Lithium–Sulfur Batteries

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Lithium–Sulfur Batteries: Electrochemistry, Materials, and Prospects

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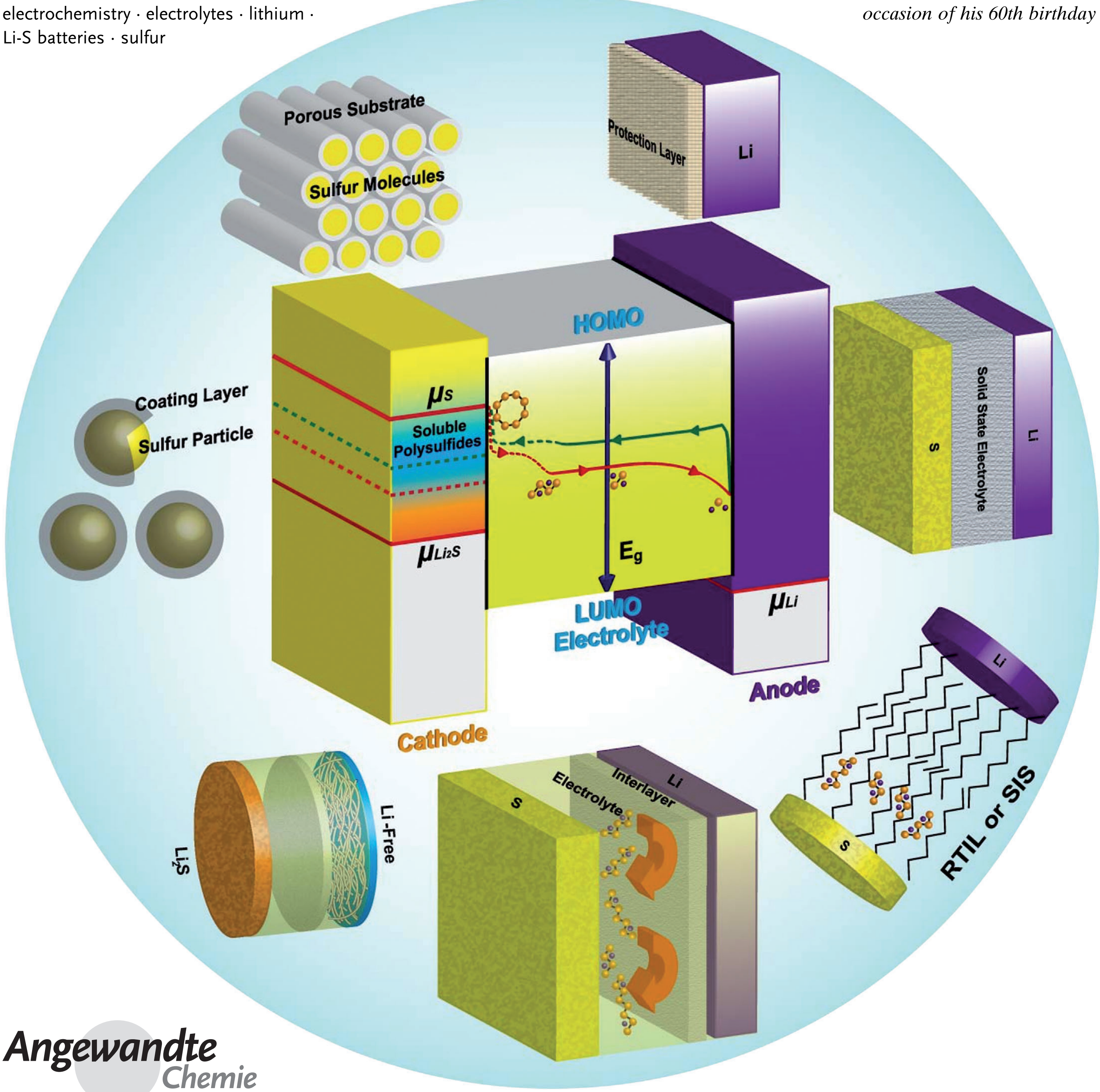
Dedicated to Professor Chunli Bai on the occasion of his 60th birthday



With the increasing demand for efficient and economic energy storage, Li-S batteries have become attractive candidates for the next-generation high-energy rechargeable Li batteries because of their high theoretical energy density and cost effectiveness. Starting from a brief history of Li-S batteries, this Review introduces the electrochemistry of Li-S batteries, and discusses issues resulting from the electrochemistry, such as the electroactivity and the polysulfide dissolution. To address these critical issues, recent advances in Li-S batteries are summarized, including the S cathode, Li anode, electrolyte, and new designs of Li-S batteries with a metallic Li-free anode. Constructing S molecules confined in the conductive microporous carbon materials to improve the cyclability of Li-S batteries serves as a prospective strategy for the industry in the future.

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1. History of the Lithium–Sulfur Battery

Since their discovery in the 1960s,[1] Li-S batteries have been considered promising for powering portable electronics. However, research ceased in the 1990s with the triumph of Li-ion batteries (LIBs),[2–6] which have more stable electrochemistry and longer lifespan. After 2000, the rapid development of emerging applications, including military power supplies, civil transportation, and stationary storage, placed higher demands on the energy density of the battery,[6–8] which resulted in the resurgent of Li-S batteries. Li-S batteries have an overwhelming advantage in energy density, with a theoretical value of about 2600 $\mathrm{Wh\,kg^{-1}}$ calculated on the basis of the Li anode and the S cathode, and is up to five times greater than that of commercial LIBs (387 $\mathrm{Wh\,kg^{-1}}$ for $LiCoO_2$/C battery).[2,8–12] The practical energy density of packaged Li-S batteries could be as high as 400 to 600 $\mathrm{Wh\,kg^{-1}}$ (two or three times higher than that of commercial LIBs), and could satisfy a traveling distance of 500 km for electric vehicles.[2,8] Furthermore, the abundance and non-toxicity of S provide Li-S batteries with improved energy economy and environmental friendliness. These qualities make Li-S batteries appealing for stationary storage of renewable energies, such as solar and wind, if long cycle life and high system efficiency can be achieved.[2,7,13] Since 2009, Li-S batteries have gained ever-increasing attention as promising candidates for the next-generation energy storage applications after Nazar et al. reported a Li-S battery with improved cycling performance.[10] Intensive efforts have been exerted in striving for significant breakthroughs in the core technology of Li-S batteries. This Review elaborates the fundamental scientific problems of Li-S batteries from both electrochemical and technical viewpoints, and summarizes the feasible solutions aiming at addressing these problems. Various strategies for improving the performances of Li-S batteries are explained, and their merits/defects are detailed to provide insights on the future development of the Li-S industry.

2. Electrochemistry of the Lithium–Sulfur Battery

A typical Li-S battery is composed of a lithium anode, a sulfur cathode, and an electrolyte in between. At the open-circuit state, the Li-S battery holds a maximum voltage (that is, the open-circuit voltage, Φ_{oc}), which is in direct proportion to the difference between the electrochemical potentials of the Li anode (μ_a) and the S cathode (μ_c) (Figure 1 a).[14] Upon discharging, S reacts with Li by a two-electron reduction process to form polysulfide intermediates (Li_2S_x, $x = 2$–8), and to generate Li sulfide (Li_2S) at the end of discharge. This process is accompanied by an increase in cathode electrochemical potential (Figure 1 b) until the battery reaches the terminal voltage (Φ, normally ≤ 1.5 V). The reverse reaction occurs when an external electric field with a certain potential difference is applied, leading to the decomposition of Li_2S back to Li and S. During this time, the cathode electrochemical potential gradually decreases till the battery voltage returns to Φ_{oc} (Figure 1 c). In contrast with the commercial LIBs, the electrochemistry of Li-S battery, which is enabled by the two-electron redox reaction, endows the two electrodes with high theoretical capacities (Li 3860 $\mathrm{mAh\,g^{-1}}$, S 1672 $\mathrm{mAh\,g^{-1}}$), thus offsetting the deficiency in average working voltage (ca. 2.1 V) and accounting for an attractively high specific energy of the battery.[2,8–11,15]

However, the electrochemistry brings noticeable problems that hinder the practical application of the battery. First, sulfur and its various discharge products (Li_2S_x, $x = 1$–8) show poor ionic and electronic conductivities, which increase the internal resistance of the battery. This increase results in a large polarization that reduces the energy efficiency of the battery. The poor conductivity also arises from the formation

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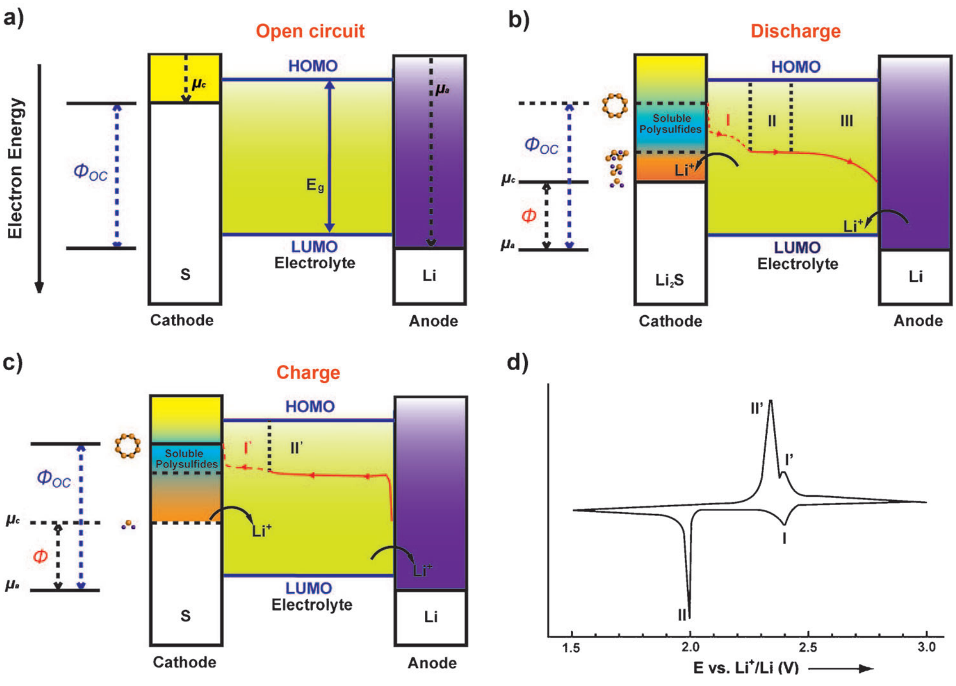
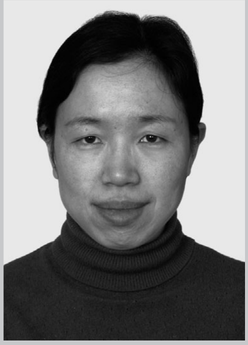


Figure 1. Electrochemistry of the Li-S battery at different stage: a) open circuit; b) discharge process; c) charge process. d) Typical cyclic voltammogram (CV) for an S cathode in a Li-S battery.

of insoluble insulation layer (mainly composed of Li_2S_2 and Li_2S) on the surface of the S particles during discharge, and impedes their further reduction, which leads to a poor active material utilization.[8,9]

The second problem lies in the electrochemical process of the Li-S battery. On the basis of previous experimental results[16–22] and theoretical analysis,[23] the prevailing electrochemical reaction mechanism between S cathode and Li anode in Li-S batteries can be ascribed as follows. Under normal conditions, sulfur exists as ring-like octatomic molecules with a chemical formula of S_8. During the discharge process (Figure 1 b), cyclo-S_8 is reduced by Li in a stepwise manner, exhibiting three distinct segments.[16,18] Segment I (from Φ_{oc} to ca. 2.0 V including a small plateau at ca. 2.35 V; Figure 1 b) accounts for a quarter of the profile, corresponding to the transformation from S_8 to Li_2S_4 (1 mol S takes up 0.5 mol Li).[8,9,18,21,23] Segment II also accounts for a quarter of the profile (plateau at ca. 2.0 V), corresponding to the reduction from Li_2S_4 to Li_2S_2,[18,20] and the last sloped segment III matches with the further reduction from Li_2S_2 to Li_2S (Figure 1 b).[16,23] During the reverse charging process, Li_2S is first oxidized to various low-order polysulfides on segment II′ and further oxidized to high-order polysulfides, and finally to cyclo-S_8 on segment I′ (Figure 1 c).[18] The redox process corresponds well with the CV of the Li-S battery, which shows two pairs of redox peaks (Figure 1 d) that match well with the plateaus on the discharge–charge profiles. However, segment III on the discharge profile



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(Figure 1 b) does not reflect in the CV, which is due to the sloped shape and the small voltage difference between segment II and segment III. The polysulfides (mainly Li_2S_4–Li_2S_8) generated on segment I and I′ can easily react with or dissolve into the organic solvent of electrolyte, leading to irreversible capacity fade of the solid cathode.[8,9,11,18,21,24] Moreover, the dissolved polysulfides can migrate onto the Li anode by a so-called shuttle effect and thereby form an electrochemically inactive layer consisting mainly of Li_2S_2 and Li_2S, further deteriorating the battery performances.[8,9,11]

The third problem is related to the volume variation of the S cathode upon cycling. In the case of the different densities of α-S_8 (2.07 $\mathrm{g\,cm^{-3}}$) and Li_2S (1.66 $\mathrm{g\,cm^{-3}}$),[16,25] S experiences a noticeable expansion of about 79 % upon Li uptake, which makes Li_2S pulverize and lose their electrical contacts with the conductive substrate or the current collector. As the fraction of “non-contact S” increases in the cathode material, significant capacity fade is observed during cycling. Although there is a distinct contradiction in the form existing (crystalline or amorphous) of the final discharge product of Li_2S between the ex situ study[16,26] and the in operando investigation,[25] the volume change of S is inevitable during cycling. This problem is crucial for practical Li-S batteries, in which the drastic volume variation of the electrodes can lead to serious safety problems.

Li anodes for Li-S batteries also suffer from several problems. The Fermi energy of Li is higher than the low unoccupied molecular orbital of the commonly used liquid electrolytes (Figure 1 a).[14] As a result, the electrolytes can be reduced on the surface of the Li anode to form a solid electrolyte interphase (SEI) layer, causing a remarkable irreversible capacity loss and low deposition efficiency of Li upon charging.[17,27–29] For practical Li-S batteries, this condition may lower the energy output of the system by requiring an excessive amount of Li to pair with S cathode.

The second problem lies in the growth of Li dendrites, which originates from an uneven deposition of Li and can cause safety problems of Li-S batteries.[30] It is worth noting that the dendrite issue is unique for the Li-S battery. The soluble polysulfides generated during cycles could react with Li,[17,30–32] which possibly suppress the growth of Li dendrite.[27,28] Nevertheless, Li anodes cycled in electrolytes with low solubility for polysulfides may still involve dendrite generation.

The third problem of the Li anode arises from the shuttle effect of polysulfides. Soluble polysulfides diffusing throughout the separator could react with Li to form the insoluble sulfides (Li_2S_2, Li_2S). The gradual growth of insulating sulfides on the Li anode during cell operation may seriously retard the rapid access of Li, and result in poor rate capability.[8,9,11,33]

Electrolyte is also an important component of Li-S battery, and the selection of appropriate electrolytes directly influences the performances of the battery. Fortunately, the operation voltage of the Li-S battery (ca. 2.1 V) is located within the electrochemical window (E_g) of most electrolytes (Figure 1 b,c),[14] indicating that a wide range of electrolytes can be chosen for Li-S batteries. However, the compatibility of the electrolyte with the electrochemistry of Li-S batteries should also be considered. Ether electrolytes have been reported to be highly active in facilitating the electrochemical reaction between Li and S. However, these electrolytes also exhibit the highest solubility of polysulfides, leading to a strong shuttle effect, as demonstrated by the fact that for Li-S batteries with ether electrolyte the charge capacity is much higher than the discharge capacity upon cycling.[30,31] Carbonate electrolytes have been shown to be reactive with the polysulfides generated on the first plateau (Li_2S_x, $x = 4$–8), leading to incomplete reduction of S.[24] Other electrolytes, such as ionic liquid electrolytes[34] and solid state electrolytes, are also involved in relieving the polysulfide shuttle,[35] but are impeded with the sluggish Li^+ diffusion owing to their high viscosity or solid-state nature.[36]

In the context of aforementioned electrochemistry characteristics of Li-S batteries, great effort has been devoted in studying both electrodes and electrolytes to enable the practical application of Li-S batteries with high energy density and long lifespans. Some effective strategies have been performed to overcome these issues concerning Li-S batteries. The following sections systematically introduce the roles and the effectiveness of these strategies on the S cathode, the Li anode, and the electrolyte.

3. The Sulfur Cathode

The sulfur cathode is a crucial component of Li-S batteries, as it endows the battery with high energy density, but this component brings serious problems as well. The poor electrochemical performances of sulfur do not make it suitable for direct use as a cathode material for Li-S batteries.[8–11,37] Different approaches have been conducted in chemical, engineering, and materials science methods to make the S cathode applicable in Li-S batteries. For example, sulfur is usually combined with a substrate with high electronic conductivity (such as carbon) to improve the electrical contact. Also, to effectively restrain sulfur on the cathode side, porous substrates are often used to adsorb the polysulfides formed in situ during the cycling process. In dealing with the volume variation problem of sulfur, elastic substrates with preserved cavities or porous structures show their advantages. The developed sulfur cathodes, varying in structures and compositions, can be generally classified into two categories, that is, the sulfur composite cathodes and the sulfide cathodes.

3.1. The Sulfur Composite Cathode

To offset its shortcomings, sulfur is always combined with other materials to construct composite materials with high conductivity and stable cyclability. Surface coating and sulfur loading are two common approaches to obtain sulfur composite cathode materials. With proper structure design, both methods can yield much improved electronic conductivity of sulfur and also effectively prevent the dissolution of polysulfides.

3.1.1. *Surface Coating*

Surface coating is an effective method for improving the electrochemical performances of electrode materials for LIBs, and is applicable to the sulfur cathode. Carbon is an ideal coating material owing to its high electrical conductivity, dense structure, and elastic nature. Thus, carbon coating has been successfully employed in enhancing the Li storage properties of various electrode materials.[38,39] However, traditional carbon coating techniques, such as chemical vapor deposition (CVD) of carbon,[40] hydrothermal,[41,42] solvothermal, and ionothermal carbon coating,[43] usually require thermal treatment at an elevated temperature of $>500\,^{\circ}\mathrm{C}$ to increase the electronic conductivity of the coating layer. This elevated temperature is apparently not suitable for sulfur because the temperature goes beyond its boiling point ($445\,^{\circ}\mathrm{C}$).[44,45] Hence, graphene (or reduced graphene oxide) serves as a feasible material to develop an effective low-temperature carbon coating technique for sulfur. With its high conductivity, large surface area, and two-dimensional morphology, graphene can easily wrap around the active sulfur particles to form a conducting network, providing excellent electrical contact to diminish the interface resistance among particles.[38] Thus, the electrochemical activity of sulfur could be improved. On the other hand, the flexibility of graphene is beneficial to alleviating the volume variation stress of sulfur during the cycling process, and its dense structure can effectively prevent the dissolution of polysulfides into the electrolyte. For example, poly(ethylene glycol) (PEG) coated submicrometer sulfur particles are wrapped with carbon black decorated graphene sheets to form the PEG-S/graphene composite material through a simple solution assembly process.[46] The PEG and graphene coating layers show a synergetic effect in trapping soluble polysulfide intermediates on the cathode, and in accommodating the volume expansion of sulfur particles during discharge.[46] Moreover, graphene sheets decorated with carbon black facilitate the electronic conduction among particles, improving the electrochemical activity of sulfur. All these factors contribute to high specific capacities of sulfur and a favorable cycle life of 100 cycles.[46] However, the inactive components (PEG, graphene, and carbon black) take up too much of the composite, and thus are not beneficial to achieving a high sulfur content. To address this issue, a one-pot scalable method was developed to synthesize a S/graphene composite[47] in which sulfur particles are in intimate contact with the conductive shrink-wrap by graphene. Given that the composite is free of any polymer buffer, the sulfur content in the final composite can be as high as 87 wt %. The validity of the graphene coating has been proven with a respectable initial capacity ($705\ \mathrm{mA\,h\,g^{-1}}$), high Coulombic efficiency (93 % after 50 cycles), and a good cycling stability of S.[47] In view of the large micrometer-sized sulfur particles in the S/graphene composite, an expectation on further improved battery performances could be made if the sulfur particle size can be decreased.

Conductive polymers,[48–51] such as polypyrrole[50,51] and polythiophene,[49] are also used for sulfur coating. Many core–shell-structured sulfur composites have been prepared in which the polymer shell facilitates the electron transfer with the conductive polymer chain, accommodates the volume variation with the elastic framework, and maintains sulfur and polysulfides inside.[49–51] The polymer coating leads to improved cycling stability of sulfur and shows significant cost advantages over graphene. Nevertheless, the bulk sulfur core still suffers from an insufficient utilization, and thus the electronic conductivity of the polymer shell should be further improved towards high-rate applications.

Recently, oxides have been demonstrated to be an effective coating material for sulfur.[52,53] For example, mesoporous TiO_2 coating layers were formed on monodispersed sulfur nanoparticles through controlled hydrolysis. This step is followed by partial dissolution of sulfur to yield S-TiO_2 yolk–shell nanoarchitectures with preserved internal space. The intact TiO_2 shell enables Li^+ to pass through and prevents the polysulfides from dissolving out. On the other hand, the large internal voids in the composite could accommodate the volume expansion of sulfur. All these improve the cyclability of sulfur, leading to Li-S batteries with a high Coulombic efficiency of 98.4 % and an impressive lifespan of over 1000 cycles.[52] As the amorphous TiO_2 coating layer is a poor electronic conductor, a large amount of carbon additive is added to improve the conductivity, which lowers the sulfur content on the cathode.

As an important technique to prepare sulfur composite cathode materials, surface coating shows distinct merits in terms of polysulfides confinement and adaptability to volume variation, while bringing about its own problems. First, the sulfur particles in the composites are usually oversized (>500 nm), which go against with the electron transport in the particle and might show adverse effect on the capacity utilization of sulfur. Second, achieving perfect coating on the sulfur particles is difficult. Some polysulfides may still dissolve out, which will inevitably deteriorate the cycling performance of sulfur. To achieve better coating of sulfur, further improvements should address these issues, such as tailing off the particle size of sulfur, or generating a layer-by-layer structure to prevent the dissolution of polysulfides. Moreover, a mixed coating of polymer and other materials with high electronic conductivity, such as graphene, is expected to strike a delicate balance between cost and effect.

3.1.2. *Sulfur Loading*

The idea of using porous substrate to host sulfur appeared in 2009,[10] when Nazar et al. firstly reported the introduction of sulfur into an ordered mesoporous carbon (CMK-3) to improve the cycling performance of the sulfur cathode (Figure 2 a,b). In fact, the strategy of combining sulfur with porous carbon substrates has been observed in other metal secondary batteries; for example, Na-S batteries, in which liquid sulfur is accommodated in a carbon felt to prepare the sulfur cathode.[54–56]

Since then, various porous substrates have been prepared for hosting sulfur.[41,57–67] Although varying in chemical composition and structure, the target of manufacturing these porous substrates is clear; that is, to achieve the best sulfur retention. According to their dimensions, the pores in porous substrates are classified into macropores (pore

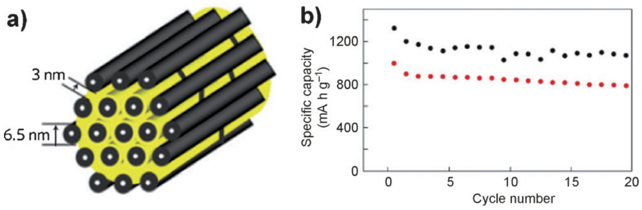

Figure 2. a) A schematic diagram of the S (yellow) confined in the interconnected pore structure of mesoporous carbon, CMK-3. b) Cycling stability comparison of CMK-3/S-PEG (upper points, in black) versus CMK-3/S (lower points, in red) at 168 mA g^{-1} at room temperature. Reproduced with permission from Ref. [10]. Copyright 2009, Nature Publishing Group.

diameter of > 50 nm), mesopores (2–50 nm), and micropores (< 2 nm). In the combination of sulfur with porous substrates, an important issue lies in the sulfur content in the composite. Since the capacity contribution by the substrate is often negligible in the operation voltage range of Li-S batteries (usually more than 1 V vs. Li$^+$/Li), the use of excessive carbon material inevitably lowers the energy output of the practical battery. To maximize the energy output of the battery, sulfur should hold a fraction as high as possible in the cathode material. Although having the largest pore volumes, macroporous substrates have been reported to be difficult to use with sulfur owing to their large size and open architecture, which is highly ineffectual in activating enclosed sulfur and restricting soluble polysulfides. To make use of macroporous substrates, a high-viscosity electrolyte could be coupled, in which the polysulfides are limited in mobility and predominately remain at the cathode.[57] In case where strong interactions are formed between the substrate and sulfur, the macroporous substrate may also be applicable. This strategy has been demonstrated by the integrations of sulfur with the conductive frameworks formed by graphene oxide[68] and carbon nanotubes,[58,59] in which the strong S–C interactions help to bind polysulfides on the substrate and improve cycling stability. However, such composites with the open structures still suffer from polysulfide dissolution and shuttle, which are not beneficial for the long-term cycling performance of Li-S batteries.

Most recent research on cathodes focused on mesoporous substrates,[60–62,69] following the early work where small carbon mesopores (3–4 nm), and a hydrophilic polymer coating provided effective confinement of sulfur to reach a reversible capacity of about 1200 mA h g^{-1} (Figure 2 a,b).[10] Compared with the macroporous substrate, the mesoporous substrate has sufficient volume to reach a high sulfur loading rate up to 70 wt % in the composite, and offers better constraint on polysulfides with stronger interactions between sulfur and the porous channels (Figure 2 b). Moreover, sulfur stored in mesoporous channels shows enhanced electrochemical activity owing to a much-diminished particle size. Among the mesoporous substrates, mesoporous carbon materials are especially promising owing to their many advantages, such as elastic properties and being lightweight and conductive, and thus the combination of sulfur and mesoporous carbon has been widely studied.[10,61,63,64,69]

Although the mesoporous carbon materials have been successful in preparing stable sulfur cathodes, the electrochemistry of cyclo-S$_8$ still exists in the systems, and the dissolution and shuttle of polysulfides cannot be eliminated. Recently, microporous carbon materials have been considered for an optimal confinement.[65,70] For example, by dispersing sulfur into microporous carbon fibers with an average pore diameter of about 1 nm, the electroactivity and cyclability of sulfur are greatly improved.[65] However, it remains a challenge to completely solve the problems resulted from the electrochemistry of cyclo-S$_8$ (Figure 3 a). Guo et al. have found that, even the carbon pore size reaches a critical value (for example, 0.5 nm), sulfur could still be loaded into the carbon channel (Figure 3 a–e).[41] Given that the pore size is less than the dimensions of cyclo-S$_8$ (ca. 0.7 nm; Figure 3 a), the ring-like configuration cannot be maintained, and sulfur can only be stored as chain-like sulfur molecules in the microporous carbon coated carbon nanotube (CNT@MPC) substrate (Figure 3 b).[41] The confined S molecules show strong interaction with the carbon wall, eliminating the unfavorable transition between cyclo-S$_8$ and S$_4^{2-}$ (during which soluble polysulfides form) and exhibiting a novel electrochemical behavior with a single output plateau at about 1.9 V, as well as one pair of redox peaks in the CVs (Figure 3 g,h).[41] Interestingly, the typical plateau at about 2.3 V (vs. Li$^+$/Li), which is ascribed to be the reduction from the common cyclo-S$_8$ molecule to the electrolyte-soluble polysulfides (Li$_2$S$_n$, $n = 4$–8), is not observed in its voltage profile. The novel electrochemistry of the confined chain-like sulfur molecules essentially solves the critical problem of polysulfide dissolution in conventional Li-S batteries. As a result, the sulfur/(microporous carbon coated carbon nanotube) (S/(CNT@MPC)) composite cathode exhibits admirable electrochemical properties in terms of specific capacity (1670 mA h g^{-1} upon the first discharge), cycling stability (1149 mA h g^{-1} after 200 cycles, Figure 3 h), and high-rate capability (800 mA h g^{-1} at 5 C).[41]

To reach a large specific capacity for the carbon/chain-like sulfur composite, a high sulfur loading rate should be guaranteed, which requires the carbon host to have a large micropore volume. However, the preparation of microporous carbon with sufficient pore volume for a chain-like sulfur content of more than 50 wt % is still challenging with current synthetic techniques.[41,65,70] Considering the benefits from both mesoporous carbon and microporous carbon, an alternative way is to load sulfur with hierarchical structured carbon substrates. For example, with potassium hydroxide as the activation agent, hierarchically micro/mesoporous carbon spheres (MPCs) can be prepared by chemical activation of hydrothermal carbon precursors (Figure 4 a).[66] The carbon substrates have a rich abundance of micropores of about 0.5 nm, and also wide distributions in the mesoporous region. The micropores enable sulfur to be stored mainly as active chain-like sulfur molecules in the composite, thus guaranteeing high capacity and good cycle stability. The mesopores increase the pore volume of carbon to achieve a high sulfur loading amount, and facilitate the smooth Li$^+$ transfer to ensure superior rate capabilities of the composite. Moreover, the pore structures of the carbon substrates can be easily

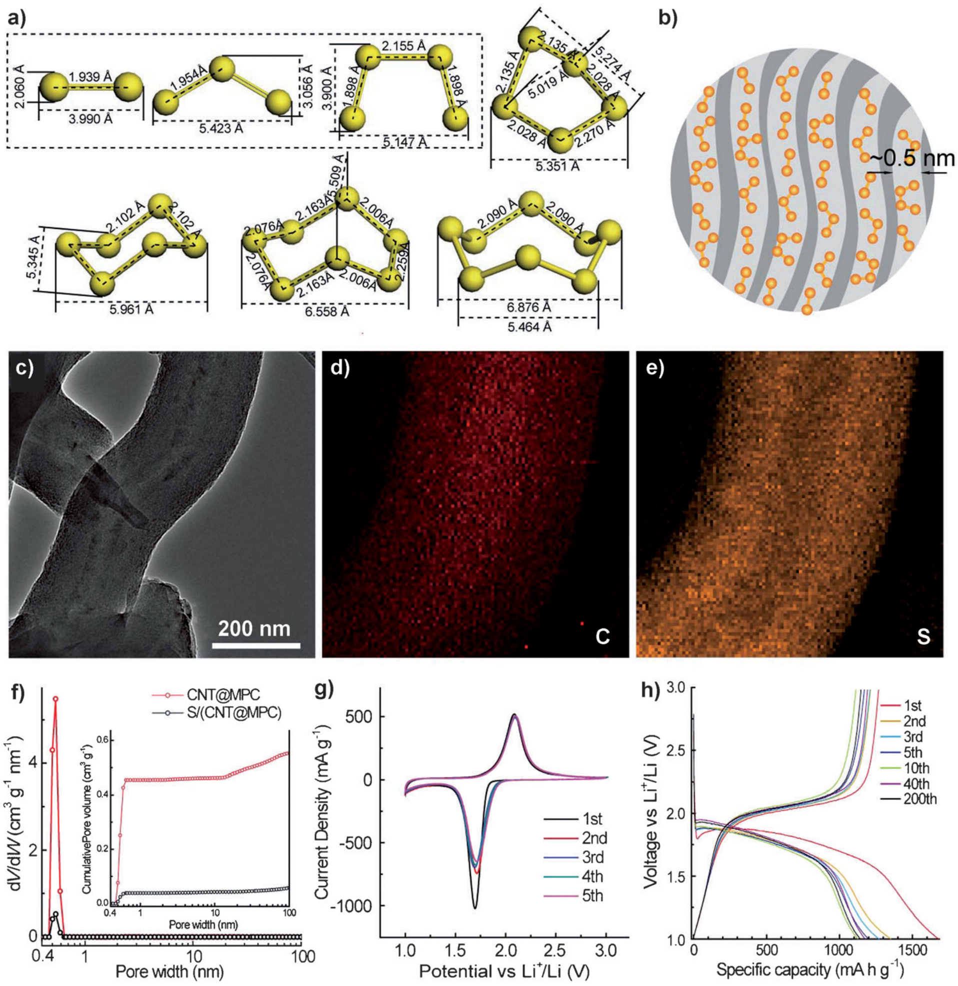

Figure 3. a) Calculation results of sulfur allotropes from S_2 to S_8.[45,71] b) Diagram showing the confined S_{2-4} molecules in the microporous carbon channels. c) TEM images of the sulfur/(microporous carbon coated carbon nanotube) S/(CNT@MPC) composite cathode. Elemental mappings of d) C and e) S of the S/(CNT@MPC) composite. f) Pore size distribution of the microporous carbon coated carbon nanotube (CNT@MPC) substrate. g) The first five CVs of the S/(CNT@MPC) composite cathode, obtained in a glyme-based electrolyte at 0.05 mV s^{-1}. h) Galvanostatic discharge–charge profiles (GDC) of S/(CNT@MPC) composite cathode at 0.1 C. Reproduced with permission from Ref. [41]. Copyright 2012, American Chemical Society.

tuned by adjusting the concentration of KOH, and it is found to be directly related with the battery performances (Figure 4a).[66] An optimized pore structure is yielded at a KOH concentration of 1 M, at which the S/MPCs cathode shows high specific capacity, favorable rate capabilities, and a long cycle life of 800 cycles at 1 C (Figure 4b). And the composite retains a high capacity and a fine cycling stability even the sulfur loading increases to 50 wt%.[66]

Recently, a more advanced hierarchically structured hollow porous carbon (HPC) has been developed for the loading of sulfur, which integrates micropores, mesopores, and macroporous hollow cavity (Figure 4c,d).[67] When loading with sulfur, the sulfur is preferentially stored as short chain-like molecules in the micropores, while the carbon mesopores facilitate the migration of Li$^+$, and the hollow structure alleviates the stresses upon lithiation/delithiation (Figure 4c).[67] With above-mentioned structural advantages, the sulfur cathode no longer involves with any polysulfide dissolution, but delivers improved electrochemical stability and kinetics. A long-life Li-S battery is assembled with the S/HPC cathode, which demonstrates a long lifespan of 600 discharge–charge cycles in a long-term cycling test lasting for 255 days.[67]

As a variant of hosting sulfur by porous substrates, the substrates can also be used as polysulfide absorbing additives for preparing the sulfur cathode, so that the soluble polysulfide intermediates can be localized on the cathode.[72–75] For example, ordered mesoporous silica substrates (SBA-15) were introduced onto the sulfur cathode, which acted as fine reservoirs to trap and to store the polysulfides formed during cycling,[72] thereby contributing to a much enhanced cyclability of the battery. Another variant is the polysulfide blocker, as demonstrated in the work of Manthiram's group, in which a microporous carbon interlayer is inserted between the battery separator and the sulfur cathode.[73] The carbon interlayer serves both as an "upper current collector" to improve the electrical contact of sulfur, and as an selective "filter" enabling the Li$^+$ flow while blocking the shuttle of polysulfides, so that stable cycling and high efficiency of the system can be maintained (Figure 5a,b).[73] Conductive carbon nanotube paper was also employed as the interlayer, which showed similar functions and effects.[74] The introduction of a carbon interlayer has been noted to reduce the sulfur fraction in the whole system, thus lowering the specific energy of the battery. Therefore, special attention should be focused on reducing the thickness and weight of the interlayer to achieve both an optimized blocking effect and a satisfied energy density of the battery.

3.2. The Sulfide Cathode

The use of sulfide as the cathode material for rechargeable Li batteries dates back to the 1970s.[76] During that time, M. S. Whittingham proposed the intercalation mechanism of Li$^+$

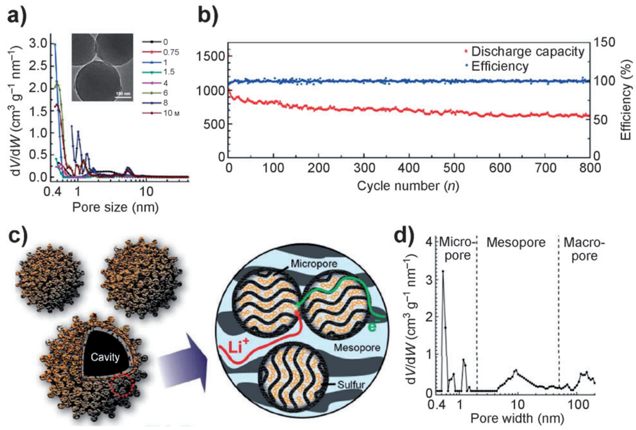

Figure 4. a) Pore size distribution of the MPC host. Inset: TEM image of MPC substrate. Scale bar: 100 nm. (b) Long-term cycling performance at 1 C. Reproduced with permission from Ref. [66]. Copyright 2013, Royal Chemical Society. c) Illustration of HPC substrate. d) Pore size distribution of the HPC host. Reproduced from Ref. [67]. Copyright 2013, Wiley-VCH.

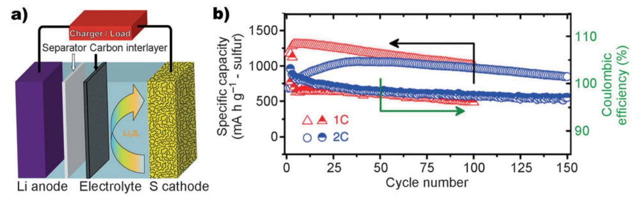

Figure 5. a) Illustration of a Li-S battery with microporous carbon interlayer. b) Cycling performance and Coulombic efficiency of the battery at 1 C and 2 C, respectively. Reproduced with permission from Ref. [73]. Copyright 2012, Nature Publishing Group.

into layered titanium disulfide (TiS_2), which was then employed as the cathode material to pair with Li anode in early Li batteries.[13,76,77] However, the intercalation sulfide cathodes suffered from their intrinsic low theoretical capacity, hindering their applications in high-energy batteries. Recently, Li sulfide (Li_2S), the final lithiation product of sulfur, has received increasing attention as a promising candidate for Li-S batteries.[78] The Li_2S cathode experiences the same but reverse electrochemical process with sulfur, and provides a large theoretical capacity (1166 mA h g^{-1}), considering the large fraction of the active sulfur. The use of Li_2S cathode obviates the need for metallic Li anodes. The cathode can be paired with various Li-free anode materials with large capacity and higher lithiation potential in assembling Li-S batteries (for example, Si, Sn, and other alloy anodes).[78–80] As a result, the common problems of Li anode, such as dendrite growth and low deposition efficiency, might be eliminated for good. These results contribute to a much enhanced battery safety.

However, the application of Li_2S cathode is still hindered by several problems. The first problem arises from the hydroscopic property of Li_2S, which makes it highly unstable in air.[81] Therefore, the preparation and storage of Li_2S should be implemented with strict isolation from ambient environment. The second problem lies in the high electronic resistivity and poor ionic conductivity (ca. 10^{-13} S cm^{-1}) of Li_2S, which makes the cathode electrochemically inactive. Cui et al. have found that, for micrometer-sized Li_2S particles, a large potential barrier (ca. 1 V) should be overcome at the beginning of charging process.[82] To enhance the Li storage kinetics, a combination of Li_2S with electronic conductors, such as carbon, is highly desired in preparing the cathode materials.[82,83] For example, the combination of micrometer-sized Li_2S particles with carbon black nanoparticles by high-energy ball milling,[83] has been confirmed as a cost-effective method to yield Li_2S-C composite cathodes with much improved electrochemical performance. After further introducing highly conductive carbon nanotubes into the composite, a high specific capacity of 1144 mA h g^{-1} (based on Li_2S mass) is obtained at a high Li_2S content of 67.5 wt %, with much improved cycling and high-rate performance.[83]

The last problem results from the electrochemistry of sulfur. Given that Li_2S shares the same but reverse electrochemical processes as sulfur, polysulfide dissolution and shuttle are also observed on the cathode. To overcome the deficiency, Li_2S is often encapsulated into porous substrates to limit the active material loss during cycling. In building a novel metallic Li-free Li_2S/Si rechargeable battery, Li_2S has been hosted into the CMK-3 mesoporous carbon for preparing the cathode,[78] which is then paired with the Si nanowire anode to assemble the battery (Figure 6a). The nanostructured designs of both electrodes assist in overcoming the issues associated with active sulfur loss and drastic Si expansion, contributing to a high specific energy (630 W h kg^{-1}, based on Li_2S mass only) and favorable cycling stability of the battery (Figure 6b).[78]

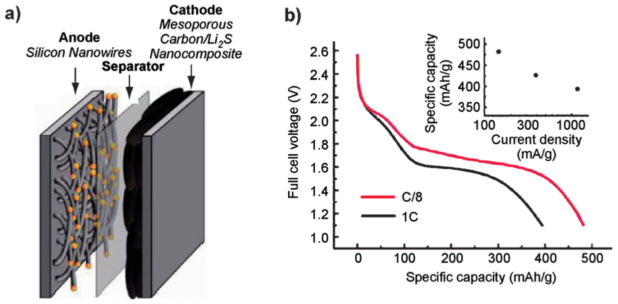

Figure 6. a) Diagram showing the structure of a Li_2S/Si battery. b) First discharge voltage profiles of the full battery with Li_2S/CMK-3 mesoporous carbon nanocomposite cathodes and silicon nanowire anodes at rates of 1 C (1166 mA g^{-1}) and C/8 (146 mA g^{-1}). The inset in (b) is a plot of the first discharge specific capacity of full cells operating at various current rates. Reproduced with permission from Ref. [78]. Copyright 2010, American Chemical Society.

Regrettably, conventional carbon processing techniques, such as CVD carbon coating and annealing (usually carried out at an elevated temperature of more than 600 °C), cannot be applied on sulfur because of its low sublimation temperature (445 °C under 1 atm).[44] Fortunately, Li_2S holds a high decomposition temperature of > 900 °C, doubling that of sulfur and warranting its processing into carbonized composites. Archer et al. developed a high-temperature carbonization technique to prepare the Li_2S/C composite cathode material, which employs polyacrylonitrile (PAN) as the carbon source, to host Li_2S species in N-doped carbon through Li–nitrile interactions.[84] The uniform distribution of Li_2S in the carbon substrate and the sequestering effect of the nanoarchitecture on higher-order polysulfides bring high-energy LIBs with great cycling stability.

The evolution from liquid electrolyte-based batteries to all-solid-state batteries has proved its validity in eliminating the polysulfide dissolution issue in Li-S batteries, yet is also applicable in Li_2S-based batteries. However, to fully utilize the capacity, the intrinsic low ionic conductivity of Li_2S should be improved.[85] Surface coating of Li_2S nanoparticles by fast ionic conductors offers an effective way to solve the problem.[86] For example, by coating Li_2S nanoparticles with a Li_3PS_4 (a Li superionic conductor) layer to form a core–shell structure, the composite exhibited a high ionic conductivity ($10^{-7}\,S\,cm^{-1}$ at 25 °C), which is six orders of magnitude higher than that of bulk Li_2S.[86] When functioning as the cathode material in all-solid-state Li-S batteries, the high Li^+ conductivity of the composite imparts a high capacity and an excellent cycling performance to the batteries, thus promises long-lasting, energy-efficient rechargeable Li batteries.

Other sulfides, such as FeS_2[87] and MoS_2,[81,88] which undergo conversion reactions with Li to yield Li_2S, are also potential cathode candidates for sulfur-based rechargeable Li batteries. For example, MoS_2 converted into Li_2S/Mo composites upon deep discharge, and the composites exhibited both high sulfur utilization and fine cycling stability owing to the high conductivity and strong polysulfide binding of Mo.[81]

Organic sulfides are also promising to be used as the cathode materials to construct sulfur-based rechargeable Li batteries.[89–92] Compared with the inorganic sulfides, the soft nature and processing compatibility of organic sulfides make them especially attractive in manufacturing flexible rechargeable Li batteries. In the organic sulfides, active sulfur is usually stored as disulfides (by the S–S bond) in the side chains of the polymer[90,93] while the carbon backbone conducts electrons for the lithiation/delithiation of the disulfides. As the disulfides are bonded to the side chain of the polymer, they are not easily released from the polymer during the electrochemical redox process, contributing to improved cycling performance.[90] However, owing to the low electronic conductivity of the polymer, the stored sulfur has a low activity, impeding its capacity utilization. With the development of organic sulfide science, it is expected that sulfides with high electrochemical activity can be synthesized, bringing about improved Li storage properties.

Apart from the above-mentioned solid cathode materials, the lithium-dissolved polysulfide systems, which utilize soluble active materials of polysulfides in ether solvent (that is, the so-called catholytes), have been revisited for Li-S batteries recently.[33,94,95] This kind of cathode materials can be dated from 1979 when Rauh et al. reported a Li/dissolved sulfur battery with a dissolved polysulfide (Li_2S_n, $n \geq 8$) electrolyte as the catholyte paired with a Teflon-bonded carbon electrode.[30] Though the utilization of soluble polysulfides as cathode materials can achieve a high reaction activity in comparison with solid sulfur electrodes, it may decrease the volumetric energy density of Li-S batteries and meanwhile bring about some severely practical problems during synthesis and battery assembly processes owing to the extraordinarily hygroscopic feature of polysulfides. Furthermore, the reduction of polysulfides on the Li metal anode and their high corrodibility are still challenges.

4. The Lithium Anode

Compared with the rapid thriving of cathode materials, the Li anode as an important component of Li-S batteries has not been comprehensively treated in current studies since the overwhelming concentration on rechargeable Li batteries from the 1970s to 1980s.[17,29,30,96,97]

The problems faced with Li anode mainly derive from the reaction of Li anode with both electrolyte solution and the soluble polysulfides. One effective approach to mitigate these problems is to isolate the highly active Li anode from electrolyte solution and soluble polysulfides through introducing a thin and stable passivation layer on Li anode. Apart from the protection of Li anode, the passivation layer should be permeable for Li^+, allowing fast transfer of Li^+ under electrical field. The passivation layer thereby functions as the solid electrolyte interphase (SEI) layer between Li anode and electrolyte solution. The protection layer can be realized on Li anode ex situ before assembling the batteries, or in situ during the operation of the batteries, through modifying the Li anode or introducing suitable additives in electrolytes. Recent progress on introducing additives in electrolytes to protect Li anode[98–100] is discussed in detail in Section 5.1.3.

4.1. Modification of the Lithium Anode

Solid polymer electrolytes with good Li^+ conductivity have been employed as a protection layer of Li anode. The protection layer covered on Li anode is synthesized by a cross-linking reaction of the curable monomer (poly(ethylene glycol) dimethacrylate) in the presence of liquid electrolyte (a mixture of tetra(ethylene glycol) dimethyl ether (TEGDME) and $LiClO_4$) and a photoinitiator (methyl benzoylformate). Compared with bare Li anode, the protected Li anode shows much improved charge–discharge characteristics. After 50 cycles, the protected Li anode shows a smoother and denser surface morphology.[101] However, owing to the sluggish Li^+ transport through polymer electrolyte, the introduction of polymer electrolyte on Li anode might compromise with the low discharge capacity at room temperature.

Apart from the polymer electrolytes to protect Li anode, sulfur powder has been reported to deposit on Li anode for the same purpose.[33] For the sulfur-deposited Li anode after several cycles, both the amount of Li_2S and that of polysulfides on Li anode are rather low compared to bare Li anode. And the cell with the sulfur-deposited Li anode shows much improved properties. The improvement is beneficial to a native SEI layer that formed on the surface of Li anode by the reduction of sulfur during contact with the electrolyte. And this protective layer prevents to generate the insoluble Li_2S at the surface of Li upon further cycling.[33]

For Li-S batteries, the utilization of the metallic Li anode suffers from serious issues, including the dendrite formation, the low deposition efficiency of Li, the deposition of insoluble Li_2S_2 and Li_2S on Li anode, and the unfavorable reaction between Li polysulfides and metallic Li during cycling. Exploring the suitable surface modifications to protect the Li anode is not an easy task, especially in maintaining high capacity and sufficient rate capability at the same time. Therefore, replacing Li anode is undoubtedly an alternative approach to avoid completely these problems related with the metallic Li anode.

4.2. Metallic Lithium-Free Anodes

Substituting the metallic Li anode for Li-S batteries means either pairing the Li-containing anode with the sulfur cathode, or matching the Li-free anode with the Li-containing cathode (for example Li_2S) to obtain new configuration of Li-S batteries. Considering the high-capacity of sulfur cathode, substituted anode ought to be high capacity to marry with sulfur cathode. Furthermore, the high lithiation potential is necessary to allow a fast charge without Li plating.[78,79,102] Naturally, high-capacity alloy anode materials (for example Si, Sn) might be the ideal candidates to fulfill this task, as the Li alloys of Si or Sn have a μ_a of 0.2 to 0.8 eV below μ_a (Li).[14]

Guo et al. replaced the metallic Li anode with the electrochemically prelithiated Si/C anode (Figure 7a).[102] After the initial discharge of Si/C microsphere in the half cell (vs. Li counter electrode), Si reacts with Li to generate Li_xSi ($x = 3.5$–4.4) alloy, which could offer sufficient Li ions for the sulfur cathode. A room temperature ionic liquid (RTIL), instead of liquid electrolyte, was used to construct a high-safety battery to promote the high thermal stability. When the prelithiated Si/C anode pairs with the S-C composite cathode in the electrolyte of 0.5 M ($Li(CF_3SO_2)_2N$) (LiTFSI) with *n*-methyl-*n*-allylpyrrolidinium bis(trifluoromethanesulfonyl)imide (RTIL-P1 A3TFSI), the as-obtained Li-S battery delivers a high initial discharge capacity of 1457 mA h g^{-1} (up to 87% of the theoretical specific capacity of sulfur) and maintain a reversible capacity of as high as 670 mA h g^{-1} after 50 cycles (Figure 7b,c). Additionally, this battery exhibits one output voltage plateau at approximately 1.5 V, which is capable of directly replacing the widely used 1.5 V primary alkaline batteries and dry cells (Figure 7b).[102] The cell configuration might be attractive in the future considering the metallic Li-free anode, the high-capacity sulfur cathode, and the high-safety RTIL electrolyte.

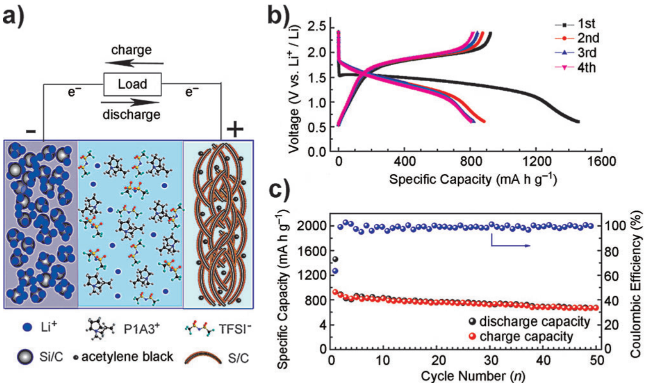

Figure 7. a) Illustration of the configuration of a Li-S battery with prelithiated Si/C anode/RTIL-containing electrolyte/S-C composite cathode. b) Galvanostatic discharge–charge profiles of the initial four cycles and c) cycle performance at a current rate of 0.1 C for the battery. Reproduced with permission from Ref. [102]. Copyright 2013, Elsevier.

Si or Sn anode matches with the Li-containing cathode (for example Li_2S) to replace the sulfur cathode.[78,79] For example, the Li_2S/C cathode is paired with the Sn/C anode across the gel polymer electrolyte, a polyethylene oxide/Li trifluoromethanesulfonate ($PEO/LiCF_3SO_3$) polymer matrix to promote the high thermal stability of the battery.[79]

Along with the aforementioned serious limitations of the metallic Li anode, safety consideration is highly important and critical for its practical application in Li-S batteries. For instance, in cases of misuse, the short circuit of Li rechargeable batteries can bring about pronounced heat dissipation, which is prone to generate dangerous "thermal runaway" and leads to the explosion of batteries.[103] Therefore, it is worthwhile to take great effort for developing metallic Li-free anodes for Li-S batteries.

5. The Electrolyte

The electrolyte, as the medium for the transfer of Li^+ between a pair of electrodes, interacts closely with both the sulfur cathode and the Li anode during the operation. The electrochemical behaviors of Li-S batteries can be dramatically different in various electrolytes, originating from the different solubility of polysulfides in various electrolyte solvents. Therefore, much attention has been given to exploring the suitable electrolytes for Li-S batteries. Liquid electrolytes, RTIL-based electrolytes, and solid state electrolytes are all involved with Li-S batteries in suppressing the internal shuttling of polysulfides and in stabilizing the Li anode.

5.1. Liquid Electrolytes

Based on the commercial success of LIBs, liquid electrolytes now take the central stage of Li-S batteries. Nevertheless, the dissolution of polysulfides in commonly used liquid electrolytes inspires the intensified research to reinvestigate electrolyte components thoroughly.

5.1.1. Solvents

Several studies on sulfur and polysulfides in nonaqueous solutions reveal that the dynamic equilibrium, redox chemistry, and kinetics of sulfur and polysulfides are strongly affected by solvent complexation,[30] resulting in the prominent influence of solvents on the electrochemical performance of Li-S batteries.[104–106] In liquid organic electrolytes, two types of aprotic solvents, carbonate and ether, are mainly utilized for Li-S batteries. Originating from the knowledge of sulfur redox chemistry, early efforts have been exerted to explore solvents with high solubility to polysulfides. Polysulfides formed during cycles are soluble for solvents with high basicity. In this regard, most ether can dissolve polysulfides very well.[30] For example, 1,3-dioxolane (DOL),[17] 1,2-dimethoxyethane (DME), and tetra(ethylene glycol) dimethyl ether (TEGDME)[107] are good polysulfide solvents. Abruña et al. conducted the systematical investigations into the interrelation between various solvents and electrochemical properties by using in situ S K-edge X-ray absorption spectroscopy.[24] For the S/C cathode materials generated by heating the mixture of elemental sulfur and carbon black at 155 °C for 10 h, low-viscosity ethereal solvents (DOL/DME) could be appropriate solvents for the electrolytes of Li-S batteries because DOL/DME can result in a more complete reduction of soluble polysulfides formed during cycles.[24] Though the electrolytes with high solubility of polysulfide enable the Li-S battery to operate with a high utilization of sulfur, even as a liquid cathode system, soluble polysulfides cause both Li corrosion and the internal polysulfide shuttle because of their relatively high mobility.[31] Note that high polysulfide solubility electrolytes may lead to a poor long-time cycling performance for the solid cathode system in Li-S batteries. The dissolution of polysulfides may not, however, be completely harmful because the soluble polysulfides in etheral electolytes could react with Li and possibly suppress the growth of Li dendrite.[31] Although ether-based electrolytes have been widely used for Li-S batteries with the target to improve the electrochemical activity of sulfur, some inherent drawbacks of ether solvents (for example, poor electrochemical stability, high volatility, particular for DME)[108] cannot be ignored definitely for the practical applications of Li-S batteries in the future.

Organic carbonate solvents, such as ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC),[41,70] are widely used in the electrolytes of commercial LIBs, but they are seldom used for Li-S batteries because carbonate-based solvents can react with reduced soluble polysulfide during the first discharge process to generate possible thioether and sulfonium functionalities.[24] Surprisingly, chain-like sulfur molecules[41] confined in tiny micropores of 0.5 nm show impressive electrochemical properties (Figure 3 f) with a carbonate-based electrolyte of 1 M $LiPF_6$ in EC/DMC (1:1 wt %). The results suggest that electrolyte solvent should be chosen with consideration for both different sulfur molecules in cathode materials and the reduced intermediate species. On the basis of the commercial success of carbonate-based electrolytes in LIBs and the outstanding electrochemical properties of chain-like sulfur molecules confined in micropores, we believe that the battery system coupled with these two features could open a new avenue to overcome the difficulties during large-scale manufacturing of Li-S batteries.

5.1.2. *Lithium Salts*

The Li salts $LiClO_4$, $LiPF_6$, $LiCF_3SO_3$ (LiTFS), and LiTFSI are commonly used for Li-S batteries. Much attention has been given to LiTFS and LiTFSI for Li-S batteries with greater thermal and hydrolytic stability compared with the popular $LiPF_6$. In contrast to the pronounced influence of different solvents on electrochemical properties of Li-S batteries, no clear difference on the electrochemical behaviors of Li-S batteries has been observed among these Li salts,[24] but the DOL/DME electrolytes with higher concentration of LiTFSI show a lower rates of Li corrosion with polysulfides and a slower shuttle phenomenon.[31] Hu et al. developed the "solvent-in-salt" electrolyte (SIS electrolyte) with ultrahigh salt concentration (7 M LiTFSI per solvent) in DOL/DME with the aim of inhibiting the Li polysulfide dissolution and stabilizing the Li anode (Figure 8 a–c).[109] For the CMK-3/S cathode, the Li-S battery with the SIS electrolyte delivers an initial specific discharge capacity of 1041 mA h g^{-1} with a high Coulombic efficiency (93.7 %) in the first cycle and a high Coulombic efficiency of nearly 100 % after the initial cycle (Figure 8 a). The possible reason for the improvement can be ascribed to the ultrahigh concentration of LiTFSI, which is almost close to saturation, hardly dissolve the soluble intermediate (Li_2S_n) and thus avoids Li polysulfides shuttle. Furthermore, the SIS electrolyte shows a lower roughness and lower damage level of the metallic Li anode compared with the pristine anode (Figure 8 b,c).[109] The unique merits of the SIS electrolyte for Li-S batteries indicate that suitable electrolytes can do significant favor to improve the electrochemical performance and safety of the Li anode, but leave the cost as a new issue.

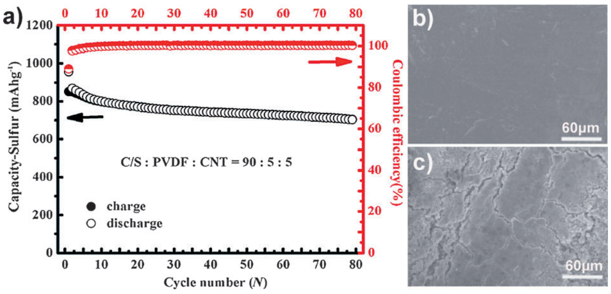

Figure 8. a) Cyclic performance and Coulombic efficiency of Li-S batteries at a current rate of 0.2 C. SEM images of b) fresh Li metal and c) Li metal with a SIS electrolyte after 280 cycles in Li deposition and dissolution experiments. Reproduced with permission from Ref. [109]. Copyright 2013, Nature Publishing Group.

However, LiTFS, LiTFSI are apt to dissolve Al substrate[110,111] and stainless-steel current-collectors,[112] resulting in the self-discharge of Li-S batteries. For instance, LiTFS dissolves Al substrate at about 2.78 V and pits at 3.0 V, whereas LiTFSI dissolves at 3.55 V.[110] The possible reason might be the reaction between TFS^- or $TFSI^-$ anion and Al or Fe. The investigation by in situ electrochemical quartz crystal microbalance further confirms that Al undergoes significant corrosion in PC containing LiTFSI, LiTFS, and $LiClO_4$, but forms a protective film in PC containing $LiPF_6$.[111] Thus, the voltage range should thus be restricted for Li-S batteries with LiTFS, LiTFSI, and $LiClO_4$ electrolytes, which may lead to the incomplete utilization of the sulfur cathode.

5.1.3. Additives in Liquid Electrolytes

The introduction of additives in liquid electrolyte mainly aims to passivate the surface of the Li anode and to protect Li from the reaction with electrolyte solution and polysulfides.

$LiNO_3$, an oxidizing additive, has been introduced into electrolytes in stabilizing the metallic Li anode by an in situ formation of a protective layer on the Li anode surface.[98] The possible reason is that $LiNO_3$ is reduced into insoluble Li_xNO_y species, and oxidizes the sulfides of solution and surface species to Li_xSO_y species, passivating the Li electrodes and thus preventing the continuous reaction between Li and polysulfides in solutions.[27] P_2S_5, another additive of electrolytes, can facilitate to form a smooth and dense passivating layer with high Li^+ conductivity on the surface of the Li anode and to prevent the precipitation of insoluble Li_2S and Li_2S_2 on Li anode.[99] P_2S_5 can react with Li_2S_x $(1 \leq x \leq 8)$ to form soluble complexes and thus converts the less soluble species of Li_2S and Li_2S_2 into highly soluble complexes. This process avoids the precipitation of Li_2S and Li_2S_2 on the anode. Moreover, the main component of the passivation layer is a high Li^+ ionic conductive glass (Li_3PS_4), which are favorite for the fast transfer of Li^+, and prevent access of the polysulfide to the surface of the metallic Li.[99]

The target of suppressing the dendrite growth of Li is another critical problem faced by the Li anode. Zhang et al. proposed the self-healing electrostatic shield mechanism to eliminate the self-amplification growth behavior of Li dendrites.[100] By introducing the selected cations (for example Ce^+, Ru^+) with the reduction potential below the reduction potential of Li^+ into electrolytes, the Li deposition morphology is altered from the commonly needlelike dendrites to mirror-like films, or films composed of merged and fine spherical particles (Figure 9).[100] During Li deposition process, these additive cations are suspected to form a positively charged electrostatic shield around the initial growth tip of the protuberances of Li, and cannot be deposited on the Li anode because of their low reduction potentials. Meanwhile, the positively charged shield formed by additives could repel the incoming Li^+ from the protrusion and force further Li^+ deposition to neighboring regions of the Li anode until a smooth deposition layer is formed.[100] The introduction of these additives in electrolytes significantly changes the morphology of deposition of Li and blocks the formation of Li dendrites without consuming these additives during the operation of batteries, but the cells with these additives might be compromised with the low rate capabilities because the additives adsorbed on the Li anode may hinder the fast access of Li^+. Thereby, the formulation of electrolytes for Li-S batteries should consider the interrelated electrochemical process of Li-S batteries.

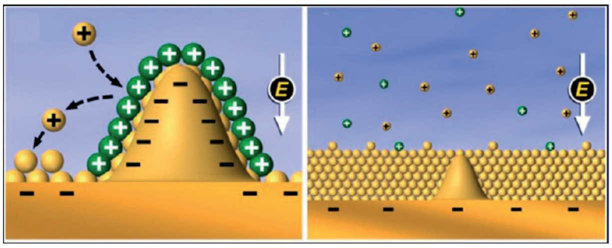

Figure 9. Illustration of the Li deposition process based on the self-healing electrostatic shield mechanism. Reproduced with permission from Ref. [100]. Copyright 2013, American Chemical Society.

Although certain progress has been achieved for liquid electrolytes for Li-S batteries, the instinct drawbacks of liquid electrolytes, which are derived from the volatile organic solvents and the high solubility of polysulfides in organic solvents, still trouble the practical application of Li-S batteries at the expense of cycling stability and safety issues. Increasing electrolyte viscosity could substantially decrease the polysulfide mobility and suppress the polysulfides shuttle, naturally, replacing liquid electrolytes with high-safety and high-viscosity electrolytes (for example, ionic-liquid-based electrolytes) may be an alternative way to mitigate the problems concerning liquid electrolytes.

5.2. Ionic-Liquid-Based Electrolytes

Low-vapor-pressure and non-flammable RTILs as the electrolyte solvent of Li-S batteries, provide the safety assets to conquer the drawbacks of liquid electrolytes with commonly used organic solvents.[34,113] Recently, much effort has been devoted to RTILs electrolytes for Li-S batteries.

A binary RTIL Li bis(trifluoromethanesulfonyl)amide/*N*,*N*-diethyl-N-methyl-*N*-(2-methoxyethyl)ammonium bis-(trifluoromethanesulfonyl)amide (Li[TFSA]/[DEME]-[TFSA]) for Li-S batteries was investigated.[36] Watanabe et al. proposed that the weak Lewis acidic/basic nature of RTILs can cause weak interactions between the cations and/or anions and Li polysulfides (Li_2S_m, $2 \leq m \leq 8$), corresponding to the low solubility of Li polysulfides in the RTIL.[36] Considering the higher viscosity of RTIL electrolytes in comparison with that of liquid electrolytes, RTIL electrolytes usually offer a sluggish mass transport and charge transfer in Li-S batteries, resulting in a low utilization of sulfur. Byon et al. combined RTILs *N*-methyl-*N*-propylpiperidinium bis-(trifluoromethanesulfonyl)imide (PP13-TFSI) with low-viscosity organic solvent DME together to provide a balance between solubility and diffusion rate of Li polysulfides.[114] In such an electrolyte, DME offers the high Li polysulfide solubility, and thus supplies a sufficient concentration of active material. RTILs PP13-TFSI has weak pairs of Lewis acid and base to alleviate the Li polysulfides solubility, and high viscosity capable of suppressing the diffusion rate of Li polysulfides. The incorporation of PP13-TFSI with DME exhibits the discharge capacity of about $1360\,mA\,h\,g^{-1}$ at 0.1 C, which is twice that observed with the neat PP13-TFSI- or DME-based electrolyte. This result suggests that the hybridization of two different electrolytes might be beneficial to the improvement of the electrochemical performance for Li-S batteries.[114]

The utilization of RTILs as the solvent of electrolytes exhibits some interesting improvements.[35,36] The high-viscosity characteristics of ionic-liquid-based electrolytes could suppress the shuttle of polysulfides at the expense of sluggish Li^+ transportation. As a result, ionic liquid electrolytes can only provide acceptable sulfur specific capacity at low rates. The batteries with ionic liquid electrolyte commonly exhibit poor rate capability. Compared with commonly used liquid electrolytes, the high cost and hard proceeding of ionic liquid still impede their industrial application for Li-S batteries.

5.3. Solid State Electrolytes

Solid-state electrolytes are the most promising electrolytes to substitute for the liquid electrolytes because of their superior voltage, temperature, and mechanical stability. In the case of Li-S batteries, solid state electrolytes have the unique advantages for their solvent-free characteristics, such as acting as the separators isolating two electrodes and maintaining the polysulfides near the cathode side.[115] Additionally, the as-assembled all-solid-state batteries have the highest safety advantages (for example, nonleakage and nonflammability) and the mitigation of the Li dendrite growth.

Gelled or solid polymer electrolytes have been investigated for Li-S batteries, such as poly(ethylene oxide) (PEO) polymer electrolyte,[116] poly(ethylene glycol) (dimethyl ether) (PEGDME) polymer electrolyte,[117] and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) copolymer.[118] Generally, the polymer electrolytes have a problem of a low ionic conductivity at room temperature, leading to the low utilization of active materials in Li-S batteries. Typical avenues, such as dispersing nanosized ceramic filler (for example ZrO_2)[115] and introducing RTIL into conventional polymer electrolytes as a plasticizer,[119,120] have been shown to improve the transport properties of the polymer electrolyte. For example, the hybrid polymer ionic liquid electrolyte, consisting of *N*-methyl-(*n*-alkyl)pyrrolidinium bis(trifluoromethanesulfonyl)imide ILs and conventional PEO-based polymer, shows the significantly improved ionic conductivity of electrolyte.[120] The cell with the hybrid electrolyte exhibits about $1000\,mA\,h\,g^{-1}$ at 0.2 C in the first cycle, and maintains a capacity retention of approximately 90 % after 50 cycles.[120] Recently, a new single-ion polymer electrolyte has been synthesized based on self-assembled polyanionic block copolymers. This polymer electrolyte exhibits the superior single-ion conductivity ($1.3\times10^{-5}\,S\,cm^{-1}$ at 60 °C), excellent mechanical properties, and an electrochemical stability window spanning 5 V versus Li^+/Li.[121] Although highly attractive for application in Li-S batteries, the polymer electrolytes still suffer from the inability resulting from the combination of the high ionic conductivities at room temperature and good mechanical properties. Along with the polymer electrolytes, inorganic solid electrolytes with high conductivity at room temperature can be considered as potential solid-state electrolytes for Li-S batteries, such as sulfide glasses Li_2S-P_2S_5, with a high conductivity of over $10^{-3}\,S\,cm^{-1}$ at room temperature.[122]

All-solid-state battery is the final target for conventional electrochemical cell, particular to Li-S batteries, in view of the unique features of solid state electrolytes. The shuttle problem of soluble polysulfides in common liquid electrolytes indicates that solid state electrolytes are the ideal electrolytes for Li-S batteries. However, most solid state electrolytes are hindered by the common problem of the low conductivities at room temperature. Developing novel solid state electrolytes with high conductivity at room temperature or combining with different electrolytes (for example solid ceramic-polymer electrolytes) could be the effective way to promote the conductivities of solid state electrolytes. The actual critical challenges impeding the application of solid state electrolytes is the high interfacial resistance between the resultant solid state electrolyte and the solid electrode in Li-S batteries. This drives more scientific and technical effort to solve the issues.

6. Summary and Outlook

In summary, we have systematically reviewed the history, the electrochemistry, and the recent progresses concerning Li-S batteries. Owing to a vast amount of publications in the field, it is hard to incorporate all the aspects in this paper, and emphasis is mainly placed on the three key components of Li-S batteries, that is, the sulfur (or sulfide) cathode, the Li anode, and the electrolyte.

The following are several key points that need to be considered for high-performance sulfur cathode materials. First, decreasing the particle size of sulfur and creating intimate contact with conductive host is necessary to improve its electrochemical Li storage activity. Second, preserving the cavity to alleviate the volume change of sulfur during cycling is of great importance in acquiring long-term cycling stability. Third, utilizing the advantages of the confinement of nanopores and surface coating of sulfur can prevent the dissolution and shuttle of polysulfide in the liquid electrolyte, but it is still a big challenge for synthesizing porous host with large pore volume of tiny pores for high sulfur loading. Fourth, substituting Li-containing cathode materials (for example Li_2S) for sulfur could obviate the need for Li-containing anodes.

In the case of Li anode, the Li surface chemistry and the nature of the Li-electrolyte interphase formed in Li-S batteries determines the Li morphology and cycling efficiency of Li. The protection of Li anode is of great importance in avoiding the formation of Li dendrites, improving the deposition efficiency of Li, and preventing the unfavorable reaction between soluble polysulfides with Li. Electrolytes also show the great influence to the performance of Li-S batteries arising from the dissolution ability of polysulfides. Solution-free solid state electrolytes could be the promising electrolyte for Li-S batteries in the future. Furthermore, suitable additives in electrolytes should be one key point to further stabilize the Li anode and to improve the utilization of both anode and cathode materials.

The development of Li-S batteries has achieved significant progress. However, more interdisciplinary effort is still needed to develop the Li-S batteries with high specific energy and good cycle life. More factors, apart from cathode materials, electrolytes, and anodes, suitable binders (for example, a mixture of styrene butadiene rubber and sodium carboxyl methyl cellulose)[123] should be considered thoroughly. Fundamental research is also necessary to explain the mechanistic details underlying the operation and limitation of Li-S batteries. It is believed that Li-S batteries could be a promising and practical technology for the applications in transportation and large-scale grid energy storage in the near future.

In the context of the similarities of the molecular structure between selenium and sulfur, and in electrochemical reaction mechanism between Li and Na, we can expect that the achievements of Li-S batteries can be extended to other novel rechargeable batteries, such as Li-Se batteries,[124] room temperature Na-S batteries,[125] and Na-Se batteries.[126] Furthermore, the scientific results of chalcogen elements in rechargeable batteries could also be utilized in Mg-S and Mg-Se batteries.[127]

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