

Review

Polymer Electrolytes for Lithium/Sulfur Batteries

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Abstract: This review evaluates the characteristics and advantages of employing polymer electrolytes in lithium/sulfur (Li/S) batteries. The main highlights of this study constitute detailed information on the advanced developments for solid polymer electrolytes and gel polymer electrolytes, used in the lithium/sulfur battery. This includes an in-depth analysis conducted on the preparation and electrochemical characteristics of the Li/S batteries based on these polymer electrolytes.

Keywords: polymer electrolyte; lithium-sulfur battery; solid polymer electrolyte; gel polymer electrolyte

1. Introduction

With the rapid exhaustion of limited resources such as fossil fuels and their global environmental issues, the modern society's sustainability depends on the development of ecological alternative power sources such as solar and wind energy, and low-emission transportation such as hybrid and electric vehicles. High energy-density batteries are an essential part of such systems and there is an insatiable demand for its improvement. Secondary lithium-ion batteries (LIBs) dominate the market for portable electronics (e.g., cellular phones, notebook computers, camcorders) [1–3], but are still not economically attractive for large scale and transportation applications.

Although tremendous progress has been achieved in the field of LIBs, the transition metal oxides and phosphates typically used as cathode materials have maximum theoretical capacity limited to about 200 mAh g⁻¹ (of which only 170 mAh g⁻¹ can be practically achieved) [4–7]. The energy limitations, along with the high cost and ecological concerns of these materials, can restrict their practical application in large scale scenarios.

An alternative technology under intense development is the lithium/sulfur battery (Li/S). Elemental sulfur has higher theoretical capacity (1672 mAh g⁻¹) and specific energy (2600 Wh kg⁻¹) than conventional cathode materials. Sulfur is also a low cost, abundant, and environmentally friendly natural resource [8], making it a very promising cathode material candidate, especially for large scale energy storage applications [9]. However, Li/S batteries suffer from inefficient utilization of cathode materials and poor cyclability [9,10], both essentially due to the insulating nature of S and the solubility of polysulfides in liquid organic electrolytes [11–14].

Successful operation of Li/S batteries has been achieved through the development of composites of sulfur with carbonaceous [5,15–23] and polymeric [24–27] materials. In these composites, the S particles are embedded into the conductive carbon or polymer matrices [5,21,28], which enhance the electronic conductivity of the composite and hinder the dissolution of polysulfides into the electrolyte [13,14,28–30].

Another strategy to improve the capacity and cyclability of Li/S batteries is the electrolyte optimization so as to reduce the loss of sulfur by dissolution in the liquid electrolyte [14,31–35]. Among the possible electrolyte modifications, replacement of the common liquid organic electrolytes with polymer electrolytes has proved promising and efficient.

Polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable to that of common liquid ionic solutions [36]. Although the study of polymer electrolyte was started in 1973 by Fenton *et al.* [37], its technological importance was appreciated in the early 1980s [38]. Since then, a large number of polymer electrolyte systems have been prepared and characterized. It is possible and convenient to group all the polymer systems into two broad categories, *i.e.*, pure solid polymer electrolyte (SPE) and plasticized or gel polymer electrolyte systems (GPE).

The first category, pure solid polymer electrolyte, is composed of lithium salts (e.g., LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂, LiC(CF₃SO₂)₃) dissolved in high molecular weight polyether hosts, (e.g., PEO and PPO) which acts as solid solvents [39]. The ionic conduction mechanism of SPE is intimately associated with the local segmental motions of the polymer. The second category of polymer electrolyte, gel polymer electrolyte, is characterized by a higher ambient ionic conductivity but poorer mechanical properties when compared with SPE. GPE is usually obtained by incorporating a larger quantity of liquid electrolyte to a polymer matrix that is capable of forming a stable gel polymer host structure.

Polymer electrolytes have several obvious advantages over their liquid electrolyte. Among the advantages of these electrolytes, they include no internal shorting, leakage of electrolytes and no non-combustible reaction products at the electrode surface existing in the liquid electrolytes [40–44]. The pre-requisites for a polymer electrolyte for lithium batteries are: high ionic conductivity at ambient and subambient temperatures, good mechanical strength, appreciable transference number, thermal and electrochemical stabilities, and better compatibility with electrodes [41–43,45]. In particular, for Li/S battery, it is expected that the polymer membrane can act as a physical barrier, which can help control

the dissolution of the sulfide anions from the cathode and also prevent the attack of the same anions at the anode [46].

Herein, this article does not intend to review the modification of cathodes or liquid electrolytes, but it focuses on the applications of polymer electrolytes in Li/S batteries. In this review, the preparation and electrochemical properties of polymer electrolytes are studied based on the catalogue of polymer electrolytes. The electrochemical characteristics of the Li/S batteries based on these polymer electrolytes, related to the performance of their cells, are also discussed here.

2. Dry Solid Polymer Electrolytes in Li/S Batteries

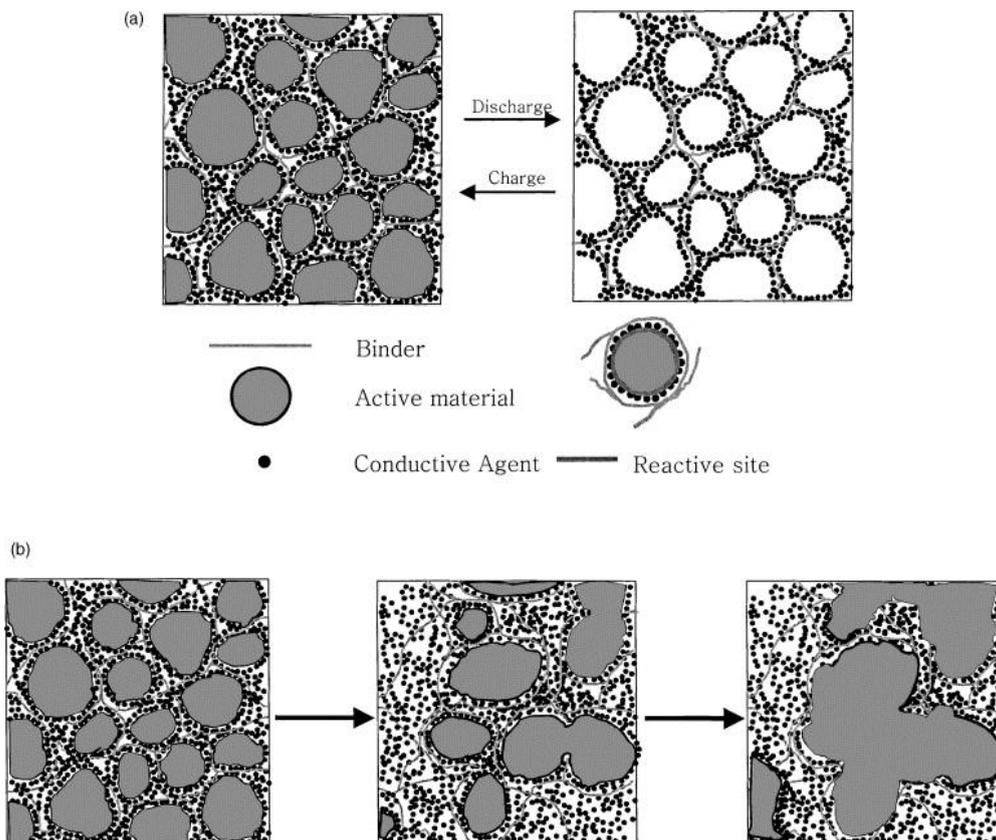
In dry solid polymer electrolytes, the polymer host itself is used as a solid solvent along with lithium salt and it does not contain any organic liquids. As a polymer host, the high molecular weight poly(ethylene oxide) (PEO)-based solid polymer electrolytes are emerging as the best candidates to be used because of their solvation power, complexation ability and ion transport mechanism directly connected with the alkaline salt (Li^+). However, the ionic conductivity of PEO-lithium salts (LiX) electrolytes at ambient temperature (10^{-7} – 10^{-6} S cm^{-1}) is not high enough for most practical applications. In order to overcome this problem, consistent research efforts have been devoted to improve the ionic conductivity of PEO- LiX ($\text{X} = \text{ClO}_4^-$, CF_3SO_3^- , BF_4^- , PF_6^- , *etc.*) solid polymer electrolytes [42,47].

In Jeon *et al.*'s study [48], LiClO_4 was chosen to dissolve in high molecular weight polymer host-PEO which acted as solid solvents. Dry polymer electrolyte made of PEO with tetra(ethylene glycol dimethyl ether) was employed into Li/S cells to study issues such as the fading capacity and low sulfur utilization. According to the change in morphologies for a composite sulfur cathode, which was obtained by scanning electron microscopy (SEM), a model for the change in morphology of the composite cathode was built as shown in Figure 1. The authors offered us a mechanism for the capacity fading was mainly due to the heterogeneity and worsening distribution of sulfur along with cycling.

Some researchers have been trying to further improve the conductivity by the use of inorganic ceramic filler such as Al_2O_3 , SiO_2 , TiO_2 and ZrO_2 in the host polymer matrix [49–57].

In Shin *et al.*'s study [58], $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ polymer electrolyte with titanium oxide ($\text{Ti}_n\text{O}_{2n-1}$, $n = 1, 2$) was introduced into Li/S system, and they not only investigated the ionic conductivity and interfacial stability of this dry polymer electrolyte but also the discharge characteristics of Li/S cells with $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ polymer electrolyte. From the results of this study, titanium oxide is a good candidate as ceramic filler in $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ dry polymer electrolyte. Titanium Oxide filler has a size of sub-micron and several micron consisting of various phases that were prepared by ball milling for 100 h, which were introduced into the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ polymer electrolyte. The addition of titanium oxide containing Ti_2O_3 , TiO and Ti_2O into the $(\text{PEO})_{10}\text{LiCF}_3\text{SO}_3$ polymer electrolyte improved the ionic conductivity due to the change of $-\text{C}-\text{O}-\text{C}-$ vibration and ionic structure of polymer electrolyte by the decrease in crystallinity of PEO polymer electrolyte, and the interface resistance between polymer electrolyte and lithium electrode was remarkably decreased by lowering the contact area between lithium and electrolyte.

Figure 1. Model for morphology change of composite cathode during charge-discharge: (a) ideal case; (b) real case [48].



In Jeong *et al.*'s study [59], $(\text{PEO})_6\text{LiBF}_4$ polymer electrolyte was prepared under three different mixing conditions: stirred polymer electrolyte, ball-milled polymer electrolyte and ball-milled polymer electrolyte with 10 wt % Al_2O_3 . The Li/S cell containing ball-milled $(\text{PEO})_6\text{LiBF}_4\text{-Al}_2\text{O}_3$ polymer electrolyte delivered a high initial discharge of 1670 mAh g^{-1} , which was better than the cells with stirred $(\text{PEO})_6\text{LiBF}_4$ polymer electrolyte or $(\text{PEO})_6\text{LiBF}_4$ ball-milled polymer electrolyte. And also the cycle performance of Li/ $(\text{PEO})_6\text{LiBF}_4$ /S cell was also remarkably improved with the addition of Al_2O_3 .

$(\text{PEO})_{20}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N-}\gamma\text{LiAlO}_2$ was prepared and introduced into Li/S battery in Wen *et al.*'s study [60]. The all-solid-state Li/S cell with PEO based polymer electrolyte operating at $75 \text{ }^\circ\text{C}$ exhibited an average capacity of 290 mAh g^{-1} in 50 cycles. The cycle-stability of Li/S polymer battery was improved by amending the method to prepare the sulfur composite cathode by blending sulfur and PEO by thermal melting at $180 \text{ }^\circ\text{C}$ in a sealed container. The SEM results confirmed the mechanism of capacity fading [48], which suggested that the capacity of Li/S polymer battery was mostly suffered from aggregation of sulfur or lithium sulfide during cycling.

This research group did a further study to combine $(\text{PEO})_{18}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N-SiO}_2$ polymer electrolyte and sulfur/mesoporous-carbon composite cathode as an all solid state polymer battery [29]. The conductivity of the PEO based electrolyte could reach $5 \times 10^{-4} \text{ S cm}^{-1}$ at $70 \text{ }^\circ\text{C}$. In the sulfur cathode, mesoporous carbon sphere with the uniform channels was employed as the conductive agent, and sulfur was penetrated into those channels by a co-heating method. By this, the prepared all solid state polymer battery showed excellent cycling performance with a reversible discharge capacity of about 800 mAh g^{-1} at $70 \text{ }^\circ\text{C}$ after 25 cycles.

In summary, the reason for the choosing PEO as the polymer host is mainly due to that PEO usually form stable dry complexes exhibiting a relatively higher ionic conductivity than other solvating polymers [61]. The sequential oxyethylene group: $-\text{CH}_2-\text{CH}_2-\text{O}-$, and the polar groups: $-\text{O}-$, $-\text{H}-$, $-\text{C}-\text{H}-$, in the polymer chains can well dissolve the ionic salts [43,44,62]. In the further study, new polymer electrolyte structures, based on the modified PEO main polymer chain with grafted polymers, block copolymers, cross-linked polymer networks, which resulted in polymer electrolytes with a lower degree of crystallinity and a low glass transition temperature T_g , can be considered to employed into Li/S battery system.

3. Gel Polymer Electrolytes in Li/S Batteries

In the point of view of dry solid polymer, the main obstacle is still the ionic conductivity, which is generally below $10^{-3} \text{ S cm}^{-1}$ and not enough for practical application. At room temperature, the all solid state Li/S batteries usually showed poor performance. As a result, gel polymer electrolytes were developed [63–65], which can be regarded as an intermediate state between typical liquid electrolytes and dry solid polymer electrolytes. In gel polymer electrolytes, the liquid component is trapped in the polymer matrix, thereby preventing leakage of liquid electrolyte. Therefore, the pore structure of the polymer membrane is the key component and is especially important for the ionic conductivity. In Li/S battery, to date, several types of polymer membranes have been developed and characterized, such as those based on poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP).

3.1. PEO-Based Gel Polymer Electrolyte

Important progress was recently made by Scrosati and co-workers [66], who built a lithium metal-free new battery version as Figure 2 shows. They also renewed the electrolyte component by replacing the common liquid organic solutions with a gel-type polymer membrane, formed by trapping ethylene carbonate/dimethylcarbonate lithium hexafluorophosphate (EC: DMC/LiPF₆) solution saturated with lithium sulfide in a polyethylene oxide/lithium trifluoromethanesulfonate (PEO/LiCF₃SO₃) polymer matrix [67]. A dispersed zirconia ceramic filler enhanced the mechanical properties of the gel and improved liquid retention within its bulk [68]. Impedance studies [69] indicate that the resistance of the as-prepared GPE is low and stable with time with a high conductivity approaching $10^{-2} \text{ S cm}^{-1}$ (Figure 3). With the assembly of the Sn/C anode, Li₂S/C cathode and PEO based GPE, this polymer battery showed a high initial discharge of about 1200 mAh g⁻¹ at 38 mA cm⁻² g⁻¹ (capacity calculated based on Li₂S mass only).

Figure 2. Sketch of the Sn/C/CGPE/ Li₂S/C polymer battery developed herein. The battery is formed by a Sn/C composite anode, a PEO based gel polymer electrolyte, and a Li₂S/C cathode. PEO = poly(ethylene oxide) [66].

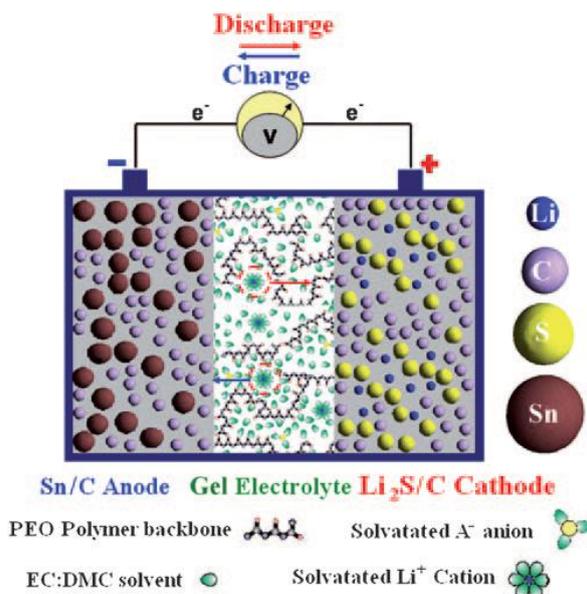
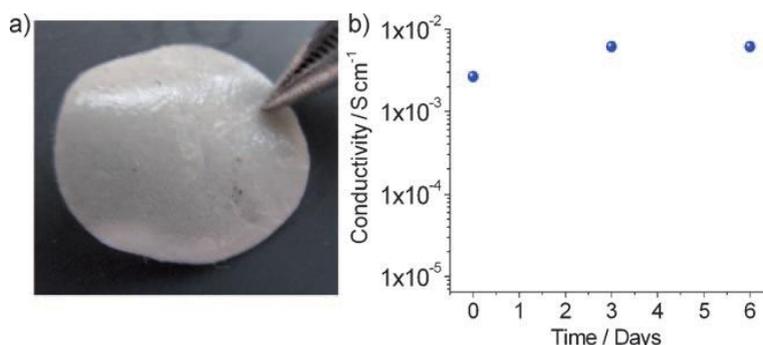


Figure 3. Characteristics of the PEO based gel polymer membrane to be used as electrolyte separator in the lithium-sulfur battery: (a) Appearance of the membrane; (b) Time evolution of the conductivity at room temperature [66].



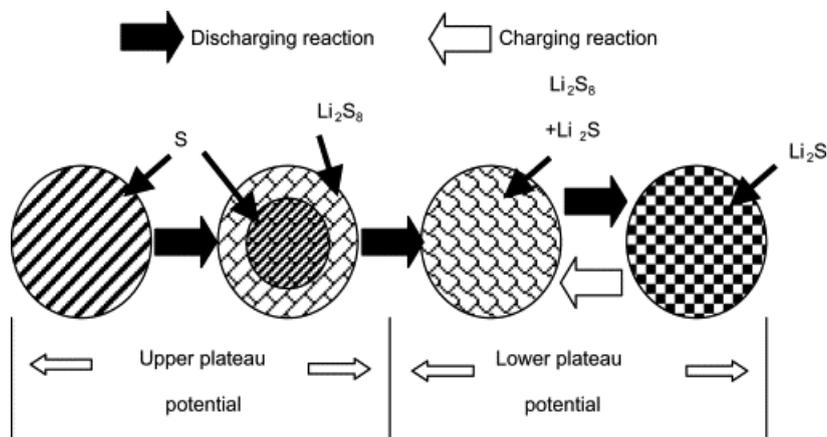
3.2. PVDF-Based Gel Polymer Electrolyte

Poly(vinylidene fluoride) (PVDF) has received great attention as a membrane material with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity [70]. By virtue of its various appealing properties, PVDF has been chosen as a suitable polymer host. PVDF-based polymer electrolytes are expected to be highly anodically stable due to the strongly electron-withdrawing functional group (–C–F). Furthermore, PVDF itself has a high dielectric constant ($\epsilon = 8.4$) for a polymer, which can assist in greater ionization of lithium salts, and thus provide a high concentration of charge carriers [39,71].

A detailed discussion regarding the discharge process of Li/PVDF/S was presented by Ryu *et al.* [72]. The PVDF gel polymer electrolyte was prepared by LiCF₃SO₃ as lithium-ion resource, tetraglyme as plasticizer, and PVDF as a gelling agent in THF solvent in Ar atmosphere. A freestanding PVDF electrolyte film was obtained after the solvent was evaporated at room

temperature. By using PVDF polymer electrolyte, the Li/S cell had two plateaus-like potential regions and a discharge capacity of 1268 mAh g^{-1} at the first discharge. The discharge capacity decreased to 1028 mAh g^{-1} and the upper plateau region disappeared after second discharge. From XRD and DSC results of the sulfur electrode, a model was built as shown in Figure 4 to suggest that elemental sulfur disappeared and changed into Li_2S_n ($n > 4$) at the upper plateau region and Li_2S was formed at the low plateau region.

Figure 4. The discharge and charge reaction model of lithium/sulfur cell [72].



3.3. PVDF-HFP Based Gel Polymer Electrolyte

Poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) has drawn the attention of many researchers due to its appealing properties. The high dielectric constant of $\epsilon = 8.4$ facilitates for higher concentration of charge carriers, and it also comprises of both amorphous and crystalline phase; the amorphous phase of the polymer helps for higher ionic conduction, whereas the crystalline phase acts as a mechanical support for the polymer electrolyte [73–75].

Shin *et al.* [76] reported the preparation and performance of PVDF-HFP gel electrolyte in Li/S batteries. The PVDF-HFP gel polymer electrolyte with tetra ethylene glycol dimethylether (TEGDME) as a plasticizer, LiCF_3SO_3 , LiBF_4 and LiPF_6 as lithium salt and acetone as solvent was prepared by solvent casting of slurry that mixed PVDF-HFP copolymer with acetone and salt using a ball-milling technique. This polymer electrolyte showed high mechanical property and good ionic conductivity ($4.99 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature). As ball-milled gel polymer electrolytes were introduced into Li/S cells with sulfur as cathode and lithium as the anode. The first specific discharge capacities with discharge rate of 0.14 mA cm^{-2} at room temperature were about 575 and 765 mAh g^{-1} . The melting temperature of crystalline PVDF-HFP was found to decrease, which may be due to the decrease of crystallinity by scission of the polymer chain during ball milling. Therefore, it was concluded that the ball-milling technique could be a very promising preparative technique for the preparation of slurry for polymer electrolytes.

In Wang *et al.*'s study [15,24], a gel polymer electrolyte was formed by trapping a liquid electrolyte of PC-EC-DEC (1:4:5 v/v) containing 1 M LiPF_6 in a dry PVDF-HFP/ SiO_2 polymer matrix. And this dry PVDF-HFP/ SiO_2 film with abundant pore structure was prepared by phase separation method. The ionic conductivity of resulting gel polymer electrolyte was about $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at room

temperature. This gel polymer electrolyte was introduced into the cells with sulfur/active carbon composite cathode and sulfur/polyacrylonitrile (S/PAN) composite, respectively. The cell with S/PAN composite cathode exhibited a specific capacity up to 850 mA g^{-1} in the initial and remained above 600 mA h g^{-1} after 50 cycles. With elemental sulfur incorporated in porous carbon, S/C composite exhibited reversible capacity of 440 mA h g^{-1} at current density of 0.3 mA cm^{-2} .

In summary, gel polymer electrolyte was considered as liquid electrolyte trapped in the polymer membrane. When the bulk of the membrane was composed of connected micropores, the ion conductivity of the gel polymer electrolyte mainly depended on the property of the liquid electrolyte. Otherwise, if the prepared membrane did not have many connected pores, the transfer of Li^+ mainly happens in the polymer membrane [77]. Therefore, in the further study, modifying the pore structure of the membrane and changing the crystallinity of the polymer matrix were developed as the most important strategies to improve Li^+ transport and ion conductivity of GPE in Li/S battery. The former was mainly achieved by optimizing the preparation methods and the latter by modifications of polymer matrix, such as blending, copolymer and cross-linking, compounding, and adding nanofillers [77].

4. Conclusions

Li/S batteries provide much hope, but also many challenges. In general, the main problem in an Li/S battery is its poor cyclic ability, which is mainly caused by polysulfides dissolving into the electrolyte. To solve this problem, the polymer electrolyte is introduced into Li/S battery. As discussed above, with employment of a dry polymer electrolyte and gel polymer electrolyte, the cell showed a better cycle performance. However, problems in Li/S batteries, such as aggregation of sulfur or lithium sulfide during cycling, could not be solved merely by modifying the electrolyte. Together with advances in anodes and cathodes, the development of polymer electrolytes with high conductivity, high compatibility and mechanical strength, can offer a promising future for Li/S batteries.

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