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Li₂S-Based Li-Ion Sulfur Batteries: Progress and Prospects

Abstract

The great demand for high-energy-density batteries has driven intensive research on the Li–S battery due to its high theoretical energy density. Consequently, considerable progress in Li–S batteries is achieved, although the lithium anode material is still challenging in terms of lithium dendrites and its unstable interface with electrolyte, impeding the practical application of the Li–S battery. Li₂S-based Li-ion sulfur batteries (LISBs), which employ lithium-metal-free anodes, are a convenient and effective way to avoid the use of lithium metal for the realization of practical Li–S batteries. Over the past decade, studies on LISBs are carried out to optimize their performance. Herein, the research progress and challenges of LISBs are reviewed. Several important aspects of LISBs, including their working principle, the physicochemical properties of Li₂S, Li₂S cathode material composites, LISBs full batteries, and electrolyte for Li₂S cathode, are extensively discussed. In particular, the activation barrier in the initial charge process is fundamentally analyzed and the mechanism is discussed in detail, based on previous reports. Finally, perspectives on the future direction of the research of LISBs are proposed.

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A Review on Li₂S-based Li-ion Sulfur Batteries: Progress and Prospects

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Key words: Li₂S cathode, activation barrier, Li-ion sulfur batteries, non-lithium-metal anodes.

Abstract

The great demand for high-energy-density batteries has driven intensive research of the Li-S battery due to its high theoretical energy density. Consequently, much progress on the Li-S battery has been achieved, although the lithium anode material is still challenging in terms of lithium dendrites and its unstable interface with electrolyte, impeding practical application of the Li-S battery. The Li₂S-based Li-ion sulfur batteries (LISBs), which employs lithium-metal-free anode, is a convenient and effective way to avoid the use of lithium metal for realization of practical Li-S battery. Over the past decade, studies of the LISBs have been carried out to optimize their performance. In this paper, the research progress and challenges of LISBs are reviewed. Several important aspects of LISBs, including their working principle, the physicochemical properties of Li₂S, Li₂S cathode material composites, LISBs full batteries, and electrolyte for Li₂S cathode, are extensively discussed. In particular, we have fundamentally analysed the activation barrier in the initial charge process and discussed the mechanism in detail, based on previous reports. Finally, perspectives on the future direction on the research of LISBs are proposed.

1. Introduction

Over the past 30 years, the practical energy density of the Li-ion battery has increased from 150 Wh kg⁻¹ to 300 Wh kg⁻¹ by using transition metal oxide as the cathode material. Current Li-ion batteries are capable of powering portable electronic devices such as cell phones, laptops, iPad tablets and digital cameras.^[1] The ever-increasing air pollution have driven the emergence of electric vehicles (EV) worldwide, triggering the requirement for higher energy density and lower cost of the battery.^[2] Nevertheless, the current Li-ion battery,^[3-4] in which the transition metal oxide^[5] is the cathode material and graphite is the anode material, has almost reached the limit for energy density after many years of efforts and cannot meet the requirements for EVs. Therefore, a new energy storage system is expected to upgrade the current Li-ion battery to power EVs.

In such a situation, Li-S batteries has attracted tremendous attention due to their tempting merits. Many researchers consider the Li-S battery as one of the most promising candidates for next generation of batteries.^[6-7] Li-S battery takes sulfur as cathode material and lithium metal as anode material^[8]. Sulfur has a high theoretical specific capacity of 1672 mAh g⁻¹. The theoretical specific capacity of lithium metal is 3861 mAh g⁻¹ and the Li-S cell has an average cell voltage of 2.15 V in the discharge process.^[8] Hence, the theoretical gravimetric energy density of a Li-S cell is 2510 Wh kg⁻¹, almost an 10 times that of the commercial one. Also, sulfur is the 10th most abundant element in the earth's crust, resulting in the higher availability and lower cost of sulfur.^[9] Over the past decade, hundreds of researchers have exerted their utmost efforts to improve the performance of the Li-S battery worldwide.^[10-11] Great progress^[12] on the Li-S battery has been achieved in the laboratory, with cycle life increasing from 50 to 1000 cycles. Unfortunately, it seems that we still have a long way to go to bring the Li-S battery to its full potential in everyday life, with the obstacles mainly derived from the safety hazards and electrolyte depletion associated with the employment of lithium metal anode in the Li-S battery.^[13] The lithium metal can easily generate lithium dendrites on the surface due to the

non-uniform deposition of lithium during the charge-discharge process. The constant growth of long, fibrous lithium dendrites can penetrate through the separator and cause a short-circuit, resulting in explosion or spontaneous combustion. In addition, the interfacial reaction between lithium metal and the electrolyte will result in the depletion of the electrolyte and lithium metal due to the unstable solid-electrolyte interface (SEI) layer, leading to fast failure of the battery. Alternatively, graphite, silicon and tin can substitute lithium metal to circumvent these issues.^[14-16] The energy density of the Li-S battery will be reduced upon the substitution of the lithium metal. Nevertheless, a big step forward has been made towards the practical application of Li-S battery if a non-lithium-metal anode is applied. In this case, researchers have proposed the concept of the Li-ion sulfur battery. There are two configurations for Li-ion sulfur batteries.^[17] In one, the element sulfur (Li-free cathode) is taken as the cathode material and the prelithiated anode as the anode material. Prelithiation is a delicate process, however, and can be greatly dependent on the cell setup. The prelithiated anode must be acquired by disassembling cells, which may damage the electrode and cause inconsistency between different cells. Moreover, the prelithiated anode is sensitive to air and should be manipulated in an inert atmosphere. Such a complicated process and strict conditions will raise the cost for manufacturing of the battery, due to the impracticality of this configuration. The other alternative is the configuration with Li_2S (lithiated sulfur) as cathode material and a Li-free anode as the anode material, greatly simplifying the manufacturing process as well as avoiding the complicated prelithiation process.

Apart from relieving safety issues and improving the stability of the anode-electrolyte interface, the LISBs has other merits. First, Li_2S shows no volume expansion in the initial charge process because Li_2S is an already “lithiated” form of sulfur, alleviating the damage to the electrode integrity from the enlarged volume and preserving good electronic and ionic pathways. Second, unlike sulfur which is highly volatile and can sublime at a slightly elevated temperature, Li_2S

has a very high melting point of 938 °C.^[18] The good thermal stability of Li₂S allows various synthesis options. For example, Li₂S/C material can be obtained through carbonizing Li₂S/polymer at 700 °C, which is impossible for sulfur. A uniform distribution of Li₂S among the carbon material and good contact between the Li₂S and the carbon material were achieved by this method.^[19] Third, Li₂S will go through the process of Li₂S→short-chain polysulfide→long-chain polysulfide→sulfur in the first charge. The amount of the highly soluble long-chain polysulfides can be controlled to relieve the shuttle effect by manipulating the upper cut-off voltage of the Li₂S cathode. Moreover, carbonate decomposition due to the attack by nucleophilic long-chain polysulfides will be avoidable because the lower upper cut-off voltage will lead to no or negligible long-chain polysulfides during the charge process.^[17, 20]

Nevertheless, the LISBs and Li-S battery also share some common challenges. Li₂S also has very poor electrical conductivity and ionic conductivity. Normally, 30-50 wt% of carbon material (conductive additive) will be added to Li₂S to increase the electronic conductivity, which decreases both the gravimetric and the volumetric energy density of LISBs. The transfer of electrons to Li₂S will be sluggish due to poor electrical conductivity. The rate capability and utilization of Li₂S will be impaired during the charge-discharge process. Low electrical conductivity is also very detrimental to cycling performance. In addition, the polysulfides will be inevitably generated in the Li₂S cathode, which will dissolve in the electrolyte and diffuse to the anode, resulting in the loss of active material and a shorter life span. In addition, the poor ionic conductivity of Li₂S will cause a high energy barrier in the initial charge process of Li₂S due to the high resistance to charge transfer at the interface between Li₂S cathode and the electrolyte, leading to electrolyte decomposition and poor cycling performance as well as low energy efficiency. Moreover, Li₂S is very sensitive to moisture in the air and must be processed in an inert gas, because it can react with moisture in normal atmosphere and produce the toxic gas hydrogen sulphide, making the processing of Li₂S more expensive and complicated than that for sulfur. To overcome the barriers to the practical application of LISBs, previous research

works focused on these hindrances using many different strategies and methods. Herein, we will go through the great efforts undertaken by many researchers and present their excellent work on LISBs in detail. Specifically, we will present a wide overview of the research on the Li_2S cathode in terms of the synthesis and working principles. In addition, the Li_2S -based full cell and electrolyte will be briefly introduced. It is worth highlighting that the energy barrier will be discussed in detail by fundamentally analysing the results reported in the previous literature. Finally, we will give some perspectives on the future research on the LISBs.

2. The Li_2S -based Li-ion sulfur battery and the properties of Li_2S

The LISB is a type of battery in which Li_2S , a lithium metal-free anode, and a non-aqueous solution act as cathode, anode, and electrolyte, respectively. **Figure 1** shows the configurations of a conventional Li-S battery and a Li-ion sulfur battery. The operation of LISBs needs to start with the charging process. During the charged process, the cathode material Li_2S will be oxidized to sulfur. Simultaneously, the Li^+ in the Li_2S will be pulled out to move from the cathode to the anode through the electrolyte. On the anode side, the Li^+ in the electrolyte will intercalate into the anode material. Overall, the electrochemical reaction of the charge process can be expressed as Equation (1), assuming that the charging is just a one-step process and the that graphite is the anode material:

When the cell is discharged, the reverse process will take place. Sulfur will grab the Li^+ in the electrolyte to reduce it to Li_2S , while the Li^+ in the anode material will be deintercalated, enter the electrolyte and migrate to the cathode. As a result, the electrochemical reaction of the discharge process can be expressed by Equation (2):

Before introducing Li_2S cathode material, it is necessary to understand the fundamental physical properties of Li_2S . Li_2S is a typical alkali-metal sulfide that possesses a face-centred cubic (fcc) antifluorite (anti- CaF_2) crystal structure^[22-23] with the space group $O_h^5 \text{Fm}3\text{m}$ and group number 225. In the antifluorite structure, the S^{2-} anions form an fcc lattice, and the Li^+ cations form a cubic lattice. Within the structure, each S^{2-} anion is coordinated with eight Li^+ cations and each Li^+ is surrounded by four S^{2-} anions,^[24] producing large cavities in the crystal structure.^[25] Similar to all other antifluorite-structured materials, Li_2S has the properties of high melting and boiling point, high enthalpy of formation, a wide band gap, high solubility in polar solvents and low density.

Because of the nature of its crystal structure, Li_2S is an electronic insulator. After an extensive search, we failed to find any experimental band-gap measurements for Li_2S . Fortunately, some papers have reported the band gap for Li_2S based on theoretical calculations. R. D. Eithiraj et al.^[20] showed that the indirect bandgap of Li_2S is 1.822 eV through first-principles calculations. They revealed that the size of the Li^+ ion is a factor that is partly responsible for the low electronic conductivity. Later, Yuriy Malozovsky^[19] predicted the electronic and transport properties of Li_2S by an *ab-initio* method. He showed that the calculated indirect band gap is 3.723 eV at 10 K.

Moreover, Li_2S also has very low Li^+ ionic conductivity. Through a first-principles study of the mechanism of Li^+ transport in Li_2S crystal, Kim et al.^[22] concluded that the transport of Li^+ mainly occurs through the diffusion of positively charged lithium vacancies, while the relatively sluggish Li^+ mobility is attributed to the low concentration of these lithium vacancies. The poor ionic conductivity of Li^+ can result in large voltage polarization in the first charge process, which will be discussed later. In order to enhance the Li^+ conductivity in Li_2S material, Simon et al.^[23] carried out experimental research on the behaviour of its ionic conductivity over a wide range of temperature. They found three regimes for the behaviour of ionic conductivity

(**Figure 2a**). In regime I, Frenkel cation disorder will dominate the concentration of charge carriers, as expected. In regime II, the extrinsic dopant is the key factor for the concentration of the charge carriers. In regime III, the ionic charge carriers will be trapped at the immobile dopant sites by electrostatic association. Subsequently, Simon et al. doped Li_2S with different elements to tune the ionic conductivity. It was found that the ionic conductivity could be increased for Li_2S doped with LiCl and MgS because the doped Cl^- and Mg^{2+} can increase the concentration of lithium vacancies by replacing more negatively charged S^{2-} and less positively charged Li^+ (**Figure 2b**). In contrast, the doping of Li_2S with LiF , LiOH , or Li_3N will attenuate the Li^+ conductivity.

3. The high overpotential voltage in the initial charge process

The operation of Li_2S cathode starts with a high overpotential voltage (activation barrier) in the initial charge.^[28-32] Such an activation barrier can spoil the electrochemical performance via decomposition of electrolyte due to the high charging voltage.^[33] Yuan et al. first investigated the mechanism behind the activation energy.^[33] It was revealed that the high overpotential originated from the large resistance to charge transfer between Li_2S and the electrolyte by applying different current densities (**Figure 3a, b**). Because of the extremely low lithium ion conductivity, the mobility of Li^+ in the solid Li_2S is very sluggish, making it difficult of the deintercalated of Li^+ to form polysulfide. Yuan et al. called the process from Li_2S to polysulfide the “nucleation of polysulfide” (**Figure 3c**). They believe that the nucleation process for polysulfides as the main cause for the high activation energy. Specifically, the Li_2S on the surface of a Li_2S particle is difficult to transform to a polysulfide because of the huge difference between the solid Li_2S and the electrolyte, so the nucleation of polysulfide can take place only when the voltage reaches a certain potential, which is similar to the case of LiFePO_4 which has an obvious overpotential voltage during the initial nucleation stage.^[34] To confirm whether their hypothesis was correct or not, Yuan et al. added some polysulfide to the

electrolyte to act as a source of polysulfide nuclei. As a result, the high overpotential voltage disappeared, implying that the hypothesis is convincing. Contrary to the hypothesis developed Yuan et al., however, Liang et al. found that Li_2S is directly transformed to elemental sulfur in the initial charge process with no polysulfide identified by in situ and operando X-ray absorption spectroscopy (XPS).^[35] In addition, Guoqiang et al.'s results, from in situ synchrotron high energy X-ray diffraction (XRD) and ex situ X-ray absorption near edge structure spectroscopy (XANES), led to the same results as those from Liang et al. because no polysulfides were tracked. Moreover, the S appeared immediately with the disappearance of Li_2S in the first charging process.^[36] Interestingly, Yongjo et al. analysed the charging barrier at the beginning of charging, believing that this barrier comes from contaminants on the surface and can be eliminated by cleaning the surface.^[37] The overpotential still exists, however, and needs to be overcome by a high cut-off voltage. The paradox shown by this previous research signals that a different and more complicated charging mechanism of Li_2S may exist. From the papers published, we can note that different methods of material synthesis can result in different activation barriers. Normally, the activation barrier is above 3.5 V if the commercial Li_2S is used as cathode material without further processing. To decrease the overpotential voltage and increase the energy efficiency, on the one hand, scientists added a redox mediator to the electrolyte to mediate the oxidation of Li_2S , which will be discussed in the section on electrolyte. On the other hand, researchers decreased the size of Li_2S to reduce the Li-ion diffusion distance and increase the surface area for the electrochemical reaction.^[19, 38-42] Yan et al. fabricated Li_2S /few-walled carbon nanotubes@reduced graphene oxide nanobundle forest by a scalable method (**Figure 4a**).^[42] The nanostructure rendered good contact between the Li_2S and the carbon matrix as well as an adequate density of reaction sites. Thus, a low overpotential voltage of about 2.6 V was achieved at 0.025 C in the initial charging process. Zhang et al.^[43] synthesized an ultrasmall Li_2S nanoparticle/graphene composite (**Figure 4b**),

where the Li_2S was anchored on the graphene through the chemical reaction between sulfur and lithium triethylborohydride (LiEt_3BH) in tetrahydrofuran (THF) solution. Through transmission electron microscopy, it was shown that the size of the Li_2S was just 8.5 nm. The activation barrier almost disappeared at 0.02 C. A one step in-situ chemical reduction method^[44] was employed by Suo et al. to synthesize nano- Li_2S with a particle size less than 100 nm (**Figure 4c**). Subsequently, the nano- Li_2S particles were coated with carbon by using a novel flowable ionic liquid as the carbon source. The activation barrier for the Li_2S @carbon is lower than that for commercial Li_2S reported in other papers in the first charge process. Cai et al.^[38] prepared nanostructured Li_2S -carbon composite cathodes in a cost-effective way through high-energy dry ball-milling of commercial micro-sized Li_2S with carbon material (**Figure 4d**). In the initial charge process in cyclic voltammetry, the current increased rapidly at 2.5 V at the scanning rate of 0.04 mV s^{-1} , indicating that the overpotential voltage was about 2.5 V, which is much lower than that for the commercial Li_2S . In addition, increasing the temperature for the operation of cells can also decrease the activation barrier. Wu et al. synthesized the Li_2S nanoparticles by the method of bottom-up assembly.^[19] The overpotential voltage reached 3.0 V when the cell was operated at room temperature at 0.05 C. In contrast, the voltage was just 2.5 V at 45 °C at the same current density. The increased temperature might accelerate the kinetics of charge transfer to reduce the activation barrier.

From the previous mechanism research and the synthesis work on Li_2S cathodes, the mechanism of Li_2S cathode activation should be separated into two parts. (i) The activation barrier at state of charge (SOC) of about 5% is attributed to the charging of a small amount of surface contamination. Some species, such as Li_2CO_3 , LiOH , Li_2SO_3 , and Li_2SO_4 with poor ionic conductivity, may form on the surfaces of Li_2S particles due to the atmosphere-sensitive nature of Li_2S .^[37] This barrier can be eliminated or relieved by reducing the handling time and processes for Li_2S materials. (ii) The activation barrier at SOC from 5% to 100% is derived

from the charge of Li_2S species. The polarization continuous to exist in the charging process due to the insulating nature of Li_2S , and this polarization mostly depends on the Li_2S synthesis method, especially regarding different chemical or thermal treatments. Because charging Li_2S with the two-phase transformation is from the outside to the inside, electrolytes can hardly penetrate the outer layer of the newly formed S and affect the inner Li_2S species. Therefore, the extraction of Li ions becomes more difficult in this process. This is the reason why smaller particle size of Li_2S results in a lower activation barrier in most cases.

4. Li_2S cathode material

4.1. Li_2S /Carbon composite material

As mentioned above, the challenges related to Li_2S cathode in the LISBs include the high overpotential voltage in the initial charging process, sluggish electronic and ionic transportation, and the shuttle effect. The overpotential voltage has been reduced to a great degree by synthesizing nano-size Li_2S , or coating the Li_2S with Li^+ -conductive material, or adding a redox mediator in the electrolyte, compared with the results reported by the early published papers. The activation barrier, in my opinion, is not currently a big issue for the practical application of Li_2S cathode material. Moreover, the high overpotential voltage is only present in the first charge process and vanishes in the following cycles. Therefore, the problems due to the high overpotential voltage are minor. The toughest and most urgent problems for Li_2S cathode material are low electronic conductivity and the shuttle effect, both of which will be very detrimental to the practically available capacity and cycle life. Hence, researchers have devoted tremendous efforts to improving the electronic conductivity and suppressing the shuttle effect for Li_2S cathode. Forming composite of Li_2S with carbon material is the most effective way to achieve these goals. First, carbon material has excellent electronic conductivity. Carbon material can provide a satisfactory electron network to transport electrons from the current collector to the active material.^[45] Second, carbon material has robust mechanical properties,

which can maintain the structural integrity of the cathode electrode during cycling.^[45] Third, the morphology of carbon material can be tailored by different synthesis methods, For example, carbon material can be made into carbon nanotubes, sheets (such as two-dimensional (2D) graphene), and hollow spheres.^[46] The diverse morphologies of carbon material can help build a more versatile electrode. Fourth, it is facile to synthesize carbon material with a porous structure,^[47] which can absorb and trap polysulfide to prevent the shuttle effect. Fifth, the surface of carbon material can be conveniently modified with other elements or groups, which can chemically bond to polysulfide to hinder the loss of active material. This means that the structure, morphology, and electronic conductivity, as well as the surface characteristics, can be systematically optimised for the Li_2S electrode when carbon material is used. Indeed, the majority of research has been focused on the development of Li_2S /carbon composite to address the challenges of Li_2S cathode material.

4.1.1 Li_2S /Graphene cathode materials

Like sulfur/carbon composite, graphene is also frequently used as conductive matrix for the Li_2S cathode material.^[48] Chen et al.^[28] achieved a binder-free three-dimensional (3D) graphene framework supporting Li_2S coated by ultra-thin Al_2O_3 films through heating Li_2S /graphene oxide sponge (Li_2S -GS) and depositing Al_2O_3 thin film on the surface of Li_2S /graphene composite by thermal Atomic Layer Deposition (ALD), as shown in **Figure 5a**. The framework can act as a good electronic and ionic facilitator, while the Al_2O_3 film can physically confine and chemically bond polysulfides to suppress their dissolution. The obtained Al_2O_3 - Li_2S -GS cell showed high specific capacity and excellent cycling stability, with a capacity of 736 mAh g^{-1} in the initial discharge and high capacity retention of 88% after 300 cycles at 0.5 C. Similarly, Li_2S /GO@C nanospheres were synthesized by embedding graphene oxide (GO) in the Li_2S nanospheres and depositing a conformal carbon layer on the surfaces

of $\text{Li}_2\text{S}/\text{GO}$ nanospheres (**Figure 5b**).^[39] The GO inside the Li_2S enables effective electron transport as well as being able to capture and immobilize polysulfide. In addition, the carbon layer on the surfaces of $\text{Li}_2\text{S}/\text{GO}$ nanospheres can physically confine the diffusion of polysulfide. The cell assembled with the $\text{Li}_2\text{S}/\text{GO}@\text{C}$ as cathode material showed a high specific capacity of 964 mAh g^{-1} at 0.2 C . In addition, it also showed excellent rate capability, delivering a discharge capacity of 584, 477, 394, and 185 mAh g^{-1} at 2.0, 3.0, 4.0, and 6.0 C , respectively. On the contrary, Li et al. thinks that many researchers employed very complicated methods to synthesize $\text{Li}_2\text{S}/\text{graphene}$ composite.^[18] Therefore he just implemented a one-pot strategy to prepare $\text{Li}_2\text{S}/\text{graphene}$ composites by calcination of graphene nanoplatelet aggregates (GNAs) and lithium sulphate (Li_2SO_4) (**Figure 5c**). The synthesis process could be clearly articulated by thermogravimetry-mass spectrometry (TGA-MS). The highly conductive host GNAs can also immobilize Li_2S due to their intimate contact. Half-cells with this material as cathode material had an initial specific capacity of 693 mAh g^{-1} . Meanwhile, they also had fast reaction kinetics as well as low polarization and good cycling performance. Qiu et al. synthesized the highly nitrated graphene- Li_2S (HNG- Li_2S) cathode by annealing GO/polyol powder at 750°C in following NH_3 gas flow^[49] and precipitated Li_2S within the carbon matrix arising from the Li_2S ethanol solution (**Figure 5d**). The high nitrogen can mediate the redeposition of Li_2S from polysulfide in the electrolyte. The cell assembled with the obtained material still possessed a specific capacity of 500 mAh g^{-1} at 0.2 C after 500 cycles, indicating the importance of optimizing the redeposition of Li_2S during the charge-discharge process. Qiu et al. also employed in-situ scanning electron microscopy (SEM) to observe the change in morphology in the initial charge process. They revealed that the Li_2S gradually disappeared at the end of charge, implying that polysulfide was generated and dissolved in the electrolyte. Their observation is consistent with the hypothesis developed by Yang,^[33] indicating the rightness of the hypothesis to some degree. Seh et al. wrapped Li_2S particles with the graphene

oxide via the favourable lithium–oxygen interactions by a facile method of sonification and centrifugation.^[50] The wrapped structure of Li₂S@Graphene oxide led to a stable cycling performance because the polysulfide was constrained chemically and physically by the GO. Graphene is a 2D sheet material with excellent electronic conductivity that can greatly enhance electron transport. Graphene has a versatile surface that can be decorated with many elements and functional groups to trap polysulfides. Nevertheless, the costly nature of graphene is impeding the large-scale production of graphene-based LISBs, so that the use of graphene in LISBs is impractical.

4.1.2 Li₂S/porous carbon cathode materials

Many other types of carbon materials have been prepared with more economically available carbon precursors.^[51] Ye et al. synthesized mesoporous Li₂S–C nanofiber composite by combining electrospinning and subsequent pyrolysis for the first time.^[41] The Li₂S and carbon formed in-situ during decomposition led to a uniform distribution of Li₂S on the carbon nanofibers. The mesopores in the composite could also trap polysulfide. The obtained Li₂S-C nanofiber material enabled a low overpotential voltage of only 2.57 V in the initial charge and improved cycling performance due to the excellent contact between Li₂S and the carbon material. Zhang et al. carbonized phytic acid-doped polyaniline hydrogel to prepare a nitrogen and phosphorus codoped carbon (N,P-C) matrix to accommodate Li₂S nanoparticles as a binder-free cathode (**Figure 6a**).^[52] The N,P-C framework enables continuous electron pathways as well as efficient lithium ion transport due to hierarchically porous channels. The phosphorus doping can absorb the polysulfide through the interaction between sulfur and the carbon framework. In addition, P element on the surface of the carbon material is able to catalyse the redox reactions of sulfur species and improve the ionic conductivity. As a result, the obtained composite shows a stable capacity of 700 mAh g⁻¹ over 100 cycles at 0.1 C and at

the areal capacity of 2 mAh cm^{-2} . Zhang et al. employed a very simple method of ball milling and pyrolysis to synthesize a $\text{Li}_2\text{S}@C$ sheet-like nanocomposite from the raw materials Li_2SO_4 and activated graphite (**Figure 6b**).^[53] The electrode was constructed on the carbon nanotube (CNT) film without adding any binder. The cell showed a high energy density of 804 Wh Kg^{-1} at 0.5 C . The method of material synthesis and cell design is simple, low-cost, scalable, and environmentally friendly, indicating a promising commercial application for LISBs. In addition, sulfur/microporous carbon (S/MC) composites^[54] were synthesized by vacuum infusion of sulfur vapour into microporous carbon which was subsequently lithiated by spraying commercial lithium metal onto the obtained S/MC composite. The $\text{Li}_2\text{S}/\text{MC}$ showed very high coulombic efficiency and stable discharge capacity over long cycling. The cell could still deliver a capacity of 650 mAh g^{-1} even after 900 cycles. Hart et al. adopted a novel method to prepare lithium sulfide-carbon composite ($\text{Li}_2\text{S}-\text{C}$) via aerosol spray pyrolysis from Li_2CO_3 /sucrose suspension, which was followed by the sulfurization of $\text{Li}_2\text{CO}_3/\text{C}$ in following H_2S gas at high temperature. The obtained $\text{Li}_2\text{S}-\text{C}$ shows a good specific capacity and tends to have better cycling stability with higher areal loading and a lower electrolyte/ Li_2S ratio. A more effective way to synthesize $\text{Li}_2\text{S}/\text{carbon}$ composite is to design a hierarchical particle-shell structure for $\text{Li}_2\text{S}/\text{carbon}$ material. The advantage of a hierarchical structure is that it can relieve the stress within the outer shells during cycling and thus preserve the structural integrity of the particles. Therefore, an intact electrode structure and excellent operation of cell could be achieved. Wu et al. constructed a nanocomposite particle-shell architecture for Li_2S cathode^[55] with three levels of enclosing hierarchy by calcination of $\text{Li}_2\text{S}@$ polyvinylpyrrolidone (PVP) composite and deposition of a carbon layer through chemical vapour deposition (**Figure 6c**). The multiple levels of hierarchy act as a robust “border wall” to physically prevent polysulfides from escaping from the cathode to the electrolyte with consequent loss of active material. The

cell showed extremely stable cycling performance, and no capacity degradation was observed over 100 cycles. It also showed very good stability even when tested for 300-600 cycles.

3D porous carbon can be synthesized by various methods using more available materials, leading to a much lower price. The pores are also very effective for confining polysulfide and lead to excellent performance. The porous carbon, however, has lower electronic conductivity than graphene.

4.1.3 Li_2S @Carbon Core-Shell cathode materials

Core-shell structures with the active material Li_2S as core and carbon layer as shell were also frequently implemented to enhance the performance of Li_2S cathode material. The carbon layer could not only act as an effective electronic conductor, but also is able to physically confine the polysulfide inside the carbon shell. Chen et al. synthesized a special structure for Li_2S cathode material (**Figure 7a**).^[56] The Li_2S /carbon black core was encapsulated in a nitrogen doped carbon shell that originated from the carbonization of PVP. Because of the effective confinement of polysulfide provided by the carbon shell and the good electronic pathway endowed by both the carbon shell and carbon black (CB), the material delivered a high initial specific capacity of 1020 mAh g^{-1} as well as an excellent Coulombic efficiency of 99.7% over 200 cycles. Moreover, the capacity decay is as low as 0.17%. The field emission transmission electron microscopy (FETEM) and elemental mapping tests revealed that the structure of $\text{Li}_2\text{S}/\text{CB}@\text{NC}$ is very robust, leading to excellent electrochemical performance. Exceptional core-shell structured $\text{Li}_2\text{S}@\text{carbon}$ has been synthesized by Nan et al. (**Figure 7b**).^[37] First, nanoparticles of Li_2S with a uniform size distribution were prepared via the chemical reaction between sulfur and lithium triethylborohydride (LiEt_3BH) in tetrahydrofuran (THF). Subsequently, the carbon layer was deposited on the Li_2S nanoparticles by chemical vapour deposition (CVD) using acetylene as the carbon source. The material showed high initial

specific capacity of 972 mAh g⁻¹ and stable cycling performance due to the durable core-shell structure. The post-test SEM indicated that the electrode had only a slight morphology change, even after 400 cycles, representing its strong capability to immobilize the polysulfide during the cell operation.

The core-shell structure is a more efficient way to constrain polysulfides than porous carbon because the shell is a more powerful physical barrier. The core-shell structure has been proved to be capable of very stable cycling performance. Nevertheless, synthesizing core-shell structures is more complicated than for porous carbon, resulting in higher cost and less viability.

4.1.4 Free-standing Li₂S cathode materials

Although some progress has been made on Li₂S/carbon composite material, as mentioned above, the practical utility of Li₂S remains still has plenty of challenges, one of which is the low mass and capacity loading of the cathode electrode due to the poor intrinsic electronic conductivity of Li₂S. Freestanding electrode may hold a solution to that problem.^[57-59] First, a free-standing electrode has a robust network of electron pathways. The electrode structure (including electron pathways and ionic transportation) can remain stable during the shrinkage and expansion of the active material. Second, owing to the 3D structure of free-standing electrode, it can accommodate a larger amount of active material within the conductive matrix, resulting in higher areal mass and capacity loading. Third, no binder is required when the electrode is fabricated because the free-standing electrode has a very good framework to hold the active material. Thus, a high percentage of active material can be accommodated in the electrode.^[29-30, 60] Yu et al. developed a method for facile production of free-standing Li₂S-based paper electrodes with high capacity loading by calcinating electrospun Li₂SO₄/PVP in flowing argon,^[29] as shown in **Figure 8a**. The in-situ formation of Li₂S resulted in ultrafine Li₂S particles and strong affinity of the Li₂S with the carbon matrix. The free-standing electrode

expectedly showed good structural stability and accelerated electrochemical reactions. It could deliver an initial specific capacity of 730 mAh g^{-1} with a Li_2S mass loading of 3.0 mg cm^{-2} . It also offered a good capacity retention at 1.0 C after 200 cycles, even when the mass loading of Li_2S was 6.0 mg cm^{-2} and 9.0 mg cm^{-2} . Fu et al. reported a novel sandwich structured Li_2S cathode with pristine Li_2S particles between two layers of self-weaving, binder-free carbon nanotube (CNT).^[30] This method is facile and cost-effective because the pristine Li_2S is used. The designed electrode architecture can facilitate ion and electron transport and confine the polysulfides. Therefore, the sandwich-structured electrode showed stable cycling performance with a Li_2S loading of 3.0 mg cm^{-2} . Mohammad et al. used the Ni foam to support ball-milled commercial Li_2S (**Figure 8b**).^[61] The advantage of this method is that it is simple and cost-effective. Most importantly, it can be scaled up for commercial production of Li_2S cathode because the preparation procedures for both the cathode composite and the electrode are facile. The Li_2S loading can reach as high as 6 mg cm^{-2} , which is required by industry. Chung et al. fabricated a shell-shaped carbon architecture through sandwiching a carbon nanofiber-carbon nanotube (CNF-CNT) ring between two CNF-CNT papers (**Figure 8c**).^[60] The Li_2S was impregnated into the empty core as the core material by injecting Li_2S dispersion inside the carbon shell. The shell carbon could provide excellent pathways for the transport of electrons and ions. The electrode could still show good electrochemical performance with the high Li_2S loading of 8.0 mg cm^{-2} and low electrolyte/ Li_2S ratio of 9/1. Moreover, the cell also showed good rate capability due to the facile accessibility to electrons and ions that was provided by the shell carbon. Wang et al. fabricated reduced graphene oxide paper by freeze-drying and annealing (**Figure 8d**). Li_2S was loaded to form nano- Li_2S /reduced graphene oxide cathode paper (nano- Li_2S /rGO paper) by drop coating of Li_2S ethanol solution on the obtained paper. The cell showed a high initial specific capacity of 1050 mAh g^{-1} . In particular, the rate capability of the cell with the Li_2S /rGO paper as cathode electrode was excellent due to the

nanosized Li_2S and good conductivity of the rGO. The cell could still deliver a capacity of 597 mAh g^{-1} at high current rate of 7.0 C as well as a high capacity of 816.1 mAh g^{-1} after 150 cycles at 0.1 C. That was because rGO paper can provide good solvent absorption to confine polysulfide.

Carbon materials have been proved effective to improve the performance of Li_2S cathode. Various $\text{Li}_2\text{S}/\text{C}$ composites and the corresponding performance is summarized in Table 1. Based on the previous publications, Most of researchers have used just one type of carbon material for Li_2S cathode. Chen et al. investigated a mixture of few-walled carbon nanotubes (FWNTs)@reduced graphene oxide nanobundle to combine the advantages of both materials.^[42] Therefore, it may be more promising to design the structure of Li_2S cathode to integrate the benefits of various carbon materials into one electrode. Carbon will continue playing an important role in the Li_2S cathode because of its high conductivity, excellent structural stability, tunable surface property, and porous nature.^[45]

4.2 $\text{Li}_2\text{S}/\text{Metal}$ composite

$\text{Li}_2\text{S}/\text{metal}$ composite should not have been mentioned here because $\text{Li}_2\text{S}/\text{metal}$ is potential for use as cathode material for LISBs. Originally, it was explored for use as a non-intercalating material in a lithium-containing cathode material for the Li-ion battery. This idea was inspired by the conversion reaction of metal sulfide as cathode material in the Li-ion battery. Nevertheless, we think that this kind of composite material may give us some hints towards exploring new utility for the LISBs. Before talking about its likely potential for LISBs, I need to introduce the research on $\text{Li}_2\text{S}/\text{metal}$ composite first. Obrovac et al. prepared a $\text{Li}_2\text{S}/\text{cobalt}$ composite to investigate its role in the Li-ion battery in different voltage ranges.^[62] It was shown that the composite transition metal/lithium sulfide could be used as a non-intercalating cathode material with a lithium source for the Li-ion battery (**Figure 9a**). Obrovac et al. also found that the cycling performance could be improved if appropriate voltage limits were

selected. Later, to understand and clarify the lithium storage properties of Co–Li₂S electrode, Zhou et al. prepared a Co–Li₂S nanocomposite thin film by pulsed laser deposition (PLD) for the first time.^[63] High resolution TEM (HR-TEM) and selected area electron diffraction (SAED) were employed to reveal that the charge-discharge mechanism of Co–Li₂S involves the formation and decomposition of Li₂S and lithium extraction/insertion from/into CoS₂. Furthermore, Fang et al. explored Li₂S/Mo as a cathode material for the LISBs for the first time.^[64] Li₂S/Mo composite was readily obtained by electrochemically converting molybdenum disulfide (MoS₂) into Li₂S and metallic molybdenum (Mo) (**Figure 9b**). It was revealed that Mo can be oxidized to sulfide above 3.0 V. The presence of Mo can enhance the cycling stability and rate capability because Mo can prevent the dissolution of polysulfide and provide good electronic conductivity for the Li₂S cathode. This gives us a new and facile method to fabricate Li₂S cathodes.

There are some advantages of Li₂S/metal composite for the LISBs. First, metal normally has higher electronic conductivity than carbon materials. Thus, Li₂S will be more electronically accessible to enhance the available capacity. Second, Li₂S/metal cathode material can be conveniently fabricated by electrochemical conversion of the commercial metal disulfide into Li₂S and the metallic element at low voltages, which is very simple and cost-effective. The distribution of Li₂S formed *in situ* is more uniform than that formed by the *ex-situ* method. Third, the transition metals usually possess a catalytic effect that can accelerate the redox reaction of sulfur species.^[65-67] Last but not the least, the metal is able to absorb polysulfide to prevent the shuttle effect due to the polar surface of the transition metal. Although Li₂S/metal composite has been rarely investigated, it is worth spending more effort on Li₂S/metal composite because of the advantages mentioned above. Li₂S/metal composite can be an alternative to Li₂S/carbon material.

4.3 Li₂S/conductive polymer composite

Conductive polymer has been intensively explored for S cathode materials.^[68-70] For example, several papers have reported the application of polypyrrole on S cathode. As a conductive additive, conductive polymer can be conducive to the cathode from the following two aspects. On the one hand, the polymers can be tailored to achieve good contact with the active material because of the flexibility and bendability of the polymer. On the other hand, functional group of the polymer can effectively absorb polysulfide inhibiting the shuttle effect and enhancing cycling performance. Much less research on Li₂S/conductive polymer composite has been carried out than that on the S cathode, with just one paper reporting the Li₂S/conductive polymer composite to the best of our knowledge. Seh et al. demonstrated an *in-situ* synthesis of Li₂S–polypyrrole composites for high-performance Li₂S cathode.^[71] High-resolution X-ray photoelectron spectroscopy (XPS) showed that the N element in polypyrrole had favourable Li-N interaction with Li₂S, enabling polysulfides to be strongly bonded to the surface of Li₂S. the polypyrrole was in intimate contact with the Li₂S to provide good electron pathways, resulting in good cycling performance and rate capability of the obtained composite.

4.4 Li₂S/mediator composite

A redox mediator is usually introduced to catalyse the redox reactions of sulfur species and interact with the polysulfide intermediates by chemical bonding or static electricity, leading to faster reaction kinetics and more stable cycling performance. Wang et al. synthesized Li₂S/TiO₂-impregnated hollow carbon nanofibers (Li₂S/TiO₂-HCFs) by electrospinning (**Figure 10a**).^[72] TiO₂ can not only catalyse the reduction of polysulfide to Li₂S but also absorb the polysulfide. Li₂S/TiO₂-HCFs delivered a discharge capacity of 851 mAh g⁻¹ at 0.1 C. The cell also showed improved cycling performance and rate capability with the specific capacity of 690 mAh g⁻¹ after 100 cycles and 400 mAh g⁻¹ at 5 C. Pourali et al. made a composite of Li₂S and transition metal carbide to obtain Li₂S/Ti₃C₂T_x because Ti₃C₂T_x has high electrical conductivity (**Figure 10b**).^[73] The cell presented better electrochemical performance than

commercial Li_2S , which is attributed to good electrical conductivity provided by $\text{Ti}_3\text{C}_2\text{T}_x$. Seh et al. coated TiS_2 on the surface of Li_2S to acquire $\text{Li}_2\text{S}@\text{TiS}_2$ through the chemical reaction between Li_2S and TiCl_4 .^[31] The TiS_2 coating layer not only has a good electronic conductivity and strong affinity with $\text{Li}_2\text{S}/\text{Li}_2\text{S}_n$ species, but also can physically prevent the diffusion of polysulfide. As a result, The cell showed very stable cycling performance over 140 cycles due to the merits provided by the TiS_2 coating layer. Wu et al. designed a delicate structure to prevent the shuttle effect by coating the nanoparticles of Li_2S with a conformal layer of LiTiO_2 (**Figure 10c**).^[74] Density functional theory (DFT) calculations revealed that LiTiO_2 has a very strong affinity to polysulfides and can facilitate the conversion reaction from long polysulfides to short polysulfides by breaking S-S bonds. The $\text{Li}_2\text{S}@\text{LiTiO}_2$ sample had high specific capacity and remarkable cycling performance over 400 cycles due to the benefits provided by the conformal layer of LiTiO_2 . The post-cycling SEM showed that the Li_2S cathode and Li anode had a smooth SEI film, indicating that the polysulfide was effectively entrapped.

5. Electrolyte

Most electrolytes for LISBs are derived from relatively mature and successful ones from the Li-S battery system because they have the same redox reactions (oxidation and reduction of S species) on their cathodes.^[25, 75] Therefore, the advanced electrolytes used in Li-S batteries also have high ionic conductivity for Li ions and chemical and electrochemical stability towards cathodes and anodes (since non-metal anodes are more stable than Li metal) in the LISB system. Only the activation problem from the use of Li_2S cathode require developing suitable electrolytes in the LISBs. Herein, we only include the liquid electrolytes for LISBs since solid electrolytes are mainly used to solve the problems arising from Li metal.

5.1 Ester-based electrolytes

The ester-based electrolytes have been proved successful in commercial Li-ion batteries due to their electrochemical inertness during operation of the Li-ion batteries, normally ranging from (0–5.0 V vs Li).^[76] The ester-based electrolytes may not be suitable for use in Li-S batteries, however. Gao et al. reported that the lithium polysulfides formed by the redox reactions can potentially react with carbonates (polypropylene carbonate (PC), EC and DEC), which is seriously detrimental to electrochemical performance, making these electrolytes incompatible with Li-S battery systems (**Figure 12a**).^[77] Recently, micropore-confined sulphur shed light on the use of carbonate electrolytes in Li-S batteries because only undissolved small-chain sulphur species are present in carbon micropores and the polysulfides are not in direct contact with carbonate electrolyte (**Figure 12b**).^[78-82] Recent work, however, showed that this compatibility between polysulfides and carbonate electrolytes may come from SEI-type films, which are formed on the surface of encapsulated S electrodes in the presence of ester-based electrolytes.^[83]

Several references have reported the use of ester-based electrolytes for Li₂S cathodes in two circumstances.^[54, 84-86] One is modifying the redox reactions by introducing transition metals or metal (M) sulphides to react with Li₂S and form Li_xMS₂ intermediate compounds on the cathode side, generally according to the following equations:^[84-86]

The possible reason why the carbonate electrolytes can function well is that no soluble polysulfide intermediate forms when these metal and metal sulphides are used.^[87] This metal driven S-Li₂S conversion leads to a compromise, however, with poor gravimetric and volumetric energy density due to relatively low redox voltage and low specific capacity of the transition metal sulphide (**Figure 12c**). The other circumstance is employing Li₂S confined in

micropores, which can be compatible with carbonate electrolytes. Unlike S, confining Li_2S in micropores is difficult due to the high melting and boiling point of Li_2S . Only micropore-confined Li_2S formed *in-situ* cathodes was prepared from S precursors and tested with carbonate electrolytes.^[54] The lower energy density and complex cathode preparation, however, weaken the motivation for using ester-based electrolytes in the presence of micropore-confined Li_2S cathodes.^[54, 88] So far, it is still unsuitable to use the ester-based electrolytes in Li-S batteries and LISBs.

5.2 Ether-based electrolytes

Ether-based electrolytes cannot be used in Li ion batteries, since the ethers will decompose above 4V, but they are very popular in Li-S batteries.^[75-76] Ethers show not only high ionic conductivity and low viscosity but also electrochemical stability towards the polysulfides and sulfur radicals.^[77, 89] In the Li-S battery system, the binary solvent consisting of DOL and DME was chosen and showed better performance than DOL or DME alone or other solvents (**Figure 13a, b**).^[77, 90] This is because DME has high ionic conductivity and improves reaction kinetics, while DOL can form a SEI on lithium anode to relieve the shuttle problem.^[90] Although the good capability towards polysulfide dissolution of DOL/DME greatly facilitates the kinetics between S and Li_2S , the increased risk of corrosion of the lithium anode and the depletion of the active sulphur cathodes are not negligible (**Figure 13c**).^[91]

DOL/DME is generally expected to be the electrolyte solvent in LISBs due to its success in Li-S batteries. The same cathodic reactions and relatively stable anodes make DOL/DME compatible and outstanding in LISBs. In 2010, an electrolyte with 1:1 DOL/DME as solvent was used in a Li_2S cathode-based cell, with the cell showing a much high gravimetric energy density of 630 Wh kg^{-1} (**Figure 13d**).^[16] After that, many researchers used the binary 1:1 DOL/DME solvents as the standard electrolyte solvent to research other types of LISB. As mentioned above, However, the lithium metal anode is unnecessary for LISBs, which means

that the anode protection becomes dispensable, so that the electrolytes can be optimized with the features of high ionic conductivity and fast reaction kinetics.

5.3. Salts and additives

Although LiPF_6 in EC/DEC normally shows good ionic conductivity in LIBs, the reactions of ester solvents and polysulfides make EC/DEC with LiPF_6 inappropriate for use in Li-S batteries.^[92] Moreover, salts such as LiPF_6 , LiBF_4 , LiAsF_6 , or LiClO_4 are not considered suitable for ether-based solvents because they are incompatible.^[75, 93] LiTFSI , which features with good temperature stability and the optimum donor number, shows high ionic conductivity and low viscosity in ether solvents.^[94-95] Therefore, LiTFSI has regularly been used as the electrolyte salt in Li-S batteries and LISBs. Despite the high initial discharge capacity in DOL/DME electrolyte with 1M LiTFSI , the goal of good cycling performance cannot be achieved due to the problems of polysulfide dissolution, the shuttle effect and lithium anode corrosion during battery operation.^[96]

Some additives such as LiNO_3 , polysulphides and LiI are used to solve these problems. LiNO_3 is generally added to the electrolytes for Li-S batteries because it protects the lithium metal anode so as to relieve the polysulfide shuttle and Li corrosion and even to help the deposition of Li metal (**Figure 14a, b**).^[97-99] Moreover, the LiNO_3 can function well by helping to form stable SEI on the Si/C anode and protecting the carbon matrix of the S/C cathode, which are important for LISBs (**Figure 14c**).^[100-101] LiNO_3 is a cheap and effective additive in Li-S batteries and LISBs, but it is an oxidation agent and can be reduced on the cathode below 1.9 V causing safety concerns and limited capacity.^[102-103] Polysulfide additives can not only compensate material dissolution and decrease the material loss on the Li anode in the initial operation of batteries, but also synergistically interact with LiNO_3 to form a SEI on the anodes (**Figure 14d**).^[104-106]

Redox mediators are chemical compounds that can act as electron shuttles to enhance electron transport from the conductive substrate to the Li_2S , resulting in accelerated redox reactions. Most importantly, the redox mediator can facilitate the oxidation of Li_2S and solve the activation problem for Li_2S cathodes (**Figure 15a**).^[107-108] LiI is one kind of redox mediator that is capable of transporting electrons from carbon to the Li_2S active material, dramatically reducing the energy barrier in the initial charge process. Moreover, LiI can substitute for LiNO_3 as a protective agent for the Li metal anode since it can also help to form a protective layer on the surface of the anode (**Figure 15b**).^[108] Like LiI , $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ and $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ additives can also work as redox mediators to reduce charging polarization below 3 V in the first charge of Li_2S cathodes (**Figure 15a**).^[107] It was revealed that $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ and $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ can effectively bridge the electron pathway between the electronic additive and the active material, reducing the energy barrier and stabilizing the cycling performance. The cell with the redox mediator showed three times more capacity than the cell without the mediator after 150 cycles. Other redox mediator additives such as InI_3 and some quinone derivatives greatly relieved the activation barrier of Li_2S cathode, increased the specific capacity, and improved the cycling performance (**Figure 15d**).^[109-110] In addition, InI_3 can help to form a protective layer on the cathode and anode to mitigate the shuttle effect and improve the cycling performance (**Figure 15c**). Whereas, the electrolyte containing P_2S_5 can interact with the Li_2S surface to increase the ionic conductivity of the Li_2S surface to reduce the overpotential voltage (**Figure 15e**).^[109] From previous research, adding the redox mediators to liquid electrolytes may be a promising way to solve the unique activation problem of Li_2S cathodes. This is because of the high mobility of electrolytes, which can continuously transport the mediators to the surfaces of Li_2S particles. In addition, protective layers will be formed on surfaces of anodes and cathodes to improve cycling performance by using mediators.

5.4 Lean electrolytes

Recently, much exciting work has been reported on reducing electrolyte usage to realise applications with practical gravimetric and volumetric energy density.^[111-114] Porous carbon matrices with low density and large surface areas, which can accommodate large amounts of electrolyte, must be used to relieve the problem of poor electrical conductivity and ionic conductivity of S and Li₂S to ensure the utilization of active materials.^[112-113] An especially insurmountable obstacle is the massive consumption of electrolytes due to the constant formation of SEI on the Li metal anode.^[115] The latter problem is fatal, causing the short life in practical application of Li-S batteries.^[112] The LISBs may be promising for the development of lean electrolyte batteries with high practical gravimetric and volumetric energy density. The electrolyte depletion in battery operation can be greatly reduced because of the Li metal-free anode in the LISBs. This may allow the LISBs to reach practical application first.

6. Li-ion sulfur full cell

To the best of our knowledge, no researcher has ever exclusively and deeply discussed the LISB full cell. The characterization of full cells is just conducted as supplementary data for the synthesized cathode material. After going through all the papers in the literature on LISB full cells, we found that lithium-free anode materials which had been investigated for the LISBs included graphite, silicon, tin, Fe₃O₄, and MnO₂ (Table 2 shows the different configurations of full cell and the corresponding performance).

Graphite is the most successfully commercial anode because it has very stable electrochemical performance. In addition, its initial Coulombic efficiency is higher than those of other anodes such as Si and Sn, which arguably makes it the most promising anode to date for LISBs, currently. Zheng et al. prepared highly stable sulfur/microporous carbon (S/MC) through vacuum infusion of sulfur vapour into the micropores of carbon,^[54] followed by the lithiation of S/MC to form Li₂S/MC via spraying lithium metal powder (SLMP) onto the S/MC. The full

cell was assembled with $\text{Li}_2\text{S}/\text{MC}$ as cathode material and graphite as anode material, 1.0 M LiPF_6 dissolved in the mixture of ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by volume) was selected as electrolyte. The full cell showed high specific capacity and very stable cycling performance, with capacity of approximately 600 mAh g^{-1} (based on the mass of Li_2S , similarly hereafter) over 150 cycles without obvious fading. Wang et al. synthesized lithium sulfide@porous carbon composites ($\text{Li}_2\text{S}@\text{PC}$) by the in-situ formation of Li_2S through the reaction between the lithium sulphate (Li_2SO_4) and the pyrolytic carbon derived from glucose.^[116] The nanosized Li_2S particles showed a uniform distribution within the carbon matrix. Wang et al. revealed that the LiNO_3 in the ether electrolyte is conducive to the cycling performance of graphite anode. Therefore, the Li-ion/sulfur full cell was assembled with lithium bis(fluoroethanesulfonyl)imide (LiTFSI) (1 M) dissolved in dioxolane/dimethoxyethane (DOL/DME) (1:1 ratio vol%) with 1 wt% LiNO_3 additive as electrolyte. The full battery shows an initial specific capacity above 500 mAh g^{-1} and a stable cycling performance at 0.1 C with capacity of 268 mAh g^{-1} after 30 cycles and 173 mAh g^{-1} after 100 cycles (**Figure 11a**). Li et al. fabricated Li_2S /graphene (LS-G) composite via the in-situ reaction between Li_2SO_4 and graphene.^[117] Considering that the Li_2S cathode electrode is not compatible with carbonate electrolyte and that the ether electrolyte will destroy the crystalline structure of graphite (G). Li et al.^[117] developed new electrolyte of solvate ionic liquids for the full cell. The full cell was assembled using LS-G BM (where BM means ball-milled) as cathode, graphite as anode and 1.0 M $(\text{Li}(\text{G}_4)_x)(\text{TFSA})/\text{HFE}$ ($x=0.6, 0.8, \text{ or } 1$), where G_4 is tetraglyme and TFSA is bis(trifluoromethanesulfonyl)amide and HFE is hydrofluoroether, dissolved in purified tetraglyme as electrolyte. It was claimed that the cell with $^{[4]}\text{[TFSA]}/\text{HFE}$ showed the highest discharge capacities of 809 and 586 mAh g^{-1} in the first and 20th cycle, with the Coulombic efficiency above 99%.

Silicon is considered as one of the most attractive anodes for the future Li-ion battery. On the one hand, silicon has a much higher specific capacity (3579 mAh g^{-1}) than graphite (372 mAh g^{-1}). On the other hand, silicon is very abundant (the 2th most abundant element in the earth's crust) and environmentally friendly.^[118] Its 300% volume change during charge-discharge, however, results in pulverization of the silicon particles, instability of the solid-electrolyte interphase, and loss of the good contact between the active material and the current collector, leading to fast capacity fading. An effective solution to relieve the volume change is to use nanosize silicon in place of bulk silicon. Recently, a variety of nanotechnologies have been implemented to synthesize different dimensions of nanosize silicon, such as nanoparticles,^[119] nanowires,^[120] nanotubes,^[121] and nanoporous networks.^[122-123] With improvement of the performance of silicon anode, there are now some works on the $\text{Li}_2\text{S}/\text{Si}$ full cell. Yang et al. prepared $\text{Li}_2\text{S}/\text{CMK-3}$ electrodes by electrochemically lithiating $\text{S}/\text{CMK-3}$ electrodes and fabricated silicon nanowires as anode by directly growing silicon nanowires on stainless steel substrates.^[116] The obtained cathode and anode were used to assemble full cell along with 1 M LiTFSI in DOL/DME (1:1 v/v) as electrolyte. The full cell showed an initial specific capacity of 423 mAh g^{-1} at C/3 with the average voltage of 1.7 V. In the cycling, it delivered about 300 mAh g^{-1} after 10 cycles and 250 mAh g^{-1} after 20 cycles at C/3 (**Figure 11b**). Jha et al. fabricated $\text{Li}_2\text{S}/\text{Si}$ full cells to investigate the activation process of Li_2S and the effects of the activation process on the cycling performance of a $\text{Li}_2\text{S}/\text{Si}$ full cell.^[124] The in-situ XRD showed that even very large Li_2S particles ($20 \mu\text{m}$) can be completely decomposed during the initial charge process. The results showed that the activation current density has an effect on the capacity and a slight influence on the cycling performance. Interestingly, the capacities of the full cell at 0.2 C and 1 C are almost identical, which is consistent with the report by Yang et al.^[116] This might indicate that the poor rate capability in Li-S batteries may be attributed to the lithium anode rather than the slow kinetics of the S cathode. Balach et al. prepared a

Mo/Li₂S-based cathode by direct lithiation of MoS₂ nanoparticles.^[125] They found that the Mo/Li₂S cathode is free of polysulfide during operation of the cell. Therefore, the carbonate-based electrolyte can be used for Mo/Li₂S-based cathode. The cathode can present good cycling performance at high Li₂S mass loading of 10.7 mg cm⁻². The Li₂S-Si full cell with 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 v/v, containing 10% fluoroethylene carbonate (FEC)) as electrolyte showed high initial specific capacity of 788 mAh g⁻¹ good cycling performance with specific capacity of 410 mAh g⁻¹, and a low fading rate of 0.32 % over 150 cycles (**Figure 11c**). Wang et al. prepared a graphene-decorated Li₂S cathode by spray-drying followed by heat treatment at high temperature.^[126] The obtained spheres of Li₂S/carbon composite were 20 μm in diameter. The Li₂S/carbon-Si Li-ion battery was assembled with 1 M (LiTFSI) in a mixture of 1,3-dioxolane and 1,2-dimethoxyethane (v/v = 1:1) with 1 wt% LiNO₃ as electrolyte. The full cell showed an initial specific capacity of 600 mAh g⁻¹ and capacity of about 350 mAh g⁻¹ after 30 cycles. Marco et al. mixed Li₂S and Mesophase Carbon Micro Beads (MCMB) to obtain Li₂S-MCMB composite by ball milling, and they prepared silicon-oxygen-carbon (Si-O-C) anode by electrodeposition.^[15] Prior to use in full cell, the anode material was rinsed in the electrolyte to be lithiated for 15 h. The full cell Li₂S-MCMB/Si-O-C battery demonstrated stable cycling performance with capacity of 280 mAh g⁻¹ over 100 cycles.

Metallic Sn is also considered a promising anode material for the Li-ion battery in terms of its natural abundance, high theoretical capacity, and environmental friendliness. Like Si, Sn also suffers from 300% volume change during intercalation-deintercalation of lithium ions,^[127] resulting in poor cycling performance. Reducing the size of Sn is also an effective way to alleviate the strain and inhibit pulverization, thus improving its life span. Jusef et al. first coupled Sn/C nanocomposite with Li₂S/C to explore the Li₂S/Sn full cell, in which a gel polymer electrolyte was used as electrolyte.^[14] The cell possessed a high initial specific

capacity of about 1200 mAh g⁻¹ (based on the mass of Li₂S only) at C/20 and retained about 840 mAh g⁻¹ after 100 cycles. Hassoun et al. prepared Li₂S-C composite by ball milling and synthesized Sn-C composite by calcinating the organometallic tin precursor tributylphenyltin (TBPT) in the inert gas argon.^[128] The polyethylene oxide (PEO)-based gel electrolyte was used as electrolyte for the full cell. The high-safety polymer Li₂S/tin lithium-ion battery showed a high specific capacity of 600 mAh g⁻¹, corresponding to an energy density of 1200 Wh kg⁻¹.

Apart from graphite and silicon, there are also some other anodes that has been explored for LISBs. Liu et al. employed SnO₂ as anode material and Li₂S-Carbon composite as cathode material to fabricate a SnO₂/Li₂S full battery.^[129] They also developed a new bifunctional additive for the electrolyte to mediate the redox reactions of sulfur species and passivate the anode surface. The SnO₂/Li₂S full battery delivered high specific capacity of 983, 878, 746, and 675 mAh g⁻¹ at 0.2, 0.4, 0.8, and 1.5 C, respectively. The full cell (**Figure 11d**) retained 647 mAh g⁻¹ after 200 cycles at 0.5 C. Yu et al. selected Fe₃O₄ as anode material to prepare a Li₂S-C/Fe₃O₄-C full cell.^[29] The cell had an initial specific capacity of 600 mAh g⁻¹ and preserved about 330 mAh g⁻¹ after 50 cycles at 0.2 C. Wang et al.^[130] also used Fe₃O₄ as anode to couple it with Li₂S@MXene/G, where G is graphene. The Li₂S@MXene/G cathode had multifunctional cooperative interfaces that could reduce the activation barrier for the initial charge and regulate the redox reactions of polysulfide conversion. The full cell delivered the specific capacity of 576 mAh g⁻¹ with the average voltage potential of 1.7 V in the first cycle. After 50 cycles, 310 mAh g⁻¹ was preserved at 0.2 C. Chen et al.^[131] fabricated a full cell with free-standing Li₂S-rGO as cathode material, MnO₂ nanoparticles as anode material, and a conventional Li-S electrolyte (LiTFSI in the mixture of DOL/DME (1:1, v/v)) as electrolyte. The MnO₂ nanoparticles reduced the diffusion distance for Lithium ion and resulted in faster charge transfer. The full cell delivered 600 mAh g⁻¹ in the first discharge process and

experienced stable cycling performance subsequently, with capacity of 450 mAh g⁻¹ after 150 cycles.

We have several anodes to choose from to match Li₂S cathode. To obtain high-energy-density LISBs, the anode should meet several requirements. First, the anode should be compatible with ether-based electrolyte because ether-based electrolyte is currently the most appropriate electrolyte for LISBs. Second, the anode material should have a lower potential for Li⁺ deintercalation and intercalation so that a relatively high voltage can be obtained for LISBs. Third, the capacity should be comparable to that of Li₂S. We believed that the challenges of LISBs are related to the challenge of finding a suitable high-energy-density anode material. Si anode meets all three requirements mentioned above and is considered as the best candidate for LISBs. Its poor cycling performance, however, hinders its practical application. Therefore, the practical application of LISBs relies on the development of a suitable high-energy-density anode material.

7. Summary and perspectives

In summary, the research status of LISBs toward the practical application of Li-S batteries has been reviewed. Unlike the conventional Li-S battery with lithium metal as anode, LISBs are more reliable and safer. The employment of graphite, silicon, or tin as anode enables the Li-S battery to circumvent the safety concerns triggered by lithium dendrites, although the commercialisation of the LISBs is still hindered by several persistent problems.

The activation barrier of Li₂S cathode in the first charge can result in low energy efficiency, which might be derived from the nucleation of polysulfide and low Li⁺ conductivity in the Li₂S. Adding a polysulfide redox mediator to the electrolyte to change the electrolyte composition can greatly reduce the overpotential voltage. The energy barrier can also be weakened by nanosizing the Li₂S particles and modifying the surface of Li₂S with a good Li⁺ conductor. Li₂S shows very sluggish Li⁺ transport within the Li₂S crystal due to the low concentration of lithium

vacancies that can be enhanced by doping with other elements. The electrical conductivity of Li_2S is improved by coupling Li_2S with conductive additives such as carbon material, conductive polymer, or metal. Carbon materials are the most frequently used for Li_2S due to their electrical conductivity, robust mechanic properties, adjustable morphology, and porous structure as well as their modifiable surfaces. Therefore, various Li_2S /carbon composites have been intensively studied, including Li_2S /graphene, Li_2S /porous carbon, Li_2S -carbon core-shell structures, and free-standing Li_2S . These Li_2S /carbon composites endow the Li_2S cathode material with dramatically improved capacity, rate capability, and cycling stability. The Li_2S /metal composites may hold the great potential to simplify the fabrication process of high-performance Li_2S due to the intrinsic merits of metals. Conductive polymer is an important alternative to carbon material, mainly because the good conductivity, excellent flexibility, and functional groups of the polymer can enable efficient accessibility to the active material.

The LISBs full cell was briefly introduced. The anode materials that have been coupled with Li_2S cathode for a full battery include graphite, silicon, tin, tin oxide, Fe_3O_4 and MnO_2 . Benefitting from the cycling stability of graphite, the Li_2S /graphite full cell shows a more stable capacity. Graphite, however, is not compatible with ether electrolyte because the layered structure of graphite can be exfoliated by ether molecules. In contrast, the silicon has high compatibility with ether electrolyte and holds great potential to match Li_2S as anode material due to its high specific capacity and high stability with ether electrolyte. The challenge behind the Li_2S /silicon full cell is the low initial Coulombic efficiency and unstable cyclability of silicon. Tin has the similar problem to silicon. Interestingly, Li_2S /tin oxide can deliver stable capacity over 200 cycles, indicating the possibly excellent compatibility of tin oxide with Li_2S cathode and ether electrolyte. Nevertheless, Fe_3O_4 and MnO_2 always only give a lower voltage level

The ester based electrolytes still have the compatibility problem with S related cathodes. Therefore, developing ether-based electrolytes seems more reasonable in LISBs at this stage. The concerns about problems from the dissolution of polysulfides could be decreased if more stable anodes, high mass loading of Li_2S cathodes, and lean electrolytes are concerned for LISBs.

Although some progress on LISBs has been achieved, there is still a long way to go before it is realized in real life. As practical application of high-energy batteries is urgently demanded, [132-133] More efforts should focus on the study of high-energy-density full batteries rather than only Li_2S cathode material. Therefore, some challenges need to be addressed to proceed toward the practical application of LISBs. First, the Li_2S active material needs to be synthesized in an inert atmosphere due to its high sensitivity to moisture, resulting in high cost. Therefore, exploring a more cost-effective synthesis method for Li_2S is worthy of more research work in the future. For instance, both Li_2SO_4 and carbon material are much more available than Li_2S . Calcination of the two chemicals can lead to $\text{Li}_2\text{S}/\text{C}$ composites. Optimization of this synthesis method seems to be a promising method to lead to large-scale production of Li_2S in a cost-effective way. Second, Li_2S needs to be paired with a non-lithium-metal anode, with the choice including graphite, silicon, and tin. It is well known that graphite has low gravimetric capacity and will undoubtedly decrease the energy density of LISBs. Silicon is considered as an ideal anode to match Li_2S owing to its high capacity. Nevertheless, the poor cycling performance of silicon will definitely impair the longevity of LISBs. It seems that improving the cyclability of silicon is related to the practical application of LISBs. Third, the mass loading of Li_2S should be increased to 6.0 mg cm^{-2} , which imposes higher requirements on the conductive additives and current collector. Carbon material is still the best candidate to meet this challenge. Free-standing carbon current collector holds the greatest potential to help achieve high mass loading of Li_2S , and it is worth devoting more effort to it. Fourth, the LISB system is still at the

embryonic stage of its development, since no mature electrolyte has been developed for it. The conventional ether electrolyte has been proved to result in poor cycling performance. Therefore, research should be encouraged to optimize the solvent, lithium salt, and additives^[131-132] to develop a highly effective electrolyte that can stabilize the interfaces of both cathode and anode. In addition, more efforts should be made towards increasing the ionic conductivity and mobility of electrolytes to help the LISBs operate with a low ratio of electrolyte/sulphur. Fifth, it is necessary to carry out a systematic investigation on the various anode materials to identify the most appropriate anode to match the Li_2S cathode, targeting the most optimised cell configuration for LISBs. Seventh, high loading of the active material and a low ratio of electrolyte to active material are required for high-energy-density LISBs, leading to practical application. Therefore, it is extremely important to explore the LISBs with high loading and lean electrolyte. Last but not least, the energy barrier should be eliminated if the LISBs need to be utilized with high efficiency. Liquid mediator is very promising to accelerate the initial oxidation of Li_2S , resulting in a lower energy barrier and higher energy efficiency. Redox mediators can be researched and explored to lower the overpotential of the first charge. Although it is very challenging to advance the practical application of LISBs, it should be firmly believed that removing the obstacles one by one can ultimately lead to what is pursued.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Li₂S cathode, activation barrier, Li-ion sulfur batteries, lithium-metal free anodes.

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Figures and Tables

Figure 1 The scheme shows the basic components and working principle of the conventional a) Li-S battery system and b) the Li_2S -based Li-ion sulfur battery (LISB) system. In Li-S batteries, a serious safety problem is caused by short-circuit of the cathode and anode due to lithium dendrite growth during battery operation. The LISB system, which is consisted of non-lithium metal anodes, is safer and can potentially deliver strong power to the electrical vehicles.

Figure 2 a) Ionic conductivity of nominally undoped single crystal Li_2S . Points are measured data; the solid line is a fit to regime II. b) Ionic conductivity of polycrystalline Li_2S doped with various mol% of LiCl , LiF or LiOH . Reproduced with permission.^[27] Copyright 2019, Wiley-VCH.

Figure 3 a) Initial potential barrier of Li_2S cathode material at C/8, C/50, C/200, and C/1000. b) Relationship between the current rate and the overpotential of Li_2S cathode. c) The model for the initial charging of Li_2S . Reproduced with permission.^[104] Copyright 2012, American Chemical Society.

Figure 4 a) Transmission electron microscope (TEM) image, high-resolution TEM (HRTEM) image and first cycle charge-discharge profiles of Li₂S/FWNTs@rGO NBF. Reproduced with permission.^[137] Copyright 2017, Wiley-VCH. b) TEM and HRTEM images, and first cycle charge-discharge curves of *in-situ* TG-Li₂S composite. Reproduced with permission.^[43] Copyright 2014, Springer Nature. c) TEM images and charge-discharge profile of Nano-Li₂S with cage-like structure. Reproduced with permission.^[44] Copyright 2015, Elsevier Ltd. d) SEM images with enlargement in insets, cyclic voltammograms, and first activation cycle at C/50 of ball milled Li₂S-C composite. Reproduced with permission.^[38] Copyright 2012, American Chemical Society.

Figure 5 a) Schematic illustration of the synthesis, TEM images, and electrochemical performance of $\text{Al}_2\text{O}_3\text{-Li}_2\text{S-GS}$ cathode. Reproduced with permission.^[28] Copyright 2017, Royal Society of Chemistry. b) Schematic illustration of the synthesis process, SEM image of $\text{Li}_2\text{S/GO@C}$ nanospheres and TEM images of GO@C after Li_2S was removed. Reproduced with permission.^[39] Copyright 2015, American Chemical Society. c) Illustration of the synthesis route for $\text{Li}_2\text{S-GNAs}$, field emission SEM (FESEM) image with corresponding elemental mapping of C and S of $\text{Li}_2\text{S-GNAs}$, and electrochemical performance of the $\text{Li}_2\text{S-GNAs}$. Reproduced with permission.^[18] Copyright 2015, Royal Society of Chemistry. d) Illustration of the synthesis method for $\text{HNG-Li}_2\text{S}$ composite, time-lapse SEM images of the activation process of Li_2S on a single-layered graphene electrode (with the red color indicating the relatively thicker Li_2S layer on graphene), and cycling performance of $\text{HNG-Li}_2\text{S}$ composite. Reproduced with permission.^[49] Copyright 2015, Wiley-VCH.

Figure 6 a) Schematic illustration of the synthesis of $\text{Li}_2\text{S}/\text{N,P-C}$, SEM image of $\text{Li}_2\text{S}/\text{N,P-C}$, cycling performance of $\text{Li}_2\text{S}/\text{N,P-C}$, digital photograph of the solution with different absorbents, and ultraviolet-visible (UV-Vis) spectra of the solution (showing the absorbability of N,P-C). Reproduced with permission.^[52] Copyright 2017, Wiley-VCH. b) FESEM and field emission TEM (FETEM) images of $\text{Li}_2\text{S}@C$ composites, schematic representation of the configuration of a cell, and electrochemical performance of $\text{Li}_2\text{S}@C$ composites. Reproduced with permission.^[53] Copyright 2015, Royal Society of Chemistry. c) Schematic of the process flow for the hierarchical C- Li_2S -C nanocomposite nanoparticles, TEM and SEM images of hierarchical C- Li_2S -C nanoparticles and electrochemical performance of hierarchical C- Li_2S -C nanoparticles. Reproduced with permission.^[55] Copyright 2015, Wiley-VCH.

Figure 7 a) Schematic illustration of the coating process for the $\text{Li}_2\text{S}@\text{C}$ spheres, SEM images, and electrochemical performance of the $\text{Li}_2\text{S}@\text{C}$ spheres. Reproduced with permission.^[32] Copyright 2014, American Chemical Society. b) Schematic diagram of PVP-assisted synthesis of $\text{Li}_2\text{S}/\text{CB}@\text{NC}$, TEM images and the electrochemical performance of $\text{Li}_2\text{S}/\text{CB}@\text{NC}$. Reproduced with permission.^[56] Copyright 2015, American Chemical Society.

Figure 8 a) Schematic illustration of the production of freestanding flexible $\text{Li}_2\text{S}@\text{NCNF}$ paper electrodes, optical image of $\text{Li}_2\text{S}@\text{NCNF}$ paper and cycling performance of $\text{Li}_2\text{S}@\text{NCNF}$. Reproduced with permission.^[29] Copyright 2017, Wiley-VCH. b) FESEM images of Li_2S composites supported on the Ni foam, and the corresponding electrochemical performances of electrodes with different Li_2S composites on Ni foam. Reproduced with permission.^[61] Copyright 2016, Elsevier Ltd. c) Schematic structure of a core-shell Li_2S cathode, SEM image of the core-shell Li_2S cathode, and cycling performance with high loading mass of Li_2S . Reproduced with permission.^[60] Copyright 2017, Wiley-VCH. d) Schematic illustration of the material preparation processes of the nano- $\text{Li}_2\text{S}/\text{rGO}$ paper, photograph of the rGO paper and nano- $\text{Li}_2\text{S}/\text{rGO}$ paper and cycling performance of nano- $\text{Li}_2\text{S}/\text{rGO}$ paper. Reproduced with permission.^[40] Copyright 2015, American Chemical Society.

Figure 9 a) Voltage curves of cells with Li₂S/Fe nanocomposite electrodes. Reproduced with permission.^[84] Copyright 2002, Electrochemical Society. b) Voltage profiles of MoS₂. Reproduced with permission.^[64] Copyright 2012, Wiley-VCH.

Figure 10 a) Schematic illustration of $\text{Li}_2\text{S}/\text{TiO}_2$ -HCF composite, optical images of sealed glass cells with Li_2S composite-Ti and pristine Li_2S cathodes after cell operations, and cycling performance. Reproduced with permission.^[138] Copyright 2018, American Chemical Society. b) Schematic representation of composite synthesis of $\text{Li}_2\text{S}/\text{Ti}_3\text{C}_2\text{T}_x$, SEM image, and cycling performance of $\text{Li}_2\text{S}/\text{Ti}_3\text{C}_2\text{T}_x$ composite. Reproduced with permission.^[73] Copyright 2018, Elsevier Ltd. c) Schematic representation of the synthesis of $\text{Li}_2\text{S}@LiTiO_2$ composite, SEM image and cycling performance of $\text{Li}_2\text{S}@LiTiO_2$. Reproduced with permission.^[74] Copyright 2018, Royal Society of Chemistry.

Figure 11 a) Schematic illustration, charge–discharge curves, and cycling performance of graphite- $\text{Li}_2\text{S}@PC$ full cells. Reproduced with permission.^[116] Copyright 2017, Elsevier Ltd. b) Illustrated structure and electrochemical performance of a $\text{Li}_2\text{S}/\text{Si}$ battery. Reproduced with permission.^[16] Copyright 2010, American Chemical Society. c) The subsequent five cycles and cycling performance of the $\text{Si}@C\text{-Li}_2\text{S}$ full-cell. Reproduced with permission.^[125] Copyright 2017, Elsevier Ltd. d) Typical charge/discharge voltage curves and cycling performance of the $\text{SnO}_2/\text{Li}_2\text{S}$ full battery. Reproduced with permission.^[129] Copyright 2017, Elsevier Ltd.

Figure 12 a) Schematic diagrams of proposed reactions between polysulfides and carbonates. Reproduced with permission.^[77] Copyright 2011, American Chemical Society. b) Representative quasi-solid-state reactions in the Li-S system. Reproduced with permission.^[83] Copyright 2017, Electrochemical Society. c) Galvanostatic charging-discharging voltage profiles of $\text{Li}_2\text{S}/\text{MoS}/\text{C}$ cathodes. Reproduced with permission.^[86] Copyright 2017, Elsevier Ltd.

Figure 13 a) Cycling performances of the S cathode in DOL or DME electrolytes. Reproduced with permission.^[90] Copyright 2010, Electrochemical Society. b) Performance comparison of S cathode in different electrolytes. Reproduced with permission.^[77] Copyright 2011, American Chemical Society. c) Representation of the polysulfide shuttle and loss of active material during charge. Reproduced with permission.^[91] Copyright 2014, Elsevier B.V. d) Specific discharge capacity of a full battery cell with a Li₂S cathode and a silicon nanowire anode. Reproduced with permission.^[16] Copyright 2010, American Chemical Society.

Figure 14 a) Cycling performance of the silicon/carbon electrode in different electrolytes. Reproduced with permission.^[100] Copyright 2016, Electrochemical Society. b) Deposition of uniform Li spherical particles in the LiNO₃ containing electrolyte. Reproduced with permission.^[99] Copyright 2019, Springer Nature. c) The mechanism responsible for the effect of LiNO₃ in the electrolyte on the sulfur electrode and the cell performance. Reproduced with permission.^[101] Copyright 2019, Elsevier B.V. d) Illustration of SEI on lithium anode cycled in different electrolytes. Reproduced with permission.^[105] Copyright 2013, Elsevier B.V.

Figure 15 a) Schematic illustration of Li_2S cathodes working with redox mediators and performance

of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$, 50 mM $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$, LiI , $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$, and $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ redox mediators. Reproduced with permission.^[107] Copyright 2014, American Chemical Society. b) Performance of the LiI redox mediator. Reproduced with permission.^[108] Copyright 2014, Wiley-VCH. c) Performance of InI_3 and LiI redox mediators. Reproduced with permission.^[129] Copyright 2017, Elsevier Ltd. d) Schematic illustration of redox mediator-assisted oxidation of Li_2S and performance of quinone-based redox mediators. Reproduced with permission.^[110] Copyright 2018, Elsevier Inc. e) Schematic illustration, SEM image, and performance of P_2S_5 assisted Li_2S cathodes. Reproduced with permission.^[109] Copyright 2014, American Chemical Society.

Table 1 Summary of the electrochemical performances of Li₂S/carbon composite cathode materials

Cathodes	Li ₂ S (wt%)	Initial discharge capacity (mAh g ⁻¹)	Current rate in cycling	Capacity retention@cycle number	Potential barrier (V)	Ref.
Mesoporous Li ₂ S–Carbon nanofiber	72%	800 (0.025 C)	1 C	64% @100	2.57 (0.025 C)	[41]
Free-standing Al ₂ O ₃ –Li ₂ S–graphene oxide sponge	58%	1028 (0.05 C)	0.5 C	88% @300	3.5–3.55 (0.05 C)	[28]
Li ₂ S/ carbon nanotubes@ reduced graphene oxide nanobundle forest	55-60%	975 (0.2 C)	0.2 C	89% @300	2.62 (0.05 C)	[42]
Li ₂ S–graphene oxide	75%	782 (0.2 c)	0.2 C	88% @150	3.5 (0.05 C)	[50]
Li ₂ S-Nitridated Graphene	66.3%	1150 (0.05 C)	0.2 C	49% @500	2.3 (0.05 C)	[49]
Li ₂ S-Lithiated Graphite	NA	800 (0.1 C)	0.1 C	91% @50	2.3-2.4 (NA)	[139]
Carbon coated Li ₂ S/graphene	80%	993 (0.5 C)	0.5 C	76% @100	2.75 (0.05 C)	[140]
(Li ₂ S)/Graphene Oxide Nanospheres with Conformal Carbon Coating	NA	964 (0.2 C)	0.2 C	71% @50	3.3 (0.05 C)	[39]
Li ₂ S/graphene	78.3%	693 (1/12 C)	1/12 C	73% @40	4.25 (0.083 C)	[18]
Li ₂ S/N,P-Codoped Carbon	62%	Over 1000 (0.1C)	0.1 C	70% @100	2.7 (0.1 C)	[52]
Hierarchical nanocomposite particle–shell architecture of Li ₂ S	60%	About 1060 (0.1 C, 45 °C)	0.5 C	100% @100	2.5 (0.1 C)	[55]
Sheet-like Li ₂ S@C nanocomposite	68%	About 860 (0.05 C)	0.5 C	91% @100	2.6 (0.05 C)	[53]
Li ₂ S-microporous carbon	43.1%	About 730 (0.1 C)	0.1 C	89% @900	NA	[54]
Li ₂ S-C composite	About 70%	About 700	0.1 C	77% @100	2.75-2.80 (0.1 C)	[141]

Nanostructured Li ₂ S-carbon composite	67.5 %	1144 (0.02 C)	NA	NA	2.5 (0.1 C)	[38]
Carbon-coated Li ₂ S Core–Shell Spheres	98 %	972 (0.2 C)	0.5 C	63% @400	2.5 (0.1 C)	[32]
Carbon-coated Li ₂ S/Carbon black	70%	1020 (0.1 C)	0.1 C	65% @200	2.6 (0.1 C)	[56]

Table 2 Summary of the electrochemical performance of LISB full cells

cathode	Anode	electrolyte	N/P ratio	Current density (1C=1166 mA / g)	Loading mass (mg cm ⁻²)	Initial discharge capacity (mAh g ⁻¹)	Capacity retention@ cycling number	Ref.
Lithium sulfide/microporous carbon	Graphite	1.0 M LiPF ₆ +EC/DEC	1.02	0.144C	NA	660	91% @150	[54]
Ball-Milled Li ₂ S/Graphene	Graphite	1.0 M Li(TFSA) in tetraglyme/HFE	NA	1/12C	2.2	809	50% @100	[117]
Lithium sulfide@porous carbon	Graphite	1 M (LiTFSI)+DOL/DM E	1.3	0.1C	0.9	470	57.4% @30	[116]
Li ₂ S@graphene nanocomposites	Graphite	1 M (LiTFSI)+D2/DOL	1.3	0.14 C	2	730	60% @200	[36]
Li ₂ S/mesoporous carbon nanocomposite	Silicon	1 M LiTFSI+ DOL/DME	1.0	1/8 C	1.1-1.4	423	51% @20	[16]
Li ₂ S/carbon mixture	Silicon	1 M LiTFSI+ DOL/DME+0.5 M LiNO ₃	NA	0.2 C	2.0	550	49% @70	[124]
Li ₂ S/C/Graphene composite	Silicon	1 M LiTFSI+ DOL/DME+1% M LiNO ₃	NA	0.086 C	<0.41	593	61% @30	[126]
Mo/Li ₂ S composite	Silicon	1.0M LiPF ₆ +EC/DMC+10% FEC	1.2	0.21 C	2.0–3.0	800	49% @150	[125]
Li ₂ S–C composite	Tin	PEO-based gel electrolyte	NA	0.13 C	NA	515	100% @80	[128]
Li ₂ S-C mixture	Tin	PEO-based gel polymer electrolyte	NA	0.033 C	NA	600	66% @32	[14]
Li ₂ S-carbonized wipes	SnO ₂	1 M LiTFSI+ DOL/DME+1% M LiNO ₃ +150 mM LiI (or 50 mM InI ₃)	NA	0.5 C	2.4	983	86% @200	[129]
Li ₂ S@NCNF paper	Fe ₃ O ₄	1 M LiTFSI+ DOL/DME+2% LiNO ₃	1.1	0.2 C	3.0	576	60% @50	[29]
Li ₂ S@MXene/graphene	Fe ₃ O ₄	1 M LiTFSI+ DOL/DME+2% LiNO ₃	0.91	0.2 C	NA	600	78% @50	[130]

Free-standing Li ₂ S- rGO film	MnO ₂	1 M LiTFSI+DOL/DME	1.5	0.2 C	1.0–1.2	587.5	80% @ 150	[131]
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The Li₂S-based Li-ion sulfur batteries system has high energy density and high safety due to the depletion of the lithium metal anode. This review systematically discusses Li₂S composite cathodes, non-lithium anodes, electrolytes and full cell configuration of the Li₂S-based Li-ion sulfur batteries. Some perspectives are proposed to further develop this battery system and to reach the practical high-energy batteries.

Keywords: Li₂S cathode, activation barrier, Li-ion sulfur batteries, non-lithium-metal anodes.

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A Review on Li₂S-based Li-ion Sulfur Batteries: Progress and Prospects