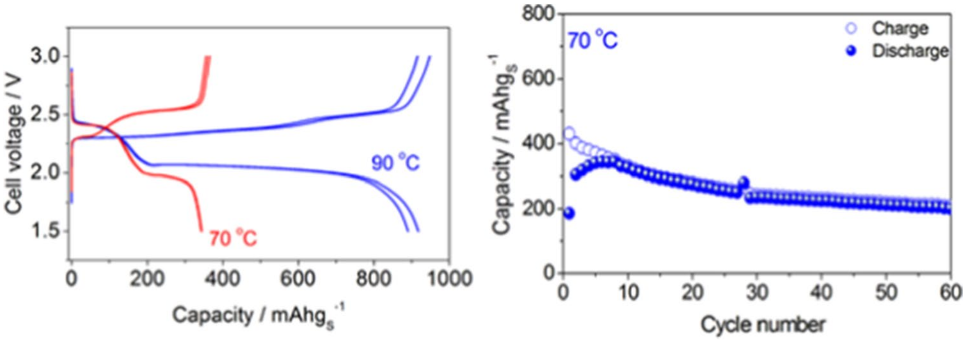

Fig. 23 Charge–discharge voltage profiles and capacity versus cycle number for a Li/CPE/S battery at various temperatures. CPE, $PEO_{20}LiCF_3SO_3Li_2S10\%ZrO_2$

as an artificial SEI is MoS_2, which successfully prevented the breakdown of the electrode–electrolyte interface and delivered high initial and final discharge capacities, 675.8 and 584.1 mAh g^{-1}. Compared to uncoated Li anode, the addition of MoS_2 layer decreased capacity fading from 27.3 to 13.6% after 200 cycles [193].

Conclusion and outlook

Due to several safety concerns, there is a big market for all-solid Li–S batteries. One of the most significant components in all solid-state Li–S batteries is the electrolyte. Ideal electrolytes depend on several criteria and requirements, which include high ionic conductivity, compatibility with electrode materials, and good mechanical properties. In addition, such electrolytes should overcome the challenges that hinder the commercialization of solid-state batteries. In this review paper, recent technologies and progress in previous years for solid-state Li–S batteries were summarized including the historical progress and technical obstacles. Many types of SSEs were reported such as inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), and glass–ceramic electrolytes (GCEs). Although these electrolytes have many advantages as discussed in this review paper, they also have several disadvantages and challenges which need to be resolved in order to proceed toward the practical application and commercialization of solid-state lithium-sulfur batteries. The different kinds of solid-state electrolytes were discussed, as well as their charge transfer, chemical properties, advantages, and challenges that hindered these electrolytes were further explored in detail. In addition, the technical challenges of the implementation of solid-state Li–S batteries were discussed in terms of preparation and design. These issues include the Li dendrite growth and low Coulombic efficiency after long-term cycling. Furthermore, extremely poor mechanical strength, huge interfacial impedance, and insufficient ionic conductivity of SSEs remain to be solved by strategic innovations. In general, ideal solid electrolytes should possess high ionic conductivity at ambient temperatures, electrical insulating properties, wide electrochemical window, and chemical stability. As of now, one of the most promising SSEs and strategies for solid Li–S batteries are GCEs and the development of gel polymer electrolytes (GPEs), respectively, due to their higher ionic conductivities even at room temperature, among others. Addition, GCEs can provide mechanical stability to solid-state Li–S batteries, which other solid electrolytes lack. Besides the advantages of GCEs mentioned above, LiPON coating on Li anode, in particular, has been shown to enhance mechanical and electrochemical stability, minimize corrosive reactions that lead to Li dendritic growth during long-term cycling, and improve cycling performance of solid-state Li–S batteries [96]. Ultimately, this strategy would allow the development of solid-state Li–S batteries for commercial applications. One downside to this is the extreme sensitivity of GCEs to air and humidity; therefore, more attention and development should be focused on resolving this issue. Furthermore, many strategies like using composite polymer electrolytes have been applied to combat other issues such as the suppression of Li dendritic growth and shuttling effect, which have proven to be effective for some. In terms of commercialization, the main factor is the cost of manufacture. Hence, researchers should focus on developing battery materials via simple and cost-effective manufacturing processes that can be easily applied into large-scale operations to enable the viable commercialization of solid-state Li–S batteries. As for GPEs, the liquid–solid hybrid nature consisting of polymeric networks provides a protective layer on electrodes, which avoids unwanted reactions that may lead to Li dendrite formation or other substances that may jeopardize the optimal functioning of batteries. Furthermore, GPEs share similar properties as both liquid and solid electrolytes, which can provide synergistic effects and enhanced practicality in commercial applications. To sum up, solid-state Li–S batteries have great potential to deliver better electrochemical performance than conventional LIBs in the market when combined with the ideal SSE. Continued efforts are needed in developing SSEs to commercialize solid-state Li–S batteries for its role in deploying clean energy and helping to achieve a carbon neutral society.

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