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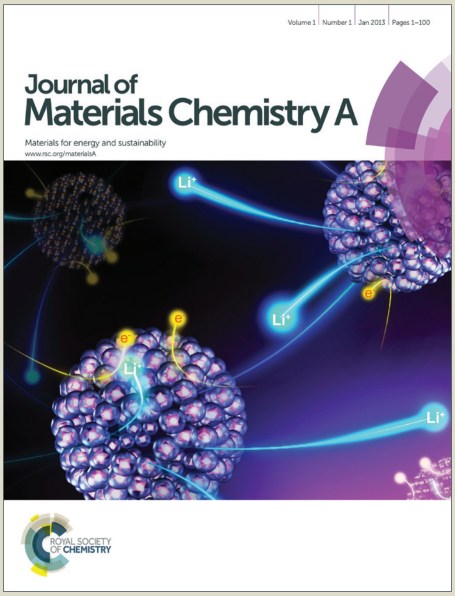

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ARTICLE TYPE

High Performance Lithium-Sulfur Batteries: Advances and Challenges

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The development of high energy batteries is highly attractive to power the future advanced communication equipment and electric vehicles. Lithium-sulfur batteries have attracted much attention in recent years due to their low cost, high theoretical specific capacity and energy density. However, lithium-sulfur batteries have not been commercialized because of their intrinsical shortcomings, including the insulation of the active cathode materials, the high solubility of lithium polysulfides in organic liquid electrolytes, and the dendrite of lithium anode. In this Feature Article, recent research progress in cathode materials, electrolytes, anode materials, and others is reviewed and commented. Some perspectives and directions on future development of lithium-sulfur batteries are pointed out based on knowledge from the literatures and our experience.

1. Introduction

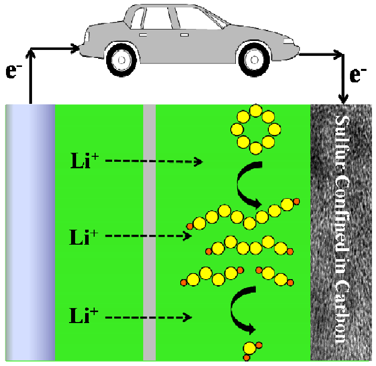
With the rapid development of modern society, widespread concern for energy storage and conversion has been paid in the new century.[1-3] In particular, lithium-ion batteries (LIBs) are promising energy storage devices due to their light weight and high energy density.[4, 5] Thus, they have revolutionized the portable electronics market during the past two decades.[6]

However, LIBs are approaching the energy density limits of the cathode materials based on the intercalation chemistry and safety concerns to support the industrial applications in electric vehicles, plug-in hybrid electric vehicles, and smart grid community systems.[7] Recently, lithium-sulfur (Li-S) batteries based on metal lithium as a negative electrode and elemental sulfur as a positive electrode have attracted considerable attention because of their high theoretical specific capacity (1672 mAh g^{-1}) and high theoretical energy density (2600 Wh kg^{-1}), assuming the complete reaction of lithium and sulfur to form lithium sulfide.[8-10] Specially, Li-S batteries can provide intrinsic protection against overcharge during the discharge process.[11] More importantly, sulfur is naturally abundant, low cost, and environmentally friendly.[12] Therefore, Li-S batteries are considered to be a promising energy storage device for next-generation high energy power system as “green batteries”.[13]

Despite these considerable advantages of Li-S batteries, they still suffer from several drawbacks that restrict their practical application.[14-16] Firstly, the utilization of active materials in cathode is low because sulfur and lithium sulfide are high insulating materials. Secondly, lithium polysulfides intermediates are soluble in organic liquid electrolytes, which lead to a loss of active materials, lithium metal corrosion and self-discharge during charge/discharge process. The so-called “shuttle effect” in Li-S batteries gives rise to severe capacity fade during extended cycling.[17] To understand fundamentally the mechanism and the impact of the components in high energy density Li-S batteries, this Feature Article reviews the recent progresses in improving the specific capacity and cycling performance of sulfur cathodes and relative development of binders, electrolytes, current collectors, anode materials, and characterization techniques to inspire possible strategies to improve the electrochemical performance and advance the practical use of Li-S batteries.

2. Cathode materials

2.1 Effect of carbon materials



Scheme 1. Illustration of the Li-S batteries (the yellow is sulfur and the orange is lithium).

Li-S batteries have two major problems. One is the insulation of the active materials. Nazar *et al.*[8] first reported a simply and broadly applicable method by encapsulating sulfur into the channel of ordered mesoporous carbon (CMK-3), where sulfur generated essentially electric contact with the conductive carbon framework. Recently, many workers pay much attention to carbon materials, which have high electric conductivity to confine sulfur for improving the utilization of the active materials

(**Scheme 1**). They include carbon nanotubes,[18] graphene nanosheets,[19] porous carbon materials[20] and so on.[21, 22] Our group reported that sulfur was encapsulated into hierarchically porous carbon (HPC) derived from the soluble starch with a template of needle-like nano-sized $Mg(OH)_2$.[23] HPC has a relatively high specific surface area of 902.5 m^2 g^{-1} and large total pore volume of 2.60 cm^3 g^{-1}, resulting that a weight percent of sulfur in S/HPC is up to 84 wt%. When evaluated as cathodes for Li-S batteries, the initial discharge capacity of S/HPC is 1269 mAh g^{-1}, which is close to double capacity of the sulfur cathode (667 mAh g^{-1}) in our previous report at the current density of 0.5 C (1 C=1675 mA g^{-1}).[24] The graphitic structure of HPC can enhance electric conductivity and its unique structure could shorten the transport pathway for both ions and electrons during prolonged cycling. Nitrogen atoms have one pair of lone electrons. Therefore, nitrogen-doped carbon materials can further improve the electric conductivity to increase the utilization of active materials. Long *et al.*[25] reported that the nitrogen doping could suppress the diffusion of polysulfide species into the electrolyte *via* an enhanced interface adsorption of the basic nitrogen-rich carbon surface and sulfur. In addition, nitrogen-doped carbon can improve the wettability of carbon materials to favor of the impregnation for electrolyte. Zhang *et al.*[26] reported that a high developed porous nitrogen-doped carbon nanotube (PNCNT) with a high specific surface area (1765 m^2 g^{-1}) and large pore volume (1.28 cm^3 g^{-1}) was synthesized from a tubular polypyrrole (T-PPY). When the S/PNCNT composite is tested as the cathode material for Li-S batteries, the initial discharge capacity is 1341 mAh g^{-1} at a current rate of 1 C. And even after 50 cycles at the same rate, the high reversible capacity still remains at 933 mAh g^{-1}.

Barchasz *et al.*[27] used chronoamperometry technique coupled with UV-visible absorption spectroscopy (UV), high-performance liquid chromatography (HPLC), and electron spin resonance spectroscopy (ESR) to investigate the electrolyte composition at different discharge potentials. The possible mechanism for sulfur reduction as follow:[28]

$$S_8 + 2e^- \rightarrow S_8^{2-} \qquad (1)$$

$$S_8^{2-} \leftrightarrow S_6^{2-} + \tfrac{1}{4}S_8 \qquad (2)$$

$$2S_6^{2-} + 2e^- \leftrightarrow 3S_4^{2-} \qquad (3)$$

$$3S_4^{2-} + 2e^- \leftrightarrow 4S_3^{2-} \qquad (4)$$

$$2S_3^{2-} + 6Li^+ + 2e^- \leftrightarrow 3Li_2S_2 \qquad (5)$$

$$Li_2S_2 + 2Li^+ + 2e^- \leftrightarrow 2Li_2S \qquad (6)$$

The sulfur reduction at around 2.3 V can be assigned to the open ring reduction of S_8 to long chain lithium polysulfides (Li_2S_x, $4 \leq n \leq 8$). These lithium polysulfides are soluble in organic liquid electrolytes, which cause severe capacity fade during repeated cycling. This is the another major problem in Li-S batteries to restrict their commercialisation. Porous carbon materials not only have excellent conductivity, but also their porous channel can effectively adsorb the active materials by physical absorption, capillary effect, to improve the performance of Li-S batteries. Archer *et al.*[29] reported a facile and scalable approach for synthesizing mesoporous hollow carbon capsules that confined elemental sulfur into the carbon framework. They first offer extended cycle life and high charge rate capability. These excellent performances result from sequestration of elemental sulfur in the carbon capsules and favorable effect in limiting polysulfide shuttling. Lou *et al.*[30] effectively confined sulfur in double-shelled "soft" carbon hollow spheres with high surface area and porosity. This carbon-sulfur nanocomposite manifests outstanding electrochemical performance when evaluated as a cathode material for Li-S batteries. The superior cycling performance and rate capability are probably attributed to the facile electronic/ionic transport, enhanced confinement of sulfur/polysulfides, and the excellent structural stability (**Figure 1**). For better confinement sulfur and polysulfides, Zhang *et al.*[31] tailored the nanostructure of graphene nanosheets in aim to create dense nanopores. The nanopores (mean pore size around 3.8 nm) of graphene nanosheets, serving as "micro-reactors" for the electrochemical reactions, suppressed the diffusion of polysulfide intermediates, which resulted in high specific capacity and excellent cycling stability.

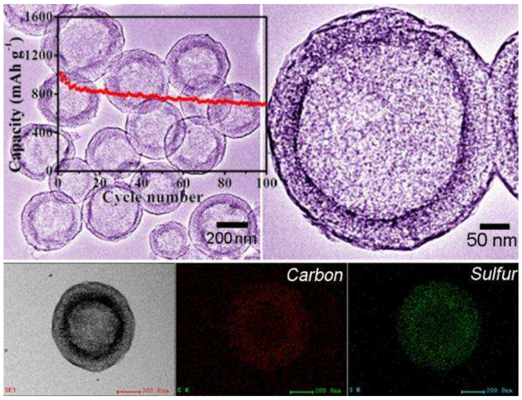
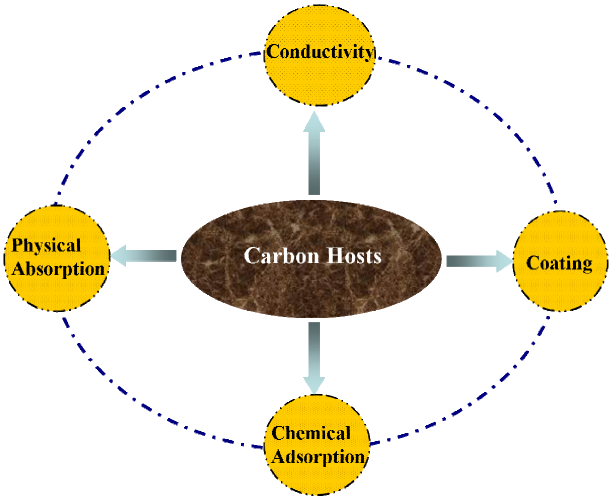


Figure 1. TEM images of the DHCS-S composite and corresponding elemental mapping of a single DHCS-S sphere. Reproduced with permission from ref. 30. Copyright 2012, Wiley-VCH.

With the decrease of pore radius in the carbon hosts, the interaction can be stronger between sulfur and the carbon hosts. Zhang *et al.*[24] reported that encapsulating sulfur into the micropores of hierarchically porous carbon nanoplates (HPCN) derived from metal-organic framework (MOF-5). The HPCN/S exhibits high specific capacities and excellent cycling stabilities owing to the good electrical conductivity of HPCN and a strong adsorption to stably trap sulfur and subsequent polysulfides during cycling, avoiding the shuttle reaction, mass loss of the active materials and the formation of the Li_2S insulating layer on the composite surface. Lou *et al.*[32] also prepared MOF-derived microporous carbon polyhedrons (MPCPs) with abundant and uniform micropores to confine sulfur for Li-S batteries. Encapsulating sulfur into the carbon micropores, Guo *et al.*[33] proposed that sulfur was mainly in the presence of the metastable sulfur allotropes S_{2-4}. The reducing of sulfur directly processes from S_{2-4} to S^{2-}, totally avoiding the unfavorable transition between S_8 and S_4^{2-}. Based on this concept, Li-S batteries exhibit unprecedented electrochemical behavior with high specific capacity and good cycling stability. This method elegantly solves the major problems in Li-S batteries. Not only the pore size distribution of carbon materials, but also the pore volume and specific surface area are key parameters.[34] The large pore volume can increase sulfur loading and accommodate the volume change of active materials. The high specific surface area has the ability to lower the real current density during charge/discharge process, increasing the specific capacity and reducing the polarization for Li-S batteries.

The carbon hosts could absorb the active materials not only by physical absorption, but also by chemical adsorption. Zhang *et al.*[35] used a chemical approach to immobilize sulfur and lithium polysulfides *via* the reactive functional groups on graphene oxide. The nanocomposite cathodes display good reversibility, excellent capacity stability, and rate capability in ionic liquid-based electrolyte, which result from a strong chemical interaction between the active materials and the carbon framework constituted by sp^2-hybridized carbon and the functional group. Zhang *et al.*[36] prepared a three-dimensional hierarchical CNTs/GO/S composite by solution-based chemical reaction-deposition method using graphene oxide (GO) and carbon nanotubes (CNTs) as precursors. They further confirmed that the CNTs/GO composite could absorb lithium polysulfides and improve the electrochemical performance of Li-S batteries by chemical adsorption.

Although the carbon hosts can absorb the active materials, the lithium polysulfides can still escape from the hosts to spread into the electrolyte. Cao *et al.*[37] reported a thermally exfoliated graphene nanosheet-sulfur composite coated with reduced graphene oxide was designed to confine the polysulfides. Yang *et al.*[38] first prepared a novel dual-mode sulfur-based cathode material. The high dispersivity of the GO in the composite is the key factors to adsorb the active materials. Furthermore, conducting polymers is also a kind of good coating layer. Gao *et al.*[39] synthesised polyaniline-coated sulfur/conductive-carbon-black *via* two facile processes. Compared with sulfur/carbon composites, the polyaniline-coated composites showed the optimum electrochemical performance, which resulted from the formation of the unique core/shell structure that restrained the severe shuttle reaction of soluble lithium polysulfides.



Scheme 2. Illustration of the effect of carbon hosts for the active materials in Li-S batteries.

The suitable carbon hosts for Li-S batteries should have high electrical conductivity, the best pore size distribution for physically absorbing polysulfides, special functional groups for chemically absorbing polysulfides, and can coat the lithium polysulfides to improve the specific capacity and cycling performance (**Scheme 2**).

2.2 Metal-Organic Framework

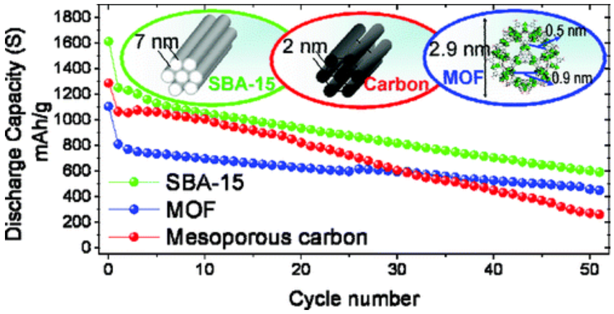


Figure 2. Cycling performance of the MIL-100(Cr)/S@155 + 50%C, mesoporous carbon/sulfur@155, SBA-15/S@155 + 55%C composite under a rate of C/10 for the voltage range between 1.0 and 3.0 V *vs* Li (the inset shows the nanostructure of these three hosts). Reproduced with permission from ref. 42. Copyright 2011, American Chemical Society.

Similar to porous carbonaceous materials, metal-organic framework (MOF) also exhibits high specific surface area and pore volume. In term of these advantages, MOF has been considered for the encapsulation of dense inorganic species in previous reports.[40, 41] Inspired by this, Tarascon *et al.*[42] used chromium trimesate MIL-100(Cr) (MIL: Materiaux Institut Lavoisier), a highly porous and hydrothermally stable MOF, as an improved confined matrix for sulfur impregnation. MIL-100(Cr) consists of an open framework of small mesopores (~2.5-2.9 nm) and micropores (~0.5 and ~0.9 nm) (as shown in the inset of **Figure 2**). During charge/discharge process, the reversible capture and release of the polysulfides by these pores and the weak binding between the polysulfides and the oxygenated framework dramatically increased the capacity retention of sulfur cathodes. Moreover, the approach was generalized to other mesoporous oxide structures. For instance, ordered mesoporous silica (SBA-15) promised the same positive effect as the MOF on the capacity retention. Recently, Xiao *et al.*[43] reported the physical and chemical interactions at molecular level between polysulfides and a Ni-based metal organic framework (Ni-MOF), Ni$_6$(BTB)$_4$(BP)$_3$ (BTB=benzene-1,3,5-tribenzoate and BP=4, 4′-bipyridyl). The capacity retention of Ni-MOF/S electrode achieved up to 89% after 100 cycles at 0.1 C. The interwoven mesopores (~2.8 nm) and micropores (~1.4 nm) of Ni-MOF provided an ideal matrix to better confine polysulfide intermediates. More importantly, the strong interactions between Lewis acidic Ni(II) center and the polysulfide base, which significantly slowed down the migration of soluble polysulfides out of the pores. However, the insulation of the MOF framework blocks the electric conductivity, which leads to low specific capacity of MIL-100/S and Ni-MOF/S systems.

2.3 Effect of oxides

Porous metal oxides also hold promising potentials in enhancing the electrochemical performance of sulfur cathodes.

The enhancement mainly realized through: (i) the catalytic effect of promoting sulfur redox reaction; (ii) the polysulfides adsorbing effect; (iii) acting as second active materials and forming mixed electric/ionic conductor.

For example, nanosized $Mg_{0.6}Ni_{0.4}O$ powders were used as additives in sulfur cathodes.[44] The nanosized oxides were expected to have the catalytic effect and the polysulfides adsorbing effect of dissociating the chemical bond. Because of the effects, the utilization and cycling stability of sulfur was improved. Meanwhile, this metal oxide also exhibited similar effects in enhancing the performance of polyacrylonitrile/sulfur (PAN/S) composite through improving the composite morphology stability and reducing the polarization of the cathode.[45] However, further researches on this oxide are still needed to understand the detailed mechanism.

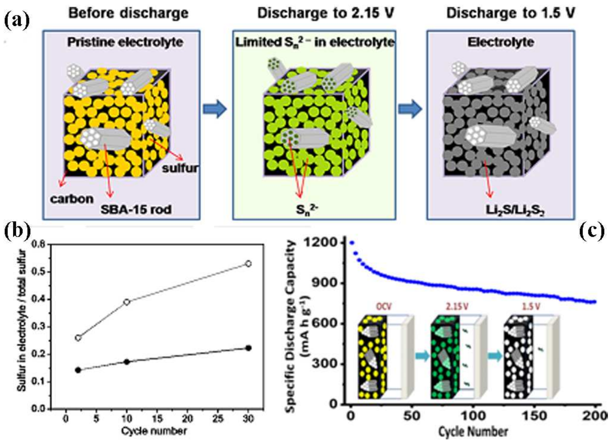


Figure 3. (a) Schematic diagram showing the effect of SBA-15 rods in the electrode on reversibly absorbing/desorbing polysulfide anions. (b) Percentage of sulfur dissolution into the electrolyte from the SCM/S cathode (open dot curve) and from the SBA-15 added SCM/S cathode (solid dot curve). Reproduced with permission from ref. 46. Copyright 2011, Nature Publishing Group. (c) Long-term cycling performance of SCM/S electrode with TiO_2 additive (the inset shows schematic illustrating the concept of polysulfide TiO_2 reservoirs). Reproduced with permission from ref. 47. Copyright 2012, American Chemical Society.

Another method to contain the polysulfides is to provide additives in the cathode matrix that can trap polysulfides. Of notable examples include the work by Nazar *et al.*,[46] who utilized mesoporous silica as an additive to a mesoporous carbon/sulfur electrode (**Figure 3a**). The silica additive was able to absorb polysulfides during intermediate discharge and release them near the end of discharge so that they could be further reduced in the mesoporous carbon. After 30 cycles, the amount of sulfur present in the electrolyte decreased by more than 30% compared with a cell consisting of no silica additive (**Figure 3b**). Based on this concept, they also increased the capacity retention of sulfur cathode through the use of nanocrystalline and mesoporous titania additives as polysulfide reservoirs (**Figure 3c**).[47] The soluble lithium polysulfides could also preferentially absorb within the pores at intermediate discharge/charge, which provided the major factor in stabilizing capacity.

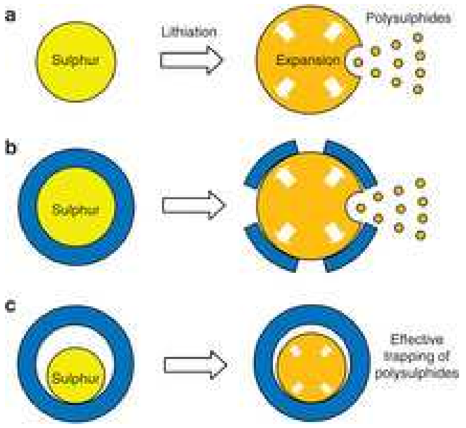


Figure 4. Schematic of the lithiation process in various sulfur-based nanostructure morphologies: (a) bare sulfur particles, (b) sulfur-TiO_2 core-shell nanostructure and (c) sulfur-TiO_2 yolk-shell nanoarchitecture. Reproduced with permission from ref. 48. Copyright 2013, Nature Publishing Group.

On the other hand, oxides could also act as passivating layer on active electrode materials, which have been widely studied for the LIBs electrode materials. Such protective layers have an enormous impact on the capacity stabilization by reducing reactivity with the electrolyte as well as inhibiting dissolution of the active materials. For example, Cui *et al.*[48] reported the rational design of a sulfur-TiO_2 yolk-shell nanoarchitecture for Li-S batteries. As shown in **Figure 4**, the internal void space in the yolk-shell nanostructure accommodated the volume expansion of sulfur, resulting in an intact TiO_2 shell to minimize polysulfide dissolution. Other amorphous oxides layers, such as V_2O_5, SiO_2, Al_2O_3 *ect.* were also coated on the carbon/sulfur surface through surface-initiated growth[49] and plasma-enhanced atomic layer deposition methods.[50] The oxide protecting layer could not only alleviate the dissolution of polysulfides, but also modify the cathode surface to inhibit the irreversible Li_2S deposition. However, these amorphous oxides are insulated, which could decrease the whole electric conductivity of the sulfur cathode. Therefore, the direct deposition of oxide coating layers on the sulfur-based electrode could be a promising strategy to alleviate the dissolution of polysulfide intermediates, but block the electric conductivity of the whole electrode.

Recently, we propose the design of sandwich nanostructured electrode for Li-S batteries.[51] Elemental sulfur was encapsulated into a TiO_2 nanocrystals (3~5 nm) decorating graphene nanosheets host (Graphene/TiO_2). Elemental sulfur occupies the inter-particle mesopores of TiO_2 nanocrystals layer and intimately contact with graphene. The sandwich structural Graphene/TiO_2/S electrode exhibits enhanced cycling stability with high specific capacity. Pore absorption of the Graphene/TiO_2 host and the on-site adsorption of the TiO_2 nanocrystals could alleviate the dissolution and shuttle of the polysulfides. More importantly, the *in situ* formed Li_xTiO_2 synergistically works with highly conductive graphene layer to facilitate easier electric/ionic transport.

In conclusion, oxides could act as effective catalysts and adsorbents to enhance the electrochemical performance of sulfur cathodes. Moreover, oxide coating on the sulfur-based composites or electrodes could be a promising avenue to optimize the electrochemical performance. The coating layers could minimize the solubility of polysulfides. More importantly, these layers could modify the composites and electrodes surface to inhibit the irreversible Li_2S deposition.

2.4 Effect of Binder

Although many efforts have been made to improve the performance of Li-S batteries, such as the design of various composite materials and cathode protection,[52, 53] there are only a few reports on the effects of auxiliary materials in the batteries, such as the binder. In fact, the binder accounting for about 1-10 wt% in electrodes has a great impact on the production process and the final properties. Therefore, it is one of the most important components in the electrodes for Li-S batteries.

In the sulfur cathode, the main effect of the binder is to enhance the contact between active materials and conductive agents and bond the active materials on the current collector.[54] On the other hand, in view of the volume expansion and contraction of the sulfur cathode during the charge/discharge process, suitable binder can play a buffer role to maintain the stability of the electrode structure.[55] In addition to the above effects, the binder needs to have the role of coating the active materials and lithium polysulfides formed in the process of discharge, thus preventing the dissolution of lithium polysulfides and then improving the cycling ability.[56] The binders used in Li-S batteries are generally high molecular polymers, which can be divided into two categories: one kind is organic solvent based binders, using organic solvent as the dispersion agent; another is the aqueous binders, using water as the dispersing agent.

Poly(vinylidene difluoride) (PVDF) is a commonly used binder which has a good adhesion property and high electrochemical stability.[8, 57] However, it is not an ideal binder for Li-S batteries. First, such a non-conductive binder increases the internal resistance of the electrode. Second, serious expansion of its volume at high temperatures will result in the destruction of the electrode. From another point of view, N-methy-l-2-pyrrolidone (NMP), which is used as the solvent to dissolve PVDF, is a toxic organic solvent. In addition, it is reported that NMP can dissolve sulfur to some extent and destroy the structure of active materials, thereby affecting the cycling performance of Li-S batteries.[58, 59]

Another popular binder is poly(ethylene oxide) (PEO), forming a solution with uniform distribution in organic solvents.[60] Lacey *et al.*[61] explored the effects of poly(ethylene oxide)-poly(ethylene glycol) (PEO-PEG) in different forms. PEO4M, PEO200K and PEG are served as binder, coating and electrolyte additive, respectively. Compared to styrene butadiene rubber-sodium carboxyl methyl cellulose (SBR-CMC) as a contrast sample binder, the results show that these three kinds of modification all increased the cycle life. They inferred that the PEO binder and coating have the same mechanism with the PEG, which is soluble in the surrounding electrolyte or forms a gel state to increase the short chain lithium sulfide solubility, thereby slowing the passivation of anode and improving cycle performance. This provides a new perspective for binders used in Li-S batteries.

The binders used above belong to organic solvent binders. Since most organic solvents are toxic and expensive, they are not suitable for large-scale industrial production. By contrast, aqueous binders with water as solvent have many advantages,[62] such as no solvent release, environmentally friendly, low cost and safety. Thus, the aqueous binder is a promising kind of binders. At present, the commonly used aqueous binders are: gelatin,[63] cyclodextrin,[64] and poly acrylic acid (PAA).[65]

Yuan *et al.*[66] reported the preparation of sulfur electrode by using water as solvent and SBR-CMC as binder. The research indicates that SBR-CMC mixture has high adhesion and strong dispersion, which facilitates the uniform distribution of the insulating sulfur with conductive carbon black to improve the sulfur utilization. The SBR-CMC binder can inhibit the agglomeration of Li_2S, thus stabilizing the cathod structure. The discharge capacity of SBR-CMC sulfur cathode is as high as 580 mAh g^{-1} after 60 cycles at the current density of 100 mA g^{-1}, while the discharge capacity of PVDF sulfur cathode is only 370 mAh g^{-1}.

The electrochemical performance of Li-S batteries used cyclodextrin was superior to the one with PVDF, polytetrafluoroethylene and gelatin (the film thickness of electrodes is 25 μm).[67] An appropriate binder for sulfur cathodes was obtained *via* a partial carbonylation of β-cyclodextrin in H_2O_2.[64] The modifide binder, carbonyl-β-cyclodextrin (C-β-CD), exhibited a high water solubility and strong bonding strength. These characteristics ensured the formation of a gel film, tightly wrapping the surface of the sulfur composite and suppressing its aggregation. The sulfur cathode with C-β-CD showed a reversible capacity of 1542.7 mAh g^{-1} and still remained at 1456 mAh g^{-1} after 50 cycles.

Zhang[68] believes that Li-S batteries are a liquid electrochemical system. During the charging process, sulfur in the electrode transforms into long-chain lithium polysulfides, which are dissolved in the electrolyte to leave a hollow structure. The oxidation of lithium sulfide to solid sulfur fills the vacancy at the finally stage. This process requires a suitable binder to sustain a stable electrode structure, preventing the collapse of the vacancy. So poly(acrylamide-co-diallyldimethylammonium chloride) (AMAC) was chosed as a binder to compare with the commonly used PEO. Since PEO is readily swelled and dissolved in organic solvents, it can not meet the requirements for Li-S batteries. While the AMAC is soluble in water and insoluble in organic solvents, it can maintain the cathode structure (**Figure 5**). The cell with AMAC binder remained a specific capacity of 652mAh g^{-1} after 100 cycles, much higher than the cell with PEO binder.

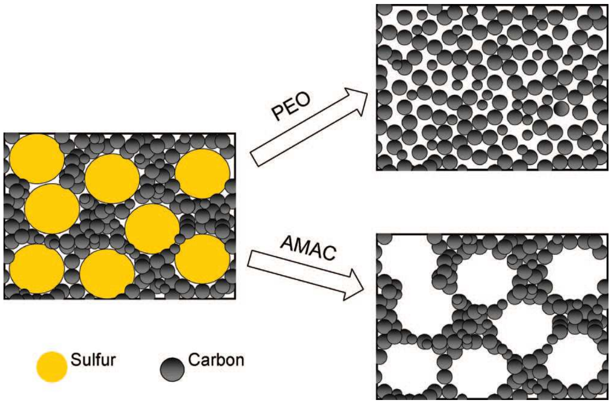


Figure 5. Schematic structure of the sulfur cathode before and after polysulfides dissolution. Reproduced with permission from ref. 68. Copyright 2012, The Electrochemical Society.

As we can see from the above work, the effects among the traditional binder, active material and the conductive agent are van Edward or hydrogen bonding force, which is far less than the covalent force. Meanwhile, since the sulfur electrode suffers from serious volume change during the cycle process, the collapse of conductive structure and the loss of intermediate products are the main factors that restrict its cycle life. Recently, there is a new point of view that is attempted to connect all the components through covalent force instead of intermolecular forces to enhance the stability of the electrode. Jin *et al.*[69] constructed a covalent bond among the electrode components in order to maintain a stability electrode through the strong intermolecular forces (**Figure 6**). Specifically, polydopamine (PD)-coated sulfur nanosheets was used as active materials, carboxylic acid functionalized multiwall carbon nanotube (MWCNT-COOH) as conductive agent and PAA as binder. Stronger covalent bonds formed by crosslinking of PD/MWCNT-COOH and PD/PAA into amide bonds were built throughout the whole electrode to firmly integrate all the individual components in the electrode together. As a result, the cathode demonstrated excellent cycling performance with a discharge capacity of 640 mAh g^{-1} after 500 cycles at a current density of 1 A g^{-1}. Besides, the discharge capacity decay after 500 cycles is only 0.021% per cycle.

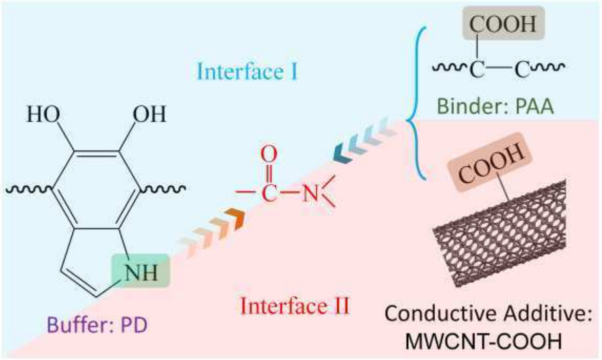


Figure 6. Schematic for the formation of amide bond between PD and PAA (named as interface I) and PD and MWCNT-COOH (named as interface II). Reproduced with permission from ref. 69. Copyright 2013, American Chemical Society.

Conductive polymer, poly(3, 4-ethylenedioxythiophene) (PEDOT), has been used as polymer binder in Li-S batteries recently.[70] Compared to PVDF as binder, PEDOT further improved the performance of Li-S batteries due to the bifunction of PEDOT with both good electrical conductivity and enhanced affinity for active materials. With the development of binders, we can come to the conclusion that binders used in Li-S batteries should meet the following requirements: 1) good bonding properties to keep the good electrical contact of the active material and conductive agent, 2) high dispersing ability to prevent the aggregation of either active materials or conductive agents, 3) good chemical and electrochemical stability without swelling and decomposition to maintain stable electrode/electrolyte interface, 4) coating effect on the electrode materials to limit the dissolution of lithium polysulfides into the electrolyte and alleviate the volume change of sulfur electrode. In addition, the binders should be environment friendly and low cost.

2.5 Effect of current collector

A nonporous aluminium (Al) foil is usually used as the current collector for Li-S batteries. The current collector accounts for about 15~20% by weight and 10~15% by cost of a battery. In addition, the Al foil suffers oxidation and corrosion at the high operating voltages of the sulfur cathode, which can cause sulfur to lose electrical contact with the current collector and increase the internal resistance of the battery.[71] Therefore, regarding Li-S batteries, an appropriate current collector is of great significance in terms of long-term cycling stability, high energy density and low cost.[72]

In recent years, using various carbon papers as current collectors draws increasing research interesting. For example, Manthiram *et al.*[73] used commercial carbon paper H-030 as the porous carbon current collect (PCCC), which showed a high porosity of 80% and low density of 0.4 g cm^{-3}. Compared to the Al foil current collector system, the PCCC system displayed longer cycle life with higher discharge capacity and Coulombic efficiency (above 94%). Other porous carbons, such as nano-cellular carbon,[74] vertically aligned carbon nanotubes,[75] three-dimensional carbon fiber,[76] carbon cloth (E-Tek, V2.02) and activated carbon cloth (Maxwell Tech.)[77] were also investigated as the current collector for Li-S batteries. These porous carbon papers provided remarkable electrolyte absorption and ensured intimate contact with the active materials. Moreover, the active sulfur loading on the porous carbon current collectors is usually up to 2~3 mg cm^{-2} or higher, which is much higher than that on Al foils (usually less than 1 mg cm^{-2}). Therefore, enhanced cycling stability with high gravimetric energy density could be achieved. But the volumetric energy density of the final cell is highly related to the thickness of the porous carbon current collector. He *et al.*[78] reported a graphene-coated polyethylene terephthalate (G-PET) as current collector. This plastic current collector (12 μm) showed the same thickness with Al foil, low weight (density of 1.37 g cm^{-3}, much less than one sixth of copper) and chemical stability against of organic electrolytes. A prototype of Li-S batteries with G-PET current collector showed an energy density of 452 Wh kg^{-1} and a capacity retention of 96.8% after 30 cycles at 100% depth of discharge.

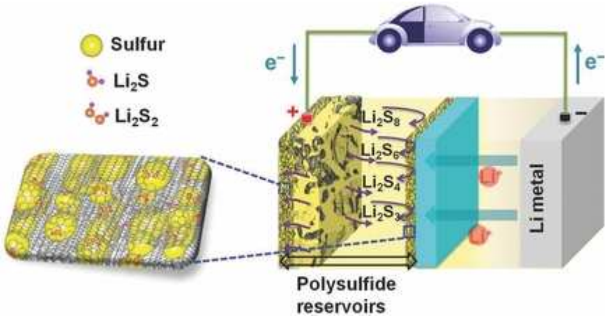


Figure 7. Schematic of a Li-S battery with sandwich structured electrode. The paler yellow color represents the reduced shuttle effect. Reproduced with permission from ref. 79. Copyright 2014, Wiley-VCH.

Recently, a unique sandwich structure with pure sulfur between two graphene membranes was designed for Li-S batteries with ultrafast charge/discharge rates and long lifetimes.[79] In this system, a graphene membrane (20 μm) was used as a current collector with sulfur coating on it (a sulfur loading up to 3~4 mg cm^{-2}), and the other graphene membrane was coated on a commercial polymer separator (**Figure 7**). The surface roughness of the graphene membrane current collector could increase the contact surface area and adhesion between sulfur and the current collector, which led to a decrease in the contact resistance, thus lowering the charge-transfer impedance. Moreover, the two graphene membranes could also accommodated sulfur volumetric expansion, store and reuse migrating polysulfides to alleviate the shuttling effect. As discussed above, porous carbon current collectors could act as advanced current collectors to achieve long-term stability with high energy density. Furthermore, they may also show promising potentials in preparing binder-free sulfur cathodes to assemble flexible batteries.

3. Electrolyte

The electrolyte used in LIBs is a medium to provide Li^+ for their operation and ensure the reversible chemical reactions. In Li-S batteries, the utilization of sulfur, the electrochemical reaction rate, even the discharge voltage and the electrode reaction mechanisms are closely related with the electrolyte component.[80, 81] Therefore, the selection of electrolyte solvents and salts is critically important. The studies of electrolyte used in Li-S batteries are also increasing year by year. Electrolyte systems can be broadly divided into three categories: organic liquid electrolyte, polymer electrolyte and all-solid-state electrolyte.

3.1 Organic liquid electrolyte

Conventional electrolyte is composed of solvents, electrolyte salts and additives. After a long time of accumulation, researchers gradually found that chain ethers solvents such as 1, 2-dimethoxyethane (DME)[82] and tetra(ethylene glycol)dimethyl ether (TEGDME),[83] have better solubility of lithium polysulfides. As Li_2S_n ($4\leq n\leq 8$) dissolved in the electrolyte increase the viscosity of the organic electrolyte, it is not conducive to the charge transfer. It is reported that the adding of cyclic ethers solvents such as 1, 3-dioxolane (DOL) can reduce the viscosity of the electrolyte.[54] At the same time, the use of DOL can prevent the lithium electrode corrosion *via* depositing a protective layer on the lithium electrode. Therefore, the appropriate deployment of electrolyte system is necessary to improve the performance of sulfur electrode.[84]

Lithium salts are another important component in electrolyte. $LiClO_4$, $LiPF_6$, $LiCF_3SO_3$ (LiFSI) and $Li(CF_3SO_2)_2N$ (LiTFSI) are popular for Li-S batteries. Compared with solvents, the species of electrolyte salts have a little effect on the cell performance. Abruna *et al.*[85] investigated the effects of different lithium salts ($LiPF_6$, $LiClO_4$ and LiFSI) as well as different mixed solvents on the performance of Li-S batteries in detail. They found that different types of lithium salts had a little effect on the performance of Li-S batteries. And solvent types were key factors that influenced the performance. When using TEGDME, DOL+DME and EMS (ethyl methyl sulfone)+DOL+DME as the solvents, Li-S batteries showed good performance. While using the electrolyte containing ester solvents, such as PC (propylene carbonate)+EC (ethylene carbonate)+DEC (diethyl carbonate), cycling performance was very poor. *In situ* X-ray absorption spectroscopy (XAS) study found that lithium polysulfides chemically reacted with the carbonate-based solvents. Ester solvents are commonly used in LIBs.[86] However, the ester solvents have adverse effects with lithium polysulfides, which is detrimental to normal electrochemical reaction.[87] Thereby, the ester electrolyte is not an ideal electrolyte for Li-S batteries.

Unlike the salts types, the lithium salts concentration has a great influence on the electrochemical properties. High concentration of lithium salts can prevent the diffusion of polysulfides by common-ion effect and high viscosity to improve the Culombic efficiency. A new electrolyte system named "salt solvent" (Solvent-in-Salt) was developed for Li-S batteries.[88] The so-called Solvent-in-Salt system referred to the solution that the salt in the volume ratio or mass ratio was higher than 50%. When used 7 mol L^{-1} LiTFSI/DOL+DME as electrolyte, Li-S batteries showed good cycle and rate performance. The initial discharge capacity was 1041 mAh g^{-1} at 0.2 C, and the capacity retention was 74% after 100 cycles. Meanwhile, the Coulombic efficiency was close to 100%. On one hand, lithium ion in the system of high lithium salts concentration was nearly saturated, inhibiting Li_2S_n ($4\leq n\leq 8$) from dissolving into the electrolyte. On the other hand, high viscosity and lithium ion transference number (0.73) caused by high lithium salts concentration alleviated the dissolved Li_2S_n ($4\leq n\leq 8$) to spread towards the lithium anode.

After exploring organic solvents and electrolyte salts, the basic problems of Li-S batteries during charge and discharge process have been solved, while the cycling performance and the Coulombic efficiency are still unsatisfactory. The shuttle phenomenon is an important reason, leading to the irreversible oxidation of active materials. In recent years, researches have tried to improve the utilization and cycling life of active materials by adding the additives into electrolyte. $LiNO_3$ is a commonly used additive. Aurbach *et al.*[89] analyzed the mechanism of $LiNO_3$ to improve the performance of Li-S batteries *via* using electrochemical impedance spectroscopy (EIS), infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and other methods. The main role of $LiNO_3$ was to protect the lithium anode because $LiNO_3$ could react with DOL and Li_2S_n ($4\leq n\leq 8$), forming a passivation layer on the surface of lithium anode. Wen *et al.*[90] also proved that $LiNO_3$ could stabilize the structure of lithium anode by a film generated on its surface. However, both the lithium anode and sulfur cathode may consume $LiNO_3$.[91] When using the $LiNO_3$-modified electrolyte, the end discharge voltage should not be too low. Otherwise, the solid-electrolyte interphase (SEI) protective layer would be irreversibly damaged.

Some other types of electrolyte additives have also been studied. Liang *et al.*[92] reported a new additive, phosphorus pentasulfide (P_2S_5) in organic electrolyte to enhance the cycling performance of Li-S batteries. P_2S_5 promotes the dissolution of Li_2S, alleviating the loss of capacity caused by Li_2S precipitation. At the same time, P_2S_5 can passivate the surface of lithium metal. The passivation layer has a dense structure that is able to conduct lithium ions while preventing the access of polysulfides to the surface of the metallic lithium, thus eliminating the shuttle phenomenon. Electrochemical tests show a reversible high-capacity 900-1350 mAh g^{-1} and high Coulombic efficiency of ≥90% at least 40 stable cycles at 0.1 C.

As can be seen from the above discussion, the major effect of electrolyte additives is so-called "*in-situ* protection" on the lithium anode. During the discharge process, the additive reacts with intermediate products and the metal lithium, forming a passivation layer on the surface of the lithium electrode, thereby avoiding the direct contact of Li_2S_n ($4 \leq n \leq 8$) with the lithium anode, and ultimately improving the performance of Li-S batteries.

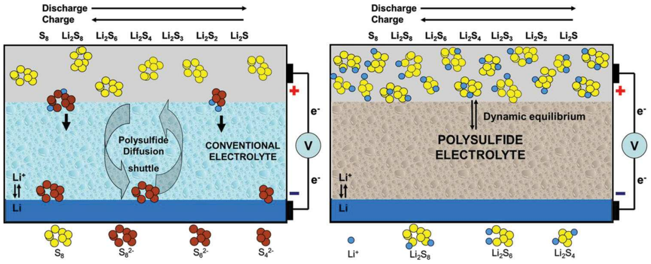


Figure 8. Schematic diagram of (left) Li-S batteries using conventional electrolyte, such as 1M LiTFSI in DME/DOL (v:v = 1:1), in which polysulfides produced at the cathode during discharge dissolve into the electrolyte; (right) Li-S batteries using the polysulfide electrolyte, in which produced polysulfides are retained at the cathode. Reproduced with permission from ref. 11. Copyright 2013, Wiley-VCH.

Lithium polysulfides are a new type of additives. Its principle is to limit lithium polysulfides on electrode/electrolyte interface by the common-ion effect, thus preventing the dissolution of lithium polysulfides. At the same time, it can contribute a part of capacity for the batteries. It should be pointed out that the use of lithium polysulfides should be combined with traditional SEI additives, such as $LiNO_3$. Belharouak *et al.*[11] followed a novel approach based on mitigating the sulfur loss by leveling the concentration gradient of the polysulfide species at the cathode/electrolyte interface (**Figure 8**). Novel electrolytes containing pre-dissolved lithium polysulfides as lithium salt along with $LiNO_3$ additive were utilized to realize the concentration gradient. It demonstrated a superior high capacity of 1450 mAh g^{-1} and almost 100% Coulombic efficiency with excellent cyclability.

Scrosati *et al.*[93] has also shown that Li-S batteries with an electrolyte formed by the addition of Li_2S_8 into the TEGDME-$LiCF_3SO_3$ electrolyte may operate with a stable high capacity approaching 1500 mAh g^{-1} for over 80 cycles. They indicated that the added Li_2S_8 provided a buffering effect according to Le Chatelier's principle, reducing the active materials dissolution during repeated cycles. Moreover, the dissolved Li_2S_8 was deposited on the cathode to compensate eventual capacity loss that resulted from lithium polysulfides dissolution during discharge.

3.2 Ionic liquid electrolyte

The commonly used DME-DOL mixed solvent has a certain characteristic of proton affinity and high donor number (DN), which leads to a high solubility of polysulfides. While the ionic liquid is liquid entirely composed of ions, it has a high dielectric constant, broad electrochemical window and high security. The studies find that the ionic liquid has a lower DN value, which leads to a low solubility of polysulfides.[94, 95]

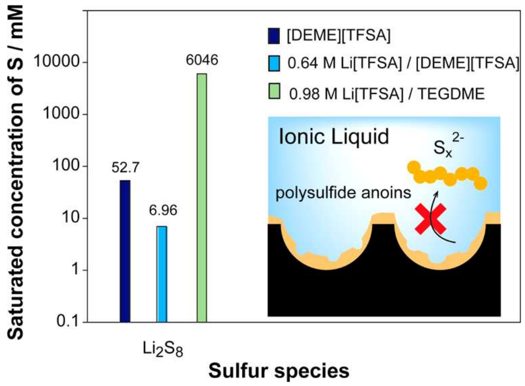


Figure 9. The solubility of Li_2S_8 in [DEME][TFSA], 0.64 M Li[TFSA]/[DEME][TFSA], and 0.98 M Li[TFSA]/TEGDME. Reproduced with permission from ref. 95. Copyright 2013, American Chemical Society.

Byon *et al.*[96] synthesized a N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) room temperature ionic liquid ammonium salt, and mixed it with DME to use as the organic electrolyte for Li-S batteries. The initial discharge capacity is about 1000 mAh g^{-1} at 0.2 C and the capacity retention is 90% after 50 cycles, showing a good cycling performance. Watanabe's group[95] synthesized N, N-diethyl-Nmethyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide (DEME-TFSI). The results showed that the charge and discharge behaviors in the ionic liquid were normal, and cycling performance was far superior to using TEGDME as electrolyte. Infrared visible spectrum and X-ray Diffraction (XRD) showed that ionic liquids could effectively inhibit the dissolution and diffusion of polysulfides (**Figure 9**). Furthermore, Xiao *et al.*[97] reported that ionic liquid could facilitate the formation of a stable SEI film on the surface of lithium anode, which effectively protected lithium metal from continuous attack by soluble lithium polysulfides.

The addition of ionic liquids on one hand can reduce the solubility of the lithium polysulfides in the electrolyte, inhibiting the loss of active materials. On the other hand, it can increase the viscosity of the solution, slowing down the diffusion of lithium polysulfides to the lithium anode. However, the elevated viscosity also reduces the diffusion speed of the lithium ions. Therefore, ionic liquids improve the cycling performance of Li-S batteries to a certain extent in small rates. The other important role of ionic liquids is the modification on the SEI quality on the anode side which alleviates the anode corrosion with cycling. Although ionic liquid electrolytes for Li-S batteries have potential applications, the complexity of their synthesis process, high cost and other reasons restrict their application in industrial production.

3.3 Gel polymer electrolyte

Gel polymer electrolyte (GPE), which composed of polymer, plasticizer and lithium salt, is a new class of electrolytes based on the liquid electrolyte. PEO, PVDF, PAN and poly(vinylidenefluoride hexafluoropropylene) (P(VDF-HFP)) are all better systems with proper porous structure. It is worth noting that although the systems have complex interactions between ion and polymer host, the solvation effects of plasticizer on ions still dominate. The ionic conduction is achieved though liquid electrolyte molecules fixed on the microstructure. The ionic conduction mechanism is similar to that in liquid, therefore the ionic conductivity at room temperature is always quite high, between 10^{-4}~10^{-3} S cm^{-1}. Compared with the organic liquid electrolyte, it has the following advantages: (1) a physical barrier to block the cathode and anode electrodes; (2) easy deformation to ensure a good contact with electrodes; (3) a certain extent to solve the security problem such as the lithium anode dendrite; (4) good chemical and electrochemical stability.

Wen *et al.*[98] prepared GPE by combining a porous P(VDF-HFP) membrane with N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (P_{14}TFSI) ionic liquid. The GPE not only ensured good safety as a physical barrier, but also decreased the solubility of lithium polysulfides in ionic liquid-based electrolytes and improved the cycling performance of Li-S batteries. Li-S batteries based on the GPE delivered an initial discharge capacity of 1217.7 mAh g^{-1} and retained a reversible capacity of 818 mAh g^{-1} after 20 cycles.

Chen *et al.*[99] proposed a novel GPE to improve the cycling performance of Li-S batteries. The GPE was formed by blending of functionalized poly(methyl methacrylate) (PMMA) and bearing trimethoxysilane groups with PVDF-HFP. The advantages of the GPE are: 1) improve stability of the GPE morphology; 2) reduce the pore size to prevent polysulfides diffusion during cycling. Therefore, Li-S batteries with the novel GPE exhibited excellent performance with a capacity up to 1050 mAh g^{-1} after 100 cycles.

Hu *et al.*[100] synthesized a poly(ethylene glycol)-borate (PEG-B) plasticizer and used it in the GPE for Li-S batteries in order to inhibit the serious migration of polysulfides. Li-S batteries using the GPE with addition of the plasticizer had an improvement in the electrochemical properties and a slow decrease of discharge capacities followed after stable cycles. The decrease of capacities was ascribed to an undesirable side reaction occurred on the GPE/Li anode interface, which caused by the diffusion of polysulfides.

Since the lithium ion conduction of GPE achieved primarily by the plasticizer, the ion conduction mechanism is similar to the liquid electrolyte. It is difficult to completely suppress the diffusion of S_2^{n-} ($4 \le n \le 8$) to the lithium anode. The cycle problems in Li-S batteries cannot be solved fundamentally.

3.4 All-solid-state electrolyte

All-solid-state electrolyte (SSE) can be divided into solid polymer electrolytes (SPE) and inorganic solid electrolytes (ISE). SPE composed of high molecular weight polymer matrix and lithium salts can be approximated as solid solution system, which is formed by dissolving lithium salts directly in the polymer matrix.[57] The transmission of lithium ion in SPE is by means of the motion of polymer segments continuously. The ionic conductivity of SPE at room temperature is low, about 10^{-8}-10^{-7} S cm^{-1} in general. It is the key factor that limits its development.

ISE, especially the glass-type electrolytes, have a high ionic conductivity at room temperature. In recent years, ISE have aroused great interests.[101] Hassoun's group[102] reported Li-S batteries using Li_2S-P_2S_5 as the glass-type electrolyte by high-energy ball milling, lithium metal as the anode and a graphite-sulfur compound as the cathode material. Electrochemical tests at 80 °C demonstrated a high conductivity of SSE as well as excellent electrochemical performance.

The ionic conductivity of cathode materials is identified as the key parameter for Li-S batteries using SSE. Liang *et al.*[103] prepared a lithium superionic sulfide (LSS) cathode by coating nanostructured lithium sulfide (NanoLi_2S) with lithium phosphorus sulfide (Li_3PS_4). The core-shell structure improved the ionic conductivity of NanoLi_2S from 10^{-11} to 10^{-7} S cm^{-1} at 25 °C. When Li_3PS_4 was used as SSE, Li-S batteries showed an excellent cyclability and rate capability.

Compared with the liquid electrolyte and GPE, SSE has two main advantages: (1) there is no leakage and flammability in SSE and the lithium dendrite can also be mitigated; (2) SSE can completely suppress the diffusion of S_2^{n-} ($4 \le n \le 8$) to the lithium anode in theory, which contributed to a better cycling performance for Li-S batteries. However, SSE still has some drawbacks such as complex manufacturing process, poor mechanical strength and large interfacial impedance.

4. Anode materials

Li-S batteries are secondary batteries, which are based on metal lithium as a negative electrode and elemental sulfur as a positive electrode. However, the lithium electrode always exists the problem of lithium dendrite. This leads to security problems to hinder the practical application of Li-S batteries. What’s more, the soluble intermediate lithium polysulfides can react with the metal lithium anode in a parasitic reaction, which cause the serious lithium anode corrosion and the low Coulombic efficiency.

Liu *et al.*[104] developed a new hybrid design by using an integrated structure composed of electrically connected graphite and Li metal as the negative electrode for Li-S batteries, which can mitigate the loss of active material and harmful parasitic reactions on the anode. At a high current density of 1737 mA g^{-1}, the Li-S batteries can deliver capacities upto 800 mAh g^{-1} for 400 cycles.

Wang *et al.*[105] firstly investigated Li-B alloy as the anode material for Li-S batteries. The unique structure of Li-B alloy can restrain the formation of dendritic lithium, reduce the interface impedance and improve the electrochemical performance for Li-S batteries. Yushin *et al.*[106] introduced a thin lithium aluminum alloy layer on the lithium surface, which can mitigate the polysulfide shuttle phenomenon and stabilize polarization during repeat cycling.

Scrosati *et al.*[107] synthesized a lithiated-silicon carbon composite to construct a new, lithium metal-free, silicon-sulfur, lithium ion batteries. The mention of sulfur-lithium ion batteries (SLIBs) may avoid the potential safety problems of lithium metal anode. The other research group, Aurbach *et al.*,[108] presented that prelithiated columnar structured amorphous silicon film served as anodes for SLIBs, which showed better capacity retention. Kaskel *et al.*[109] reported balanced and stable SLIBs by using prelithiated silicon-carbon as well as prelithiated all-carbon as anodes. The SLIBs without dendrite formation and electrolyte decomposition deliver a specific capacity upto 1470 mAh g^{-1}.

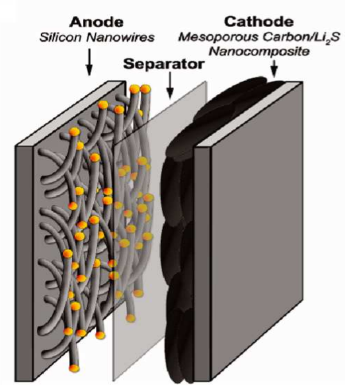


Figure 10. Schematic diagram of battery structure. Reproduced with permission from ref. 110. Copyright 2010, American Chemical Society.

The other kind of SLIBs is full battery cells based on Li_2S cathodes and silicon or tin anodes. Cui *et al.*[110] reported SLIBs consisted of a Li_2S/mesoporous carbon cathode and a silicon nanowire anode (**Figure 10**). The theoretical specific energy and the theoretical volumetric energy density of the SLIBs are four times that of state-of-the-art battery technology and about twice that of the $LiCoO_2$/graphite system, respectively. Scrosati *et al.*[111, 112] developed new SLIBs with safety, high capacity and high energy density, which used Li_2S-C composite as cathode and tin-carbon composite as anode. The new system of SLIBs delivered a specific energy upto 1100 Wh kg^{-1}.

5. Characterization techniques and others

There have been many researches about the modification of the components in Li-S batteries. However, there are only a small amount of reports to analyze the working mechanism and the limitation factors of Li-S batteries by characterization techniques. The analysis of polysulfides, the structural and morphological changes have been studied by inductively coupled plasma-Optical emission spectrometer (ICP-OES) measurement, liquid chromatography coupled with mass spectrometry (LC-MS),[113] transmission X-ray Microscopy,[114] *in situ* XRD,[115] and UV/Vis in Operando Mode.[116] New characterization techniques need to further develop, which can qualitatively and quantitatively detect these reactions that occur at the sulfur cathod and the lithium anode. Thus, the content of soluble lithium polysulfides (Li_2S_8, Li_2S_6, Li_2S_4, and Li_2S_3) into the electrolyte can be determined. Adding these lithium polysulfides based on the above results in the fresh electrolyte can limit lithium polysulfides from the cathode on electrode/electrolyte interface by the common-ion effect, which can suppress the shuttle effect and improve the electrochemical stability. Based on these new characterization techniques, researchers can simulate the dynamic models of the polysulfides diffusion in electrolyte and the polysulfides deposition on electrode surfaces. Thus, this can help to understand fundamentally the mechanism and the impact of the components in Li-S batteries, which provide a theoretical basis to suggest possible strategies to improve the electrochemical performance.

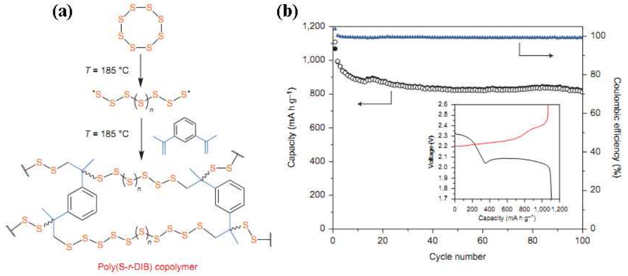


Figure 11. (a) Synthetic scheme for the copolymerization of S8 with DIB to form chemically stable sulfur copolymers. (b) Battery cycling data for poly(S-r-DIB) (10 wt% DIB, C/10 rate) showing the discharge capacity (open circles), charge capacity (filled circles) and Coulombic efficiency (blue triangles) with the inset showing a typical charge/discharge profile. Reproduced with permission from ref. 12. Copyright 2013, Nature Publishing Group.

In addition to the conventional means above, there are also some new and unique ways to improve the electrochemical performance of Li-S batteries. With regard to cathode materials, some new active materials, such as polysulfides,[117-120] poly(acrylonitrile)-sulfur composite,[38, 121-128] lithium superionic sulfide,[103] lithium polysulfidophosphates,[129] and poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB), **Figure 11**)[12, 130] instead of the traditional sulfur cathode materials. The special structure using interlayer is designed to block polysulphides migration,[131-134] which can improve the cycle stability of Li-S batteries. Polysulfide flow batteries (**Figure 12**)[135, 136] and charge operation controls[137-139] offer tremendous improvement to advance the practical use of Li-S batteries.

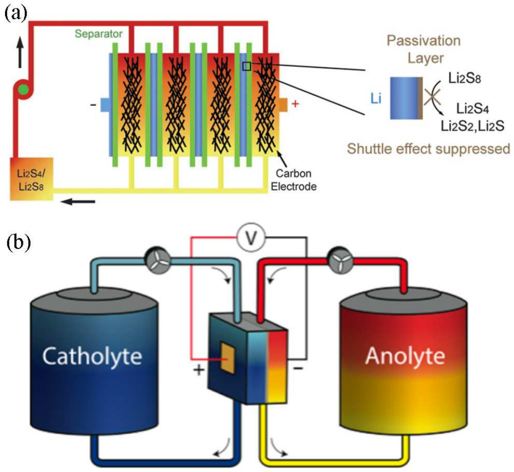


Figure 12. (a) The schematic illustrating the structure of the Li/PS battery. Reproduced from ref. 135. Copyright 2013, The Royal Society of Chemistry. (b) Flow batteries combine a current-extracting stack, through which redox active solutions flow, with storage tanks and pumps. Reproduced with permission from ref. 136. Copyright 2014, American Chemical Society.

Outlook

In the Feature Articles, we mainly summarize the recent development on cathode materials, electrolytes, and anode materials for Li-S batteries. The carbon hosts can improve the electric conductivity of sulfur cathodes and trap polysulfides by physical absorption, chemical adsorption, and coating. The oxides could further improve the electrochemical performance for Li-S batteries. Binders and current collectors are also quite important in terms of cycling ability. The electrolytes and additives have significant roles in promoting the practical use of Li-S batteries. The metal lithium anodes in Li-S batteries replaced by new anodes, such as silicon, can emerge novel generation batteries, sulfur-lithium ion batteries, which avoid security issues from the lithium dendrite.

In summary, there have been significant advances on Li-S batteries in recent years. However, challenges are always present. The polysulfides cannot be completely suppressed to dissolve into the electrolyte, which lead to poor cycling stability. Some perspectives and directions on future development of lithium-sulfur batteries are pointed out based on knowledge from the literature and our experience: (1) The new active materials mentioned above have a low electronic conductivity. Future explorations of these active materials would greatly benefit from efforts to improve their electronic conductivity with carbon materials or conducting polymer. (2) Using new anodes replace the metal lithium anodes to obtain a secure system. (3) Exploiting novel electrolytes and additives for Li-S batteries to suppress the rapid capacity fade during charge-discharge cycles. Especially, the solid-state electrolyte could be an effective strategy to solve this problem. However, superior performance at room temperature remains to be solved. (4) The special structure for Li-S batteries and polysulfide flow batteries should reduce their complexity to use widely. (5) It is quite important to explore the mechanism of Li-S batteries during the charge/discharge process by modern physical characterization techniques. (6) Not only the specific capacity, but also the energy density with high loading of sulfur should be improved. Therefore, development of novel hosts with new binders, electrolytes, current collectors, anode materials combined with special configurations for Li-S batteries will come into being unprecedented performance, which makes Li-S batteries for future wide applications in the field of automobiles, unmanned aerial vehicle and other stationary energy storage.

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Notes and references

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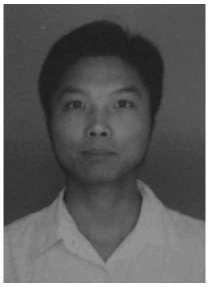
Biography & photograph



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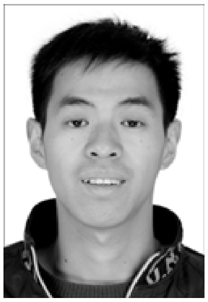

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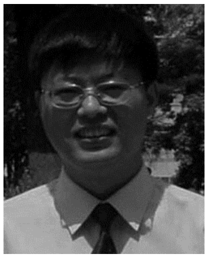

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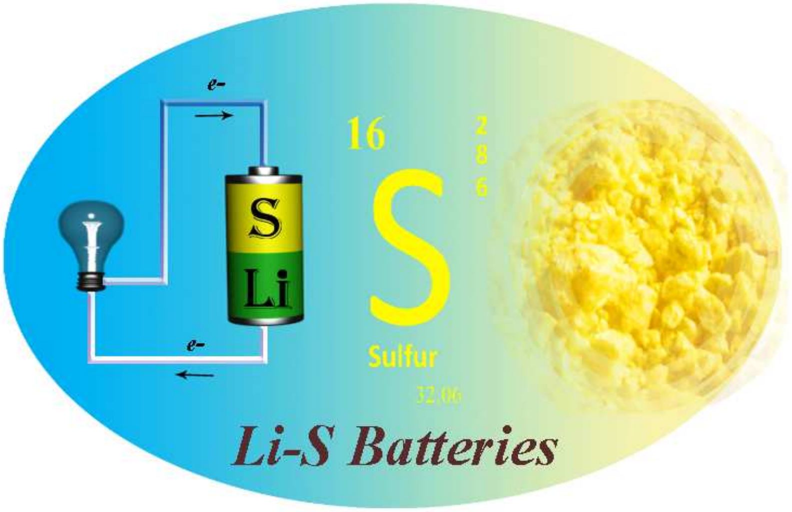
TOC figures



TOC text

This Feature Article reviews the recent progresses of Li-S batteries to advance their practical use.