Review Article
Lithium Sulfide as Cathode Materials for Lithium-Ion Batteries: Advances and Challenges

Luoting Zhou,1,2 Wenkui Zhang,1 Yangfeng Wang,1 Sheng Liang3, Yongping Gan,1 Hui Huang,1 Jun Zhang,1 Yang Xia,1 and Chu Liang1

1College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China
2School of Textile and Apparel, Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province, Shaoxing University, Shaoxing 312000, China
3School of Energy Materials and Chemical Engineering, Hefei University, Hefei 230601, China

Correspondence should be addressed to Sheng Liang; liangsh@hfuu.edu.cn and Chu Liang; cliang@zjut.edu.cn

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Due to the ever-growing demand for high-density energy storage devices, lithium-ion batteries with a high-capacity cathode and anode are thought to be the next-generation batteries for their high energy density. Lithium sulfide (Li2S) is considered the promising cathode material for its high theoretical capacity, high melting point, affordable volume expansion, and lithium composition. This review summarizes the activation and lithium storage mechanism of Li2S cathodes. The design strategies in improving the electrochemical performance are highlighted. The application of the Li2S cathode in full cells of lithium-ion batteries is discussed. The challenges and new directions in commercial applications of Li2S cathodes are also pointed out.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronic equipment, electric vehicles, and large-scale energy storage devices due to their relatively high energy density and long cycle life. Currently, the intercalation-type lithium storage materials with high cycling stability are employed as the main cathode and anode materials for commercialized LIBs. However, the intercalation-type cathode materials such as LiFePO4, LiMnO4, and LiCoO2 suffer from low theoretical capacity (<200 mAh·g−1), which fail to meet the ever-increasing need of higher energy density. Lithium-sulfur (Li-S) batteries as the representative of nonintercalation-type lithium storage materials have very high energy density (2600 W·h·kg−1), more than 8 times that of currently commercialized LIBs [1, 2], and are regarded as one of the most promising secondary batteries with high energy density.

Both sulfur and its fully lithiated state of Li2S can be used as active cathode materials for Li-S batteries. A sulfur-based composite cathode should be coupled with the lithium metal or lithium-containing anode. The low electronic and ionic conductivity is the intrinsic characteristics of elemental sulfur, leading to low specific capacity and poor rate performance. The various soluble lithium polysulfides (3 ≤ n ≤ 8) are produced during charging and discharging. The shuttle effect of dissolved lithium polysulfides results in active material loss and rapid capacity fading. The volume change is as high as 80% in the conversion of S (2.07 g·cm−3) into Li2S (1.66 g·cm−3). The repeated volumetric expansion and contraction will accelerate the cathode pulverization and the loss of electronic contact [3–6]. Lithium sulfide (Li2S), as the fully lithiated state of sulfur, can not only deliver a high theoretical specific capacity (1166 mAh·g−1) but also avoid the volumetric expansion, resulting in a more stable microstructure and electrochemical performance [7]. The high melting point (938°C) and solubility in some organic solvents make Li2S more advantageous in the synthesis of composites.

Despite the above differences between the S cathode and the Li2S cathode, the greatest challenge of Li-S batteries is the safety problems caused by using the metallic lithium anode. The internal short circuit arising from the formation of lithium dendrites is the major risk for Li-S batteries [8]. However, the Li2S cathode can be used in LIB pairing with safer lithium metal-free anodes (e.g., graphite, silicon, and Sn).
for its lithium composition, which can avoid the safety problems caused by lithium metal anodes. Compared with the Li-S batteries, the LIBs using the Li2S materials as cathodes can reach an energy density as high as that of Li-S batteries, which is several times that of the current commercial LIBs which use intercalation-type cathode materials such as LiFePO4, LiMnO2, and LiCoO2, and advance in safety by avoiding the use of lithium metal anodes. The above advantages make lithium sulfide a promising cathode material for LIBs.

Like elemental sulfur, Li2S suffers from the shuttle of lithium polysulfides and low electronic and ionic conductivity as well. High initial kinetics barrier during charging is another problem for Li2S cathode materials. Many strategies have been reported to improve the electrochemical lithium storage performance of Li2S as cathode materials for secondary batteries. This review summarizes recent progress in Li2S-based composite cathode materials. First, we summarize the activation process during initial charging and reversible lithium storage mechanism of Li2S. The strategies for improving the electrochemical performance of the Li2S cathode for lithium-ion batteries (half cells) are then highlighted. Finally, we discuss the design and progress in Li2S-based cathode materials for lithium-ion batteries (full cells). We hope that this review will provide a fundamental understanding on the lithium storage mechanism of the advanced cathode materials.

2. Activation and Lithium Storage Mechanism of Li2S Cathodes

As the fully lithiated product of sulfur, Li2S exhibits a same lithium storage mechanism except the initial activation process, which can only be observed in the first delithiation process of Li2S. The activation process and reaction mechanism of Li2S are illustrated in Figure 1 [9]. During the initial charge (Figure 1(a)), the voltage rises to 3.45 V and then rapidly drops to about 2.4 V, representing the initial potential barrier from phase nucleation of polysulfides. Subsequently, a long voltage plateau is seen at ~2.4 V, and then the voltage gradually increases to 3.4 V and goes up to 4.0 V rapidly. It is believed that the activations are related to the phase nucleation of polysulfides and charge transfer during the oxidation of Li2S in the first charge process. The oxidation of Li2S is achieved through the direct charge transfer between the solid Li2S and conducting materials. The potential barrier is found to be strongly dependent on the current density in the activation (Figures 1(b) and 1(c)). It should be noted that the potential barrier is quite weak at a very small current density of C/1000 (approaches the zero current), whereas the potential barrier increases rapidly when the current density is over C/200, as shown in Figure 1(b). This result means that the delithiation process of Li2S is thermodynamically favorable but kinetically unfavorable.

As shown in Figure 1(d), the first charging process can be divided into four steps.

Step 3 (in the middle of charging):

\[ y\text{Li}_2\text{S}(s) \rightarrow \text{Li}_2\text{S}_y(l) + (2y - 2)\text{Li}^+ + (2y - 2)e^- \]  \hspace{1cm} (2)

\[ \text{Li}_2\text{S}_y(l) \rightarrow \frac{y}{8}\text{Li}_2\text{S}_8(l) + \left(2 - \frac{y}{4}\right)\text{Li}^+ + \left(2 - \frac{y}{4}\right)e^- \]  \hspace{1cm} (3)

Step 4 (at the end of charging):

\[ \text{Li}_2\text{S}_y(l) \rightarrow \frac{y}{8}\text{Li}_2\text{S}_8(l) + \left(2 - \frac{y}{4}\right)\text{Li}^+ + \left(2 - \frac{y}{4}\right)e^- \]  \hspace{1cm} (4)

A high potential barrier in steps 1 and 2 can be attributed to the phase nucleation of polysulfides, in which a large amount of energy is needed to increase charge and ionic conductivity. In step 3, the disappearance of potential barrier and the formation of polysulfides cause faster charge transfer because charge can move rapidly between Li2S, lithium polysulfide, and electrolytes. At the end of charging, potential barrier is not seen due to the existence of a single lithium polysulfide phase. The activation barrier can disappear by adding lithium polysulfides into the liquid electrolyte, further demonstrating the activation barrier arising from the nucleation of polysulfide. During the first discharge process, a short plateau at 2.3 V and a long plateau at 2.1 V can be observed, corresponding to the reaction of S with Li to form long-chain lithium polysulfide (Li2S8, 4 ≤ n ≤ 8) and the reaction of lithium polysulfide with Li to form insoluble lithium sulfide (Li1Sn, 1 ≤ n ≤ 2), consistent with the sulfur cathode. In the following cycles, the activation barrier disappeared and the voltage profile is the same with the sulfur electrodes. The delithiation and lithiation behaviors of Li2S can be seen in the cyclic voltammetry (Figure 1(b)) [9].

The activation barrier is associated with the particle size of Li2S. Liang et al. decreased the particle size of Li2S from 10–20 μm to ~1 μm through a facile ball milling process. The interfacial and charge transfer resistance of Li2S was decreased after ball milling and carbon-coating treatment, and the initial activation potential was reduced from 3.38 to 2.99 V [10]. Higher voltage is required to extract the lithium ion from the interior of Li2S with large particles due to the long lithium-ion diffusion distance and slow charge transfer. Small particles can not only shorten the diffusion distance of lithium ions but also accelerate the charge transfer and chemical reactions by increasing the contact areas with the electrolyte. Figure 2 shows the CV curves of Li2S with three particle sizes. Combined with SEM images and CV curves, it can be concluded that the activation potential of Li2S decreases with the particle sizes (Figure 2) [11]. A native layer effect as another important potential factor was proposed to explain the activation of Li2S [12]. Li2S is sensitive to moisture and air to generate H2S and a stable LiOH layer accompanied by an unstable S-H layer. These unique layers result in low lithium-ion diffusivity and severe capacity fading, which can be removed by two typical methods of high-temperature annealing and mechanical ball milling of Li2S [12, 13].

Another avenue to reduce the activation potential is to add facilitating additives such as polysulfides and redox...
mediators. The added polysulfides are thought to contribute to the phase nucleation of polysulfides in the Li2S cathode during the initial charge process. Xu et al. added a small amount of polysulfides into DME to form a Li2Sx-based electrolyte. When contacted with the long-chain Li2Sx, Li2S can spontaneously oxidize to low-order Li2Sx which significantly reduces the energy required for the nucleation of polysulfides. As a result, the activation barrier during the initial charge process was likely eliminated [14]. Redox mediators (RMs) can enhance the electron transfer in the Li2S cathode by the following steps: (1) RMs are electro-oxidated at the electrode surface; (2) the oxidated redox mediators (RM+) diffuse deeper into the Li2S cathode materials; (3) the inner Li2S is oxidated by the RM+; and (4) RMs diffuse back to the electrode surface to be recycled. The activation potential of the Li2S cathode can thus be reduced for the enhanced charge transfer. Meini et al. used three kinds of RMs with different oxidation potential for testing: $E_{RM} < E_{Li2S}$ (cobaltocene), $E_{RM} = E_{Li2S}$ (dibenzenechromium), and $E_{RM} > E_{Li2S}$ (decamethylferrocene, LiI, and ferrocene), and found that only the RMs whose oxidation potential is higher than that of Li2S can work effectively. The activation potential of the Li2S cathode during the initial charge was reduced to $\sim 2.75$ V by using decamethylferrocene as the RM [15]. These results provide new ideas for reducing the activation barrier of Li2S.

Figure 1: (a) Charge-discharge profile of the Li2S electrode in the initial three cycles. (b) CV curves of the Li2S electrode. (c) Initial potential barrier at different current. (d) Overpotential at different current rates. (e) Initial charging process of Li2S [9].
3. Improvement of Lithium Storage Performance of the Li$_2$S Cathode in Half Cells

Li$_2$S suffers from low electronic and ionic conductivity, high activation barrier, and the shuttle of lithium polysulfides, resulting in the poor electrochemical performance. In this section, we focus on the strategies for improving electrochemical properties of Li$_2$S cathode materials. Table 1 lists the electrochemical performance of various lithium sulfide cathodes for lithium-sulfur batteries. The electrochemical performance of Li$_2$S composites is found to strongly depend on the modified materials and mass loading of Li$_2$S.

3.1. Li$_2$S-Metal Composites. Transition metal sulfides (FeS$_2$, CuS, CoS$_2$, etc.) have been widely used as the cathode materials in Li-S batteries. After lithiation, the transition metal sulfides finally convert into a mixture of transition metal and Li$_2$S, in which the transition metal is uniformly dispersed in the Li$_2$S. The electronic conductivity of Li$_2$S is increased by the uniformly dispersed transition metal. Dahn et al. directly mixed the transition metal and Li$_2$S by ball milling and demonstrated that the Li$_2$S-M (M=Co, Fe) nanocomposite with average grain sizes of ~10 nm is electrochemically active. The Li$_2$S-Fe cathodes displayed a high reversible capacity of 600 mAh·g$^{-1}$ [16]. Pure Li$_2$S is difficult to work in all-solid-state batteries as the cathode material for its insulative nature. The addition of highly conductive metallic materials can effectively improve the electronic conductivity. Tatsumisago et al. used a mechanical milling synthesis to prepare Li$_2$S-Cu active materials with various molar ratios [17]. Li$_2$S did not react with Cu during the mechanical milling (Figure 3(a)). The conductivity improved by the addition of Cu successfully allowed the


| Cell type | Modified material | Cathode material | Current density | Capacity (mAh g\(^{-1}\)) | Voltage (V) | Li\(_2\)S content (wt. %) | Mass loading (g cm\(^{-2}\)) | Ref. |
|-----------|-------------------|------------------|----------------|-----------------------------|-------------|---------------------------|-----------------|------|
| Half cell | Metal | Li-S/Fe | 64 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 300-90 | [16] |
| Carbon materials | Li-S/C nanocomposites | Li2S-C nanocomposites | 88.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 411-90 | [17] |
| Carbon materials | Li-S/C-CNT nanocomposites | Li2S@C | 166.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 402-90 | [18] |
| Carbon materials | Li-S/C-PVP | Li2S-C-PVP | 233.2 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 309-90 | [19] |
| Carbon materials | Li-S/C-CNT | Li2S-C-CNT | 590.8 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [20] |
| Carbon materials | Li-S/C-SiC | Li2S-C-SiC | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [21] |
| Carbon materials | Li-S/C-GO | Li2S-GO | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [22] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [23] |
| Carbon materials | Li-S/graphene nanocomposites | Li2S-graphene nanocomposites | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [24] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [25] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [26] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [27] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [28] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [29] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [30] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [31] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [32] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [33] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [34] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [35] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [36] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [37] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [38] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [39] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [40] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [41] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [42] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [43] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [44] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [45] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [46] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [47] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [48] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [49] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [50] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [51] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [52] |
| Carbon materials | Li-S/graphene | Li2S-graphene | 617.6 mA cm\(^{-2}\) | 0.0 | 0.1-3 | 62.2 | 6.2 | 958-90 | [53] |
| Cell type | Modified material | Cathode material | Current density | Capacity (mA·g⁻¹)@cycle number | Voltage (V) | Li₂S content (wt. %) | Mass loading | Ref. |
|-----------|-------------------|------------------|----------------|--------------------------------|-------------|----------------------|-------------|------|
| Full cell | Carbon materials  | Li₂S-mesophase carbon microbeads | 232 mA·g⁻¹ | 280@50 | 0.1–2.75 | 50 | — | [54] |
| Full cell | Carbon materials  | Li₂S/mesoporous carbon nanocomposites | 389 mA·g⁻¹ | 234@20 | 1.2–2.6 | 58.9 | 1.1–1.4 mg·cm⁻² (Li₂S) | [55] |
| Full cell | Carbon materials  | Li₂S/graphite | 97.2 mA·g⁻¹ | 410@100 | 0.5–3.5 | 80.6 | 2.2 mg·cm⁻² (Li₂S) | [56] |
| Full cell | Carbon materials  | Li₂S-rGO | 232 mA·g⁻¹ | 472@150 | 0.2–2.6 | 55 | 1.0–1.2 mg·cm⁻² (Li₂S) | [57] |
insulative Li$_2$S being rechargeable in the all-solid-state batteries. As shown in Figure 3(b), the 75Li$_2$S·25Cu electrode not only delivers a high capacity (∼300 mAh·g$^{-1}$ after 30 cycles) but also exhibits a high coulombic efficiency (∼97% at the 30th cycle).

Li$_2$S-metal composites exhibit higher electronic conductivity and better electrochemical performance compared with pure Li$_2$S. However, the limitations of Li$_2$S-metal electrodes are gradually revealed. Firstly, transition metals usually used in Li$_2$S-metal electrodes cause the low energy density of cells due to the high density of transition metals. Secondly, the irreversible reactions between metals and intermediate products from the charge/discharge process of Li$_2$S result in the loss of active materials and the capacity fading. Thirdly, a serious electrochemical polarization is accompanied by the charge-discharge process of the Li$_2$S-metal electrode, which is associated with its rate performance. More attentions have been focused on other Li$_2$S-based composites (such as Li$_2$S-carbon, Li$_2$S-conducting polymer, and Li$_2$S-sulfide) because of the unsatisfactory electrochemical performance of Li$_2$S-metal.

3.2. Li$_2$S-Carbon Composites. Carbon materials with rich structural diversity, stable chemical properties, high conductivity, abundant reserve, and low density are considered one of the most promising materials used in the energy storage field (such as hydrogen storage, lithium-ion battery, and supercapacitor). As the typical representatives of carbon materials, activated carbon, carbon nanotubes, graphene, and porous carbon have been widely used in the Li$_2$S electrode with excellent electrochemical performance. The carbon materials can contribute to the electronic conductivity and prevent the diffusion of lithium polysulfides. According to the combination mode of Li$_2$S with carbon, we can divide it into four main methods: (1) physical mixing: the Li$_2$S-carbon mixtures were obtained by the most straightforward method of mechanical milling; (2) diffusion and precipitation: in the liquid state, Li$_2$S can be easily diffused into the interior of carbon materials and reserved inside by the following evaporation process; (3) pyrolysis and carbon coating: the pyrolysis reaction of organics under high-temperature and anaerobic conditions is utilized to prepare carbon layer-coated Li$_2$S-carbon composites; and (4) in situ reaction. Different from aforementioned methods, there is no readymade carbon or Li$_2$S and the Li$_2$S-carbon composites are in situ synthesized by one-pot reaction of a mixture of lithium sources, sulfur sources, and carbon sources.

3.2.1. Physical Mixing. Physical mixing of Li$_2$S and carbon is regarded as the simplest and most direct method to obtain Li$_2$S-carbon mixtures. Cai et al. reported a typical physical mixing method for preparing the nanostructured Li$_2$S-carbon composite by high-energy ball milling (Figure 4(a)) [18]. After ball milling, the size of Li$_2$S particles reduced from about 20 μm to about 400 nm (~50 times), and the carbon black is uniformly dispersed on the Li$_2$S surface, as illustrated in Figure 4(a). The morphologies of commercial Li$_2$S and ball-milled Li$_2$S-carbon composite can be observed by scanning electron microscopy (Figures 4(b) and 4(c)). The reduced size of Li$_2$S and uniform dispersion of conductive carbon on the Li$_2$S surface can effectively reduce the lithium-ion transmission distance and increase electronic conductivity, leading to the good electrochemical performance of Li$_2$S-carbon.

In addition to the mixing function, mechanical ball milling is also widely used to reduce the Li$_2$S particle size for further processing [10, 19–21]. For example, Chen et al. used high-energy ball milling to obtain the precursor of Li$_2$S-plus-C composites (Figure 4(d)), which showed a smaller particle...
size and higher electrochemical activity [19]. It should be noted that the physical mixing is difficult to obtain a composite of which Li$_2$S enters the interior of carbon materials, and the naked Li$_2$S suffers from the serious shuttle effect of lithium polysulfides.

3.2.2. Diffusion and Precipitation. Li$_2$S has good solubility in solvents such as ethanol and tetrahydrofuran. As a result, a simple liquid infiltration-evaporation method was widely used to synthesize the Li$_2$S-carbon composite [22–27]. The synthesis process mainly includes three steps: (1) the preparation of the Li$_2$S solution; (2) the infiltration; and (3) the evaporation of the solvent and nucleation of Li$_2$S. This method requires a high specific surface area and porosity of the carbon material (e.g., graphene, carbon nanotube, and porous carbon) to get a higher Li$_2$S content and better dispersion of Li$_2$S in the composite. The synthetic schematic of the Li$_2$S-carbon composite using different carbon materials is displayed in Figure 5 [22–24]. Li$_2$S solution was usually slowly added into the carbon materials until the solvents had visibly evaporated to ensure rapid nucleation of Li$_2$S with a small size [26, 27]. Zhou et al. successfully synthesized a freestanding Li$_2$S-coated graphene cathode through the above method. It showed a reduced initial charge voltage barrier and a high capacity of 403 mAh·g$^{-1}$ after 300 cycles at 0.5°C. The cross-linked, porous network structure provides not only the homogeneously dispersed nucleation sites but also the fast electron/ion transfer channels.

Li$_2$S can also be synthesized by a solution-based chemical infiltration method through the following disproportionation reaction of Li$_2$S$_6$ [28, 29, 58]:

$$\text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S} + \left(\frac{5}{8}\right) \cdot \text{S}_8$$  

(5)

The chemical infiltration method is similar to the liquid infiltration-evaporation method. Li$_2$S$_6$ solution is prepared firstly and then absorbed by the carbon materials. During the evaporation process of the solvent, the disproportionation reaction occurred, Li$_2$S and sulfur were formed inside carbon, and extra sulfur was removed by a heat treatment. Strubel et al. reported that the as-prepared Li$_2$S showed a smaller size and higher initial discharge capacity with better cycle stability compared with Li$_2$S prepared by an ethanol-based liquid infiltration-evaporation method [29]. Li$_2$S$_3$ solution is also used to synthesize such a kind of Li$_2$S-carbon composite instead of Li$_2$S$_6$ solution [30].

In addition, it is noteworthy that the lithium-triggered chemical reduction is also an effective method to prepare the Li$_2$S-carbon composite. The Li$_2$S$_8$ solution was dropped to the lithiated graphite paper and then assembled into a cell with the lithium metal. The open-circuit voltage of the cell linearly increased from 60 mV to 2.12 V, indicating that Li$_2$S$_6$
was slowly in situ converted to Li$_2$S by the following reaction:

$$\text{Li}_2\text{S}_6 + 10\text{Li}^+ \rightarrow 6\text{Li}_2\text{S}$$  \hspace{1cm} (6)

Only 48.4% Li$_2$S$_6$ converted to Li$_2$S because of the insoluble Li$_2$S and Li$_2$S$_2$ formed on the surface of graphite, blocking the pathway for the further reduction reaction [59]. Zheng et al. infiltrated sulfur into the microporous carbon at first and then adopted a similar chemical reduction method to convert the elemental sulfur in porous carbon into Li$_2$S using the lithium metal [60]. Li$_2$S can easily enter the interior of the carbon materials owing to the fluidity of the liquid but still suffers from the polysulfide shuttle for the exposure to the liquid electrolyte.

### 3.2.3. Pyrolysis and Carbon Coating

Carbon layer coating is an effective strategy to reduce direct contact between the electrolyte and Li$_2$S, and to block the shuttle of lithium polysulfides. It is the most common method to prepare carbon-coated Li$_2$S by utilizing the pyrolysis reaction of organics. Liang et al. dispersed the ball-milled commercial Li$_2$S in the polystyrene solution and obtained the uniform size (≈1 μm) carbon-coated Li$_2$S particles followed by a pyrolysis process. The formed carbon layer not only helped confining the lithium polysulfides but also prevented the Li$_2$S particles from agglomerating. The as-prepared Li$_2$S-C composites showed excellent cycling stability with an average decay rate of 0.18% per cycle over 200 cycles [10]. More complicate carbon-coating structures were designed to improve the electrochemical performance of Li$_2$S [31–35]. Wu et al. prepared a hierarchical particle-shell architecture Li$_2$S-C composite (Figure 6) with remarkable long-term cycling performance. In this case, nanosized Li$_2$S particles were embedded into the conductive carbon matrix and then coated by a graphitic outer shell through a CVD method. The
hierarchical particle-shell architecture can obviously reduce the internal stresses within outer shells caused by the volume changes during the charge/discharge process and enhance the mechanical stability of the composite. The multilevel protection for Li$_2$S effectively mitigated polysulfide dissolution and achieved excellent cycling performance ($\sim$700 mAh·g$^{-1}$ after 600 cycles at 0.5°C) [34].

However, the excessive use of carbon can seriously affect the specific capacity of composite materials. To prepare a dense and effective carbon layer for Li$_2$S particles is the goal for many researchers. Suo et al. successfully prepared a nanoscale carbon cage for Li$_2$S clusters through the two steps of polymerization (350°C) and carbonization (600°C) processes. During the polymerization stage, the agglomerated Li$_2$S particles were departed into Li$_2$S clusters for the shrink of [Emim]-[N(CN)$_2$]. The dense outer carbon layer ($\sim$5 nm) was then formed during the carbonization stage. The as-prepared carbon-coated Li$_2$S clusters also exhibited a high initial capacity of 826 mAh·g$^{-1}$ at 0.1°C and an excellent capacity retention of 82% after 500 cycles at 1°C [33].

Based on the advantages mentioned above and its simple processing, the pyrolysiss carbon layer-coating method is also widely used to enhance the physical protection for Li$_2$S in other Li$_2$S-carbon composites as an auxiliary measure. For example, the Li$_2$S-3D porous carbon composites prepared by a liquid infiltration-evaporation method are often followed by a coating treatment for the exposed Li$_2$S [36, 37, 61]. Tu et al. successfully prepared a 3D reduced graphene oxide material embedding carbon-coated Li$_2$S particles through a one-step liquid solution-evaporation-carbonization method. The electrochemical performance of the above Li$_2$S-carbon composite is much better than that of the 3D-rGO-Li$_2$S composite without carbon coating [36].

### 3.2.4. In Situ Reaction

In fact, both mechanical milling and a liquid solution-evaporation method are merely physically mixing Li$_2$S and carbon materials. The poor physical contact between Li$_2$S and carbon materials, as well as the high cost of commercial Li$_2$S particles, is still limiting the practical applications of the Li$_2$S-carbon composites. In recent years, facile synthesis methods of Li$_2$S particles have been developed based on the reduction of sulfur using various reducing agents (LiH, LiEt$_3$BH, etc.). The as-prepared Li$_2$S particles show good electrochemical performance with ultrasmall size ($\sim$8.5 nm) [38]. But a further carbon mixing treatment is still needed to enhance the electronic conductivity. In situ synthesis of the Li$_2$S-carbon composite is a promising new avenue to be developed.

Just like the combustion reaction of metallic magnesium in carbon dioxide, metallic lithium can also be burned in carbon disulfide vapor. Li$_2$S/carbon can be obtained by the following reaction:

$$4\text{Li}(l) + \text{CS}_2(g) \rightarrow 2\text{Li}_2\text{S}(s) + \text{C}(s)$$

It is seen that Li$_2$S and carbon, as the only two products of the combustion reaction of the Li metal with CS$_2$, combined to be a composite just like a "combination reaction" [39, 40]. Tan et al. prepared Li$_2$S particles wrapped by few-layer graphene (10–20 layers) with a capsule-like nanostructure using the above method. The single-crystalline Li$_2$S core was completely coated by the graphene, and the active mass loading is achieved to be $\sim$10 mg·cm$^{-2}$. In the first charging, the composite exhibits 1600 mAh·g$^{-1}$ (specific capacity of sulfur) with a coulombic efficiency of 72.5%. A reversible capacity $>$600 mAh·g$^{-1}$ and a high areal capacity $>$4.2 mAh·cm$^{-2}$ remained after 200 cycles [39]. Though the above "combination reaction" has 100% utilization of raw materials in theory, the reaction temperature above 600°C is
too high. Liang et al. used LiH instead of the lithium metal as the reducing agent:

$$4\text{LiH}(s) + \text{CS}_2(g) \rightarrow 2\text{Li}_2\text{S}(s) + \text{C}(s) + 2\text{H}_2(g) \quad (8)$$

The reaction temperature was lowered below 250°C and the reaction time was as short as 5 seconds, which are the lowest reaction temperature and the shortest reaction time reported to date for the in situ synthesis of Li$_2$S-carbon composites, as shown in Figure 7 [41].

Li$_2$SO$_4$ can be reduced by carbon to directly synthesize Li$_2$S-carbon materials through the following reaction [62]:

$$\text{Li}_2\text{SO}_4 + x\text{C} \rightarrow \text{Li}_2\text{S} + x\text{CO} \quad x = 1 - 4; \; y = 1 - 2$$

(9)

Such a facile, cost-effective method has attracted the attention of many researchers [42–48, 62–64]. Through the above method, Li$_2$S can be combined with carbon in various structures by dispersing Li$_2$SO$_4$ in different carbon matrices. Wang et al. fabricated the nanosized Li$_2$S embedded into porous carbon composites through a one-pot carbonization-reduction method, as shown in Figure 8. The glucose and Li$_2$SO$_4$ mixture was first heated to 600°C for the carbonization, and the Li$_2$SO$_4$ particles were homogeneously distributed in the carbon matrix without turning into Li$_2$S. Then, the temperature went up to 800°C, and Li$_2$SO$_4$ totally converted into Li$_2$S. It is believed that the glucose carbonization can effectively inhibit the growth or aggregation of nano-Li$_2$SO$_4$, which is the key to form homogeneously distributed Li$_2$S-porous carbon composites [43]. More novel structures, such as one-dimensional fibers, two-dimensional sandwich plates, and three-dimensional networks, were also synthesized through the similar method [42, 46, 47].

The Li$_2$S-carbon composites exhibit a broad application prospect in lithium ions batteries because more and more advanced preparation technologies will be developed. The most Li$_2$S-carbon study focused on the construction of a stable material structure, simple synthesis method, and high active material loading and utilization, but the weak affinity toward polar Li$_2$S and polysulfides for the nonpolar nature of carbon has still not been fundamentally resolved [65]. It is believed that the study of compounds of Li$_2$S-other materials with strong binding is necessary to figure out better solutions for both high capacity and rate performance.

3.3. Compound of Li$_2$S with Polar Chemical Binding. Many materials with polar functional groups such as metal oxide, metal sulfide, and polymer materials have been applied in the Li$_2$S compounding [49, 50]. Chen et al. coated ultrathin Al$_2$O$_3$ layers (~1 nm) onto the Li$_2$S-graphene oxide sponge by an atomic layer deposition (ALD) technique. The three-dimensional graphene oxide contributes high electronic conductivity to the composites, and the Al$_2$O$_3$ layers effectively suppress the dissolution of lithium polysulfides through the strong binding between Al$_2$O$_3$ layers and Li$_2$S$_x$. As a result, long-term cycling stability (high capacity retention of 88% after 300 cycles at 0.5°C) and high rate performance were achieved simultaneously [50]. LiTiO$_2$ is believed to exhibit a strong binding to the lithium polysulfides and to induce the conversion of long polysulfides into short polysulfides, which have lower solubility in electrolytes. LiTiO$_2$ can be synthesized by the following reaction at 650°C:

$$\text{TiO}_2 + \text{Li}_2\text{S} \rightarrow 2\text{LiTiO}_2 + \text{S}_8$$

(10)

When the TiO$_2$ particles and Li$_2$S were simultaneously dissolved in anhydrous ethanol, the formed LiTiO$_2$ particles were uniformly distributed within the Li$_2$S agglomerates. The as-synthesized product showed unsatisfactory electrochemical performance. Wu et al. adjusted the preparation using titanium isopropoxide as the liquid titanium source instead of TiO$_2$ particles. In such a solution situation, the Li$_2$S nanoparticles got nucleated first due to the lower solubility in ethanol during the early stage of solution evaporation and immediately got wrapped by Ti species in the further evaporation, forming a core-shell structure and reducing agglomeration. The LiTiO$_2$-coated Li$_2$S particles ranging from 100 to 200 nm showed remarkable cycling stability and good rate performance. In addition, the formation of Ti-S bonding is proved to be beneficial for the conversion reaction of Li$_2$S into polysulfides by lowering the activation barrier. Compared with commonly used grapheme, a multilayered Ti$_3$C$_x$ material fabricated by Liang et al. exhibited better chemical absorption of polysulfides as the Li$_2$S host, and the activation barrier of the Ti$_3$C$_2$-Li$_2$S composite cathode decreased to 2.85 V, a 0.6 V potential lower than that of the graphene/Li$_2$S composite cathode [51].

Metal sulfide is another popular material used in the Li$_2$S composite for its sulfur composition and strong chemical interaction toward lithium polysulfides. He et al. used the metal sulfide (TS, TS=NiS, CoS, MnS) to decorate the carbon sponge. The uniformly dispersed polar 0D metal sulfide nanodots accelerate the Li-S redox reaction and absorb the lithium polysulfides through the strong binding. The 1D carbon nanowires cross-linked with 2D graphene nanosheets avoid aggregation and construct a 3D porous and conductive network, which not only facilitate the electronic and ionic conduction but also provide enough space for hosting Li$_2$S (Figure 9). Among the above metal sulfides, CoS has the highest electrocatalytic effect and exhibits an outstanding electrochemical performance with a high areal capacity of 8.44 mAh cm$^{-2}$ [66].

Cui’s group coated the Li$_2$S particles with a TiS$_2$ shell (~20 nm) using a chemical reaction method:

$$\text{TiCl}_4 + 2\text{Li}_2\text{S} \rightarrow \text{TiS}_2 + 4\text{LiCl}$$

(11)

As calculated, the binding energy between Li$_2$S and TiS$_2$ is 10 times higher than that of Li$_2$S with carbon-based graphene. Due to the high electronic conductivity of TiS$_2$, the electronic conductivity of the Li$_2$S-TiS$_2$ composite is 10 times higher than that of the pure Li$_2$S. The Li$_2$S-TiS$_2$ composite delivered stable specific capacities (700, 650, 608, 595, and 560 mAh g$^{-1}$) at different C rates (0.2 C, 0.5 C, 1 C, 2 C, and 3 C). Other transition metal disulfides such as ZrS$_2$ and VS$_2$ were also investigated using the same reaction mechanism:
MCl₄ + 2Li₂S → MS₂ + 4LiCl  \quad M = Ti, Zr, and V

(12)

The calculated binding energies of ZrS₂ and VS₂ with Li₂S are 2.70 and 2.94 eV, respectively, which are 9-10 times higher than that of Li₂S with carbon-based graphene [52].

The conducting polymer is believed to be the ideal material for the Li₂S composites because of its high electronic conductivity, soft nature, and sufficient polar function groups [53, 67–69]. Polypyrrole has been the most popular conductive polymer in recent years. When coupled to Li₂S in a Li/S or lithium-ion battery, the N atoms in polypyrrole can interact strongly with Li₂S, leading to a uniform and complete coating of Li₂S by polypyrrole with strong adhesion. The core-shell structure and Li-N interaction between the polypyrrole and lithium polysulfides effectively avoid the polysulfide species dissolution into the electrolyte, enabling the Li₂S-polypyrrole cathode to maintain a stable capacity performance of 785 mAh g⁻¹ after 400 cycles [53].

Besides the design of active Li₂S composites, binder and electrolyte modification is another avenue to avoid the polysulfide dissolution. There are various functional groups in the polymer binders. Seh et al. selected poly(vinylpyrrolidone) as the optimal binder for the Li₂S cathode based on the binding energies between the functional groups and lithium polysulfides calculated by ab initio simulations. The high binding energy of >C=O groups in PVP with Li₂S and lithium polysulfides results in a uniform dispersion of the active material and carbon in the electrode slurry and inhibition of polysulfide dissolution [70]. However, the strong binding between PVP and Li₂S will cause a boosted initial potential barrier for the inhibition of lithium-ion diffusion. According to Liu’s results, this could be alleviated by using a PVP and polyethylene oxide (PEO) mixed binder for the excellent ionic conductivity of PEO [20]. Wang et al. adopted a two-phase organic electrolyte system: the cathode electrolyte (carbonate) and anode electrolyte (ether) were separated by an ion-conducting glass ceramic separator. The polysulfides could be well constrained on the cathode side without shuttling [71].

To achieve the full theoretical capacity of 1167 mAh g⁻¹, a high initial charge potential of 4.0 V Li for the Li₂S cathode is needed. However, the commonly used ether-based electrolyte solutions are unstable at such a high potential [72]. A lower cutoff of 3.6 V Li is usually employed for the stable running of Li-S batteries despite a lower utilization of Li₂S. Additions of redox mediators (decamethylferrocene, LiI, and ferrocene) [15], P₂S₅ [73], and lithium polysulfides [14] for the electrolyte were reported to be effective in enhancing the Li₂S utilization. Redox mediators can be electrooxidized on the electrode surface and diffuse into the interior to oxidize the inactive Li₂S. The Li₂S cathode can thus be completely activated by the above reversible redox reactions at a low initial charge potential. The initial charge shows a flat potential plateau implying the proceeding of the reversible redox reactions [71]. A similar behavior can be seen while adding P₂S₅ into the electrolyte, and intermediate sulfur- and phosphorus-containing species will be formed on the Li₂S surface, which can assist the surface charge transfer [73].
4. Preliminary Exploration of the Li$_2$S Cathode in Full Cells

A lithium metal anode suffers from the safety problems for the excessive formation of lithium dendrites. A lithium sulfide cathode can avoid the use of lithium metal anodes and pair with the lithium metal-free anodes (Si, Sn, graphite, transition-metal oxides, etc. [54–57, 74–79]) to assemble the full cells. Si has a high theoretical capacity of 4212 mAh·g$^{-1}$, which can pair with Li$_2$S (1166 mAh·g$^{-1}$) to form a full cell with high energy density [54, 55]. Yang et al. prepared a Li$_2$S-mesoporous carbon cathode to pair with the silicon nanowire anode. The theoretical specific energy of the Li$_2$S/Si full cell can reach 1550 Wh·kg$^{-1}$, 4 times that of the commercialized LIBs (LiCoO$_2$/graphite and LiFePO$_4$/graphite). The initial discharge specific energy reached 630 Wh·kg$^{-1}$. However, the Li$_2$S-Si full cell showed a rapid capacity fading compared to the Li$_2$S/Li half cell, which is probably related to the loss of the lithium source during cycling arising from the irreversible reaction and deep discharge or overcharge of Li$_2$S or silicon for the uncontrollable single electrode voltage [55].

Graphite is a more commercial choice for the anode of the Li$_2$S full cell for its low cost, mature production process, and stable electrochemical performance (one Li atom can be
accommodated per six C atoms with 9%-13% volume change during graphite lithiation). The Li$_2$S/graphite full cell delivered an initial discharge capacity of 1006 mAh·g$^{-1}$ and a long cell life with 500 cycles [74]. However, the graphite anode is highly electrolyte-selective. On the one hand, the commonly used Li-ion carbonate electrolytes are suitable for the graphite, while the polysulfides are reactive in it. On the other hand, the graphite anode is unstable in the ether electrolytes, which are used in the Li-S batteries during cycling. Wang et al. found that the cycled graphite particles can be partly exfoliated by the DOL/DME solvent molecules, but the exfoliation of graphite was alleviated when adding LiNO$_3$ into the electrolyte [43]. Li et al. used HFE (1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether) diluted solvate ionic liquids (ILs) as the Li$_2$S/graphite full cell electrolyte. The ILs showed high Li$^+$ transportation, stabilized the lithiation/delithiation of graphite, and had a low solubility of polysulfides [56].

Among the transition-metal oxides, MnO$_2$ shows a considerable theoretical capacity of 1232 mAh·g$^{-1}$, which matches well with that of the Li$_2$S cathode. The theoretical specific energy of the Li$_2$S/MnO$_2$ full cell can reach 1020 Wh·kg$^{-1}$. As shown in Figure 10, the Li$_2$S/MnO$_2$ full cell assembled by the Li$_2$S-rGO cathode and rGO-MnO$_2$ anode exhibits long charge/discharge plateaus, a high initial discharge capacity of 587.5 mAh·g$^{-1}$, a capacity retention of 80.5% after 150 cycles, and a high specific energy of 827.3 Wh·kg$^{-1}$ (455.0 Wh·kg$^{-1}$ cathode) [57].

![Figure 10: (a) Initial charge-discharge profiles. (b) Cycling performance of the Li$_2$S/MnO$_2$ full cell [57].](image)

### 5. Conclusions and Outlook

To meet the ever-growing demand for high-density energy storage devices, lithium-ion battery cathodes with high specific capacity are the bottlenecks of present LIBs. Li$_2$S is regarded as one of the most promising cathode materials for next-generation lithium-ion batteries due to its high theoretical capacity of 1166 mAh·g$^{-1}$. However, the commercial applications of the Li$_2$S cathode are limited by its high initial activation barrier, shuttle of lithium polysulfides, and low electronic and ionic conductivity. Much progress has been made in tackling the above challenges. This review gives a systematical summary on the recent progress in the activation and lithium storage mechanism of Li$_2$S, the improvement of lithium storage performance of Li$_2$S in half cells, and the preliminary exploration in full cells. Strategies for improving the electrochemical performance are emphasized. Li$_2$S composites can exhibit better cycling and rate performances by the introduction of conductive materials, construction of the structure, and chemical binding for inhibiting the shuttle of lithium polysulfides. According to the combination mode of Li$_2$S with carbon, Li$_2$S-carbon composites are synthesized by the following 4 methods: (1) physical mixing, (2) dissolution and precipitation, (3) chemical carbon layer coating, and (4) in situ reaction.

Li$_2$S cathode materials have attracted much attention for the high theoretical capacity. Despite the efforts made to improve the electrochemical performance, more electrochemical improvements are needed for the wide commercial applications. The commercial Li$_2$S is too expensive because it is synthesized in the organic solvents. Further works can be devoted to the large-scale synthesis of Li$_2$S-based composites at low temperatures from low-cost and sustainable raw materials. The high-performance and low-cost electrolytes are also needed for developing lithium-ion batteries. Better understanding of the activation mechanism of the Li$_2$S cathode in full cells is required. Among the modified Li$_2$S composites, nanoscale Li$_2$S-carbon composites can effectively reduce the activation barrier and improve the cycling performance. The future development trend of Li$_2$S composites is likely to be the specific structure design and
functional groups introduced to increase the mass loading of active Li$_2$S and effectively inhibit the shuttle of lithium polysulfides. The electrochemical performance of the Li$_2$S cathode coupled with the lithium metal-free anode should be further improved for developing next-generation lithium-ion batteries with both high energy density and safety.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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