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Application of MoS₂ in the cathode of lithium sulfur batteries

 Yanyun Liu,^a Chunjuan Cui,^{ab} Yue Liu,^a Wei Liu^a and Jian Wei^{ac}

Molybdenum disulfide (MoS₂) with a two-dimensional layered structure can effectively inhibit the shuttle effect of lithium–sulfur batteries (Li–S batteries). It contains metal–sulfur bonds and combines with polysulfides through electrostatic bonds or chemical bonds. In this paper, the structure and properties of MoS₂ are briefly introduced, and the research progress on the design, preparation, structure and properties of MoS₂ as a cathode material for Li–S batteries in recent years is reviewed. The effects of MoS₂ structure and its composition with carbon materials or metallic oxides on the performance of the electrode materials are analyzed. Finally, the existing problems and possible future research directions are pointed out.

1. Introduction

With the development of social economy and the continuous increase of the population in the world, the total amount of energy consumed by humans and society is increasing. Traditional energy production and consumption has caused global warming and ecological environmental destruction. At the same

time, according to current energy consumption patterns, global fossil energy will be exhausted in the future. Therefore, energy storage and transformation is the key to coping with the climate crisis and achieving sustainable development of human society.¹

Li–S batteries are rechargeable and generally consist of a sulfur-based cathode, binder, separator, organic liquid electrolyte, lithium anode and current collector. A schematic diagram of a Li–S battery is shown in Fig. 1.²

The working principle of Li–S batteries is shown in Fig. 2.³ During the discharging process, sulfur in the solid phase (S_{8(s)}) is firstly dissolved in the electrolyte and then transforms to S_{8(l)}. Then S_{8(l)} is gradually reduced to high-order lithium

^aSchool of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China. E-mail: cuichunjuan@xauat.edu.cn

^bShaanxi Metallurgical Engineering Technology Research Center, Xi'an, 710055, China

^cSchool of Materials Science and Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China



Liu Yanyun graduated from the School of Materials Science and Engineering, Shaanxi University of Science and Technology in 2015. She is currently a student in the School of Metallurgical Engineering of Xi'an University of Architecture and Technology for her Master's degree. She is mainly focusing on the research of lithium sulfur batteries.



Cui Chunjuan obtained her M.E. degree and PhD degree in Materials Processing Engineering from Northwestern Polytechnical University and is now serving in the School of Metallurgical Engineering, Xi'an University of Architecture and Technology. She is currently a professor and doctoral supervisor. She performed collaborative research in 2013–2014 at the University of Kentucky, USA.

She has published more than 50 journal papers, and more than 30 of them were indexed by SCI and EI. She has also published an academic monograph on metal solidification theory and application technology. Her team's research interests are theory and technology of directionally solidified metal matrix composites, and lithium sulfur batteries.



polysulfides (Li_2S_n , $4 \leq n \leq 8$), which are easily soluble in the electrolyte and diffuse from the cathode to the electrolyte. As discharge continues, the high order lithium polysulfides are further reduced to low order lithium polysulfides (Li_2S_2 and Li_2S) which are less soluble in the electrolyte. During the charging process, the discharge products (Li_2S_2 and Li_2S) are gradually oxidized to high order lithium polysulfides and eventually oxidized to elemental sulfur.

Metallic lithium has very high electro-negativity while possessing the lowest density among all metals, leading to its highest specific capacity (3861 mA h g^{-1}).⁴ Element sulfur has a theoretical specific capacity of 1675 mA h g^{-1} .⁵ Thus, Li-S batteries can reach high theoretical gravimetric and volumetric energy densities of 2500 W h kg^{-1} and 2800 W h L^{-1} , respectively. Given a complete reaction to Li_2S , the energy densities are 3–5 times as high as those of commercial lithium-ion batteries.^{6,7} Moreover, sulfur also has the advantages of low cost, non-toxicity and high storage capacity as compared with that of conventional lithium-ion batteries.⁸ Furthermore, Li-S batteries have more possibility of commercialization than

lithium-air batteries. Therefore, Li-S batteries have good application prospects in energy storage to reduce the use of fossil fuels and protect the environment.

2. Research situation of Li-S batteries

The development of Li-S batteries was initiated in 1962. Herbert⁹ was the first person to have the idea to use sulfur as the cathode in Li-S batteries. General Motors also proposed to use sulfur as an active material for thermal batteries and put the batteries into early electric vehicle projects.¹⁰ In 1976, Whittingham *et al.*¹¹ successfully researched Li-TiS₂ secondary batteries using layered TiS₂ as the cathode and metal lithium as the anode. However, it failed to be commercialized due to safety problems such as “lithium dendrites”. In 2009, Nazar¹² with his team in Canada stimulated attention toward Li-S batteries when they successfully compounded high performance cathode materials of Li-S batteries with ordered mesoporous carbon CMK-3 and sulfur. At present, the representative manufacturers of Li-S batteries in the world are Sion Power, Poly plus and Moltech in the US, Oxis in the UK and Samsung in Korea, among which the US is expected to reach 500 W h kg^{-1} as the energy density of Li-S batteries in the coming years.

Although Li-S batteries have many advantages, there are many factors that have gravely hindered their commercialization, for example, the insulating nature of sulfur and the lower electronic and ionic conductivity of the discharging products result in poor electrode reaction kinetics,¹³ and polysulfides formed in the cathode can be easily dissolved in the electrolyte and aggregate into the anode through the diaphragm during the charging and discharging processes. The redundant reaction is called the “shuttle effect” of polysulfides and results in capacity loss and cycling decay.^{14–16} The volume expansion of sulfur during charging and discharging can be up to 80%. This causes



Liu Yue graduated from the School of Metallurgical Engineering, Xi'an University of Architecture and Technology in 2019, majoring in metal material engineering. He is currently a student in the School of Metallurgical Engineering of Xi'an University of Architecture and Technology for his Master's degree. His main direction is lithium sulfur battery research.



Liu Wei graduated from the School of Material Engineering of Xi'an Aeronautical University in 2018. She is currently a graduate student in the School of Metallurgical Engineering, Xi'an University of Architecture and Technology. Now, she is mainly focusing on the research of high temperature oxidation and corrosion of the directionally solidified Ni-Si eutectic composites.



Wei Jian obtained his M.E. degree and PhD degree in Materials Processing Engineering from Northwestern Polytechnical University and is now serving in the School of Metallurgical Engineering, Xi'an University of Architecture and Technology. He is currently a professor and doctoral supervisor. As a professor in the School of Materials and Mineral Resources of Xi'an University of

Architecture and Technology, he is mainly engaged in the research of one-dimensional nanomaterials, lithium-ion batteries and fiber composite materials. He has published two university planning textbooks and more than 50 academic papers. He is also the Director of the Youth Working Committee of the China Society of Materials Research.



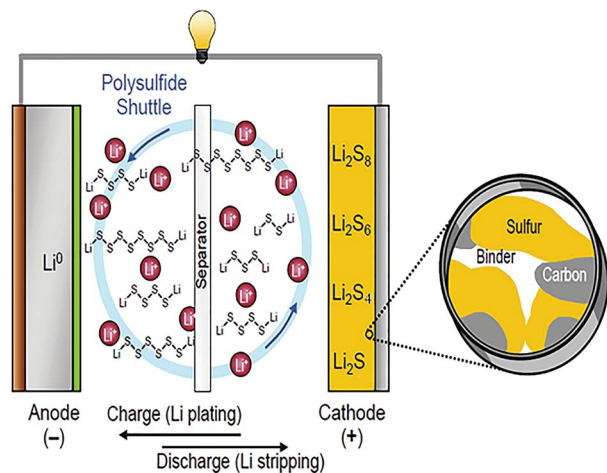


Fig. 1 Schematic diagram of a Li-S battery.²

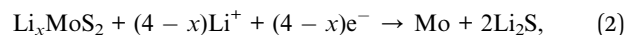
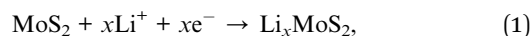
the powdering and collapse of the electrode material and worsens the electrical contact between the electrode material and the collector. The decline of the lithium storage capacity will be accelerated to some extent as a result.¹⁷

There are two main research points in order to promote the commercialization of Li-S batteries. The first one is improving the conductivity of the cathode through compounding with high conductivity materials during the preparation of the initial electrode materials. The second one is adding materials that have high adsorption for polysulfides to inhibit the dissolution of polysulfides. Carbon materials have been paid more attention in recent years due to their excellent electrical conductivity, non-toxicity, and effective inhibition of the shuttle effect. However, the physically weak bonding between carbon and polysulfides is not strong enough to completely inhibit the shuttle effect. Instead, the application of transition metal sulfides can effectively solve this problem. The metal-sulfur bonds can combine with polysulfides through electrostatic or chemical bonds,¹⁸ which can effectively inhibit the dissolution of polysulfides. The emergence of metal sulfides, such as MoS₂, has attracted researchers' attention.

3. Research situation of MoS₂ as a cathode material of Li-S batteries

MoS₂ is a kind of typical graphene-like two-dimensional layered transition metal sulfide. It has a high theoretical storage capacity of 670 mA h g⁻¹ when it reacts with Li⁺ according to the conversion reaction (MoS₂ + 4Li⁺ + 4e⁻ → Mo + 2Li₂S), which is much higher than that of graphene (372 mA h g⁻¹).¹⁹ Each layer is composed of S-Mo-S by covalent bonding in a hexagonal sandwich-like structure. In other words, each layer of Mo is sandwiched between two layers of S atoms, and the layers are connected by weak van der Waals forces.²⁰ A schematic diagram of the structural unit is shown in Fig. 3.²¹

This special structure makes the interaction forces inside the layer strong, while the interaction between layers is relatively weak, and this makes it easy for external substances to be embedded.²² At the same time, double-layer MoS₂ also has good storage capacity of charge, and the Mo atoms have an oxidation state from 2 valence to 6 valence. High theoretical lithium storage capacity is produced by these characteristics.²³ When used as the cathode material of Li-S batteries, the electrochemical reactions between MoS₂ and Li⁺ are shown as follows:²⁴⁻²⁶



The strong adsorption of MoS₂ can prevent polysulfide groups from dissolving in Li-S batteries. Thus, it can ensure lower volume expansion and better cycling stability over several thousands of charge/discharge cycles. Fig. 4 illustrates the polysulfide immobilization and conversion processes on the surface of nitrogen-doped carbon@MoS₂ (NC@MoS₂). It is found that MoS₂ can accelerate the redox reaction kinetics through strong adsorption of polysulfides, fast electron transfer and catalysis for fast redox.

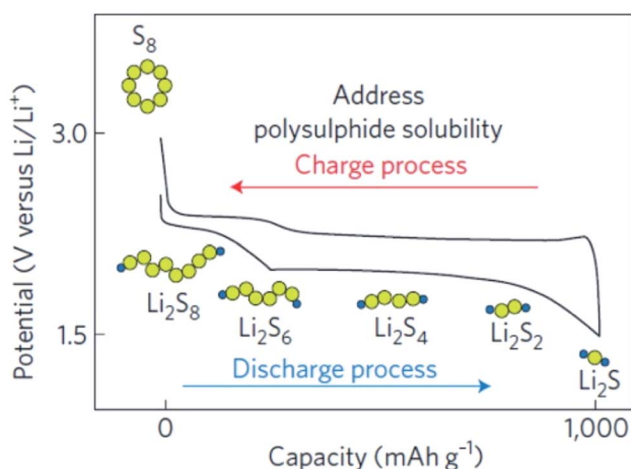


Fig. 2 Voltage profiles of a Li-S battery.³

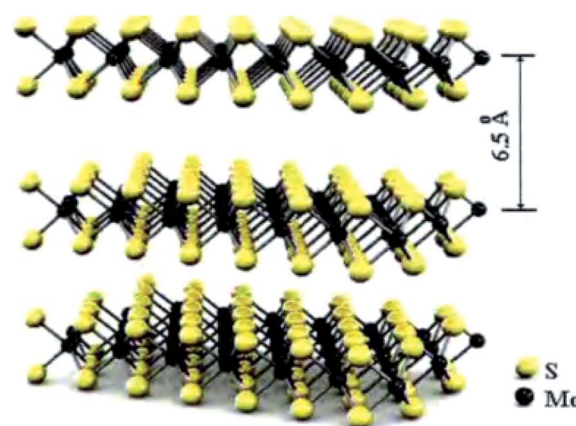


Fig. 3 Structural unit diagram of MoS₂.²¹



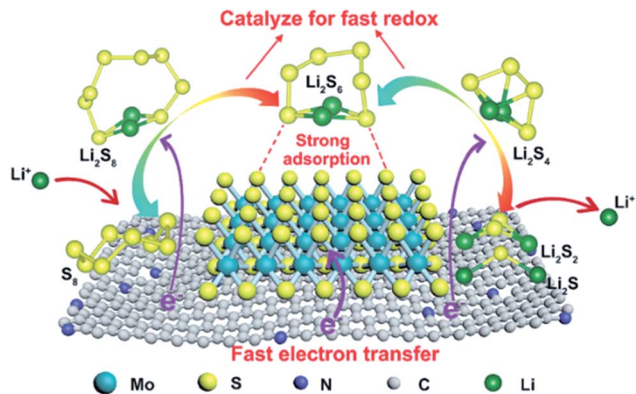


Fig. 4 Polysulfide immobilization and conversion processes on the surface of NC@MoS₂.²⁷

Wu²⁷ proposed density functional theory (DFT) calculations to explore the catalytic effect of NC@MoS₂ on polysulfide demobilization and conversion. Soluble long-chain polysulfide Li₂S₆ was chosen as the prototype for calculations. Fig. 5(a–c) display the optimized geometries of Li₂S₆ adsorption on carbon matrix, NC, and MoS₂ (001) surfaces. The adsorption energies for NC and MoS₂ are -0.66 and -0.57 eV respectively, which are larger than that of a pure carbon matrix. This indicates

a stronger polysulfide adsorptivity. Therefore, MoS₂ possesses superior anchoring ability for polysulfides.

Then, symmetric cells with a Li₂S₆ catholyte were assembled to study the transition kinetics of polysulfide conversion. As shown in Fig. 5(d), CP-NC@MoS₂ electrodes exhibit a decreased charge-transfer resistance, implying enhanced reaction kinetics of polysulfide conversion. Fig. 5(e) shows the CV curves of Li₂S₆ symmetric cells recorded at 50 mV s⁻¹ within a voltage window of -1.0 V to 1.0 V. The CP-NC@MoS₂ electrode shows significantly increased redox currents, further confirming faster redox kinetics in the soluble region.

Remarkably, the effective polysulfide adsorption ability and high electronic conductivity of MoS₂ enable fast redox of Li–S batteries. Therefore, MoS₂ plays a dominant role in the redox reaction kinetics of polysulfide conversion.

Fig. 6 shows the energy profile of polysulfide conversion on a MoS₂ (001) surface.²⁸ It was confirmed that MoS₂ participates in the polysulfide conversion and accelerates the kinetics of the polysulfide redox reactions in Li–S batteries. The polysulfide conversion on the MoS₂ (001) surface undergoes a “lithiation–cleavage–lithiation–cleavage–lithiation–cleavage” mechanism from the reactant S₈@MoS₂ to the product Li₂S@MoS₂. The polysulfides need to coordinate with the MoS₂ surface to accelerate electron transfer, and the system energy decreases significantly after reduction. The fast conversion of the soluble

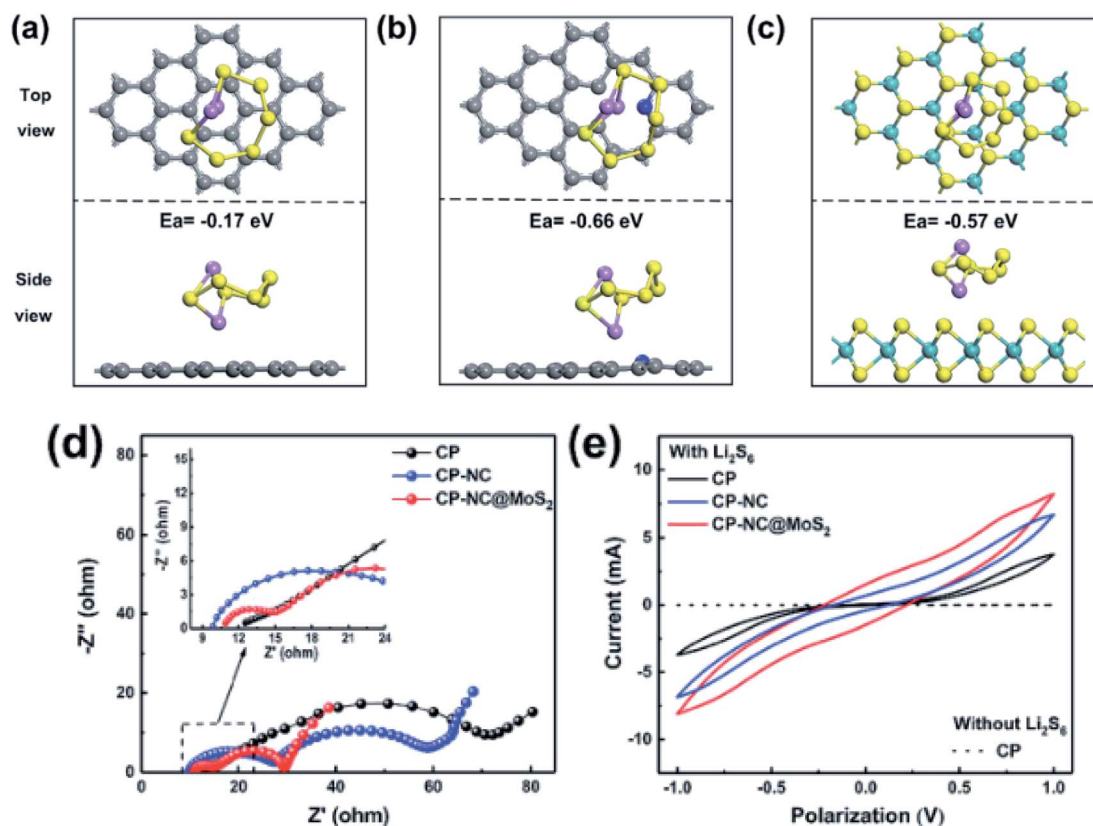


Fig. 5 Optimized geometries of Li₂S₆ on (a) carbon matrix, (b) NC, and (c) MoS₂ (001) surfaces, in which grey, yellow, blue, purple, and green spheres represent C, N, S, Li, and Mo, respectively; Nyquist plots (d) and CV (e) curves of Li₂S₆ symmetric cells employing CP, CP-NC, and CP-NC@MoS₂ as working electrodes.²⁷



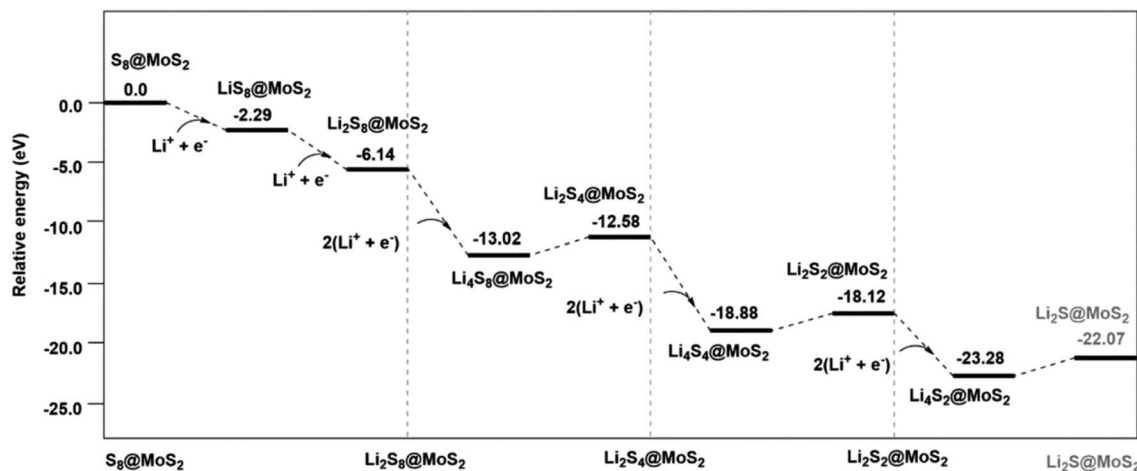


Fig. 6 Energy profile of the polysulfide conversion mechanism on the MoS₂ (001) surface.²⁸

polysulfides decreases their accumulation in the sulfur cathode and inhibits their subsequent loss from the cathode. The suppression of this loss mechanism leads to a more sustained cyclability.^{29,30}

3.1 Effect of MoS₂ structure on electrical properties

A change in the MoS₂ structure has a great influence on the capacity and cycling stability of electrode materials.³¹ Therefore, optimizing the structure of MoS₂ nanomaterials can effectively improve the electrochemical performance of Li-S batteries. There are three main types: one-dimensional MoS₂ like nanotubes, two-dimensional MoS₂ like nanosheets, and three-dimensional MoS₂ like nanoparticles, nanoflowers and other special nano-structured cathode materials.

3.1.1 One-dimensional MoS₂ nanomaterials. Qiu³² synthesized tubular MoS₂/S composites with a template method. The tubular structure has double the surface area and is favorable for the fixation and infiltration of sulfur into the MoS₂ nanotubes as shown in Fig. 7. The initial capacity of the tubular MoS₂/S composites can reach 650 mA h g⁻¹ at 100 mA g⁻¹. However, the reversible specific capacity decreases to

450 mA h g⁻¹ after 50 cycles. The electrochemical properties are not good. MoS₂ and sulfur can be compounded to some extent, but sulfur cannot well penetrate into the tube to form a MoS₂/S composite, and only mixing of the two phases can occur.

However, Qiu did not point out the mechanism of inhibiting the shuttle effect of MoS₂ nanotubes in Li-S batteries. There are few reports on the application of one-dimensional MoS₂ nanomaterials in Li-S batteries at present, and further study in this area is required. If MoS₂ nanotubes with a mesoporous structure can be synthesized, the loading rate of sulfur and the cyclic properties of the electrode materials will be greatly improved. This structure contributes to the inflow of sulfur through the micropores of the MoS₂ nanotubes at 155 °C (at 155 °C, the S₈ is mainly short linear sulfur chains, and the viscosity of molten sulfur is the lowest³³). On the one hand, MoS₂ nanotubes have double the surface area, so the loading of sulfur is increased, and more reactive sites are provided for the electrochemical reaction. On the other hand, in the process of electrochemical reaction, molybdenum polysulfides can be controlled or adsorbed inside the MoS₂ nanotubes, which can inhibit the shuttle effect of Li-S batteries.

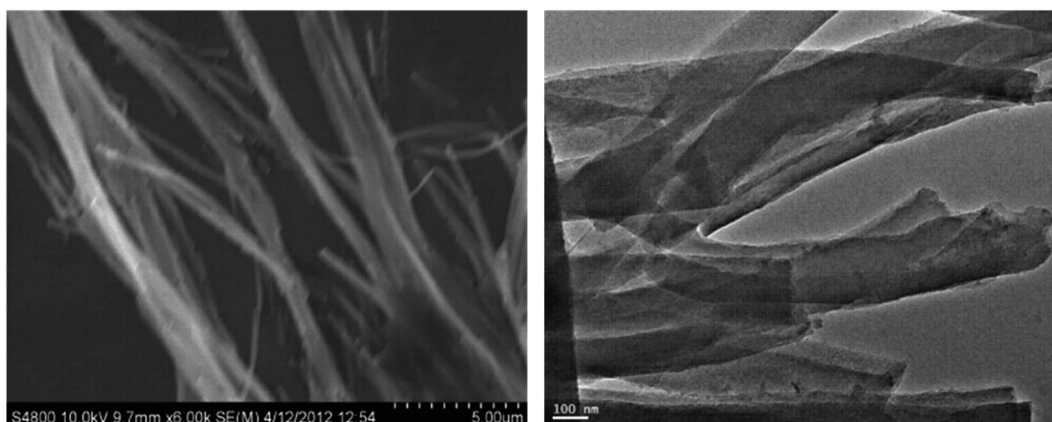


Fig. 7 TEM image of MoS₂ tubes.³²



3.1.2 Two-dimensional MoS₂ nanomaterials. Two-dimensional nanomaterials have been extensively studied due to their special structures and excellent physical properties, such as high specific surface area. Two-dimensional structures can form networks through overlapping and stacking. They also have a large surface area which can provide more reactive sites and an open pore structure. These properties are very helpful for enabling effective anchoring of polysulfides and enhancing the reaction kinetics.³⁴

Zhao³⁵ proposed a MoS₂/mesoporous carbon hollow sphere (MCHS) structure as an efficient sulfur cathode in order to deal with the shuttle effect, avoid active material loss and prevent performance decay of Li-S batteries. Ultrathin multi-layer MoS₂ nanosheets are uniformly distributed in the mesoporous carbon hollow spheres, enhancing the physical adsorption and chemical entrapment functionalities towards the soluble polysulfides. Polar MoS₂ can trap polysulfides *via* strong chemical bonds, so the polysulfides are largely fixed and remain inside the conductive MCHS as shown in Fig. 8. Benefiting from these structural advantages, the sulfur-impregnated MoS₂/MCHS cathode presents remarkable electrochemical performance.

Zhao³⁶ studied MoS₂ nanosheets by liquid phase exfoliation. As shown in Fig. 9, the layered MoS₂ nanosheets can achieve a good coordination with graphene and control polysulfides on graphene. Yu³⁷ deposited an ultrathin layer of MoS₂ (10–40 nm) nanoflakes by a liquid-based self-assembly method in the cathode of Li-S batteries. The results show that the reversible specific capacity reaches 1010 mA h g⁻¹ at 0.5C, and the capacity fading is 0.11% per cycle over 400 cycles. The MoS₂ interlayer inhibits polysulfide diffusion across the separator and remarkably improves the battery performance. Moreover, the MoS₂ films with a high density of catalytic active edges can achieve high areal sulfur loading.

There are still many researchers studying the application of two-dimensional MoS₂ in Li-S batteries.^{38–41} Many properties of two-dimensional MoS₂ are highly sought after for application in batteries. Two-dimensional MoS₂ has a large surface area, while maintaining a low size, especially thin-layer MoS₂, which can provide more active sites, and the electrode materials and

electrolyte can fully contact each other. This is helpful to realize fast electrochemical reaction kinetics. In addition, the thin layer of MoS₂ can achieve a good match with graphene, improving the capacity of the electrode materials.⁴² At the same time, it can effectively inhibit the shuttling of polysulfides. At present, the preparation methods of thin layer MoS₂ mainly include the stripping method,⁴³ high temperature solid phase method,^{44,45} template method⁴⁶ and hydrothermal method.⁴⁷ The MoS₂ layers are connected with each other by weak van der Waals forces, and delamination can be realized in theory. However, the prepared MoS₂ in most actual exploration processes is a small amount of thin layer only in the liquid state. Therefore, it is difficult to realize a large number of thin layer products of MoS₂, which has become the main difficulty in their exploration.

3.1.3 Three-dimensional MoS₂ nanomaterials. For three-dimensional nanomaterials, electrons can move freely in all three dimensions. Different morphologies, such as nanoparticles and nanoclusters, have diverse properties.

At present, the design of nano-core-shell structures has become a research hotspot. This is because the core structure can provide supportive materials for the synthesis of MoS₂ shell structures, which can fix polysulfides inside the shell, effectively inhibiting the dissolution of polysulfides, and improving the material's reversible cycling performance. Cheng⁴⁸ synthesized a core-shell structured MoS₂@S cathode material through a chemical route using MnCO₃ as a template, as shown in Fig. 10. A picture of the core-shell structured MoS₂@S is shown in Fig. 11. The initial discharge capacity of the material is 800.6 mA h g⁻¹ at 1C rate, and the capacity retention rate is 79% after 200 cycles. For comparison, a MoS₂/S cathode was also synthesized. It is found that the electrochemical performance of the core-shell structures MoS₂@S cathode is much improved as compared with the MoS₂/S composite. The high capacity and cycling stability of MoS₂@S cathode materials are attributed to the mechanical inhibition and chemical combination of the polar MoS₂ shell with lithium polysulfides, which further illustrates that the core-shell structure of MoS₂@S can effectively inhibit the shuttling of polysulfides.

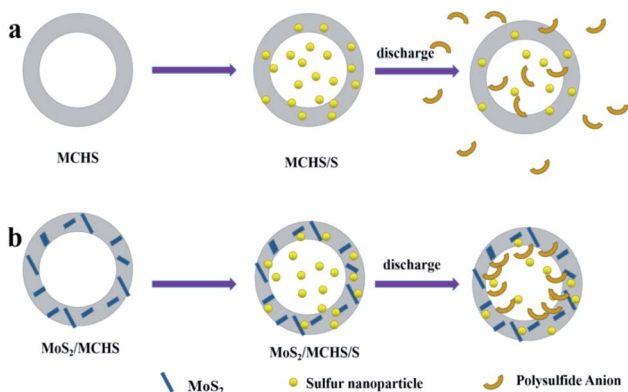


Fig. 8 Proposed adsorption mechanism of polysulfides for the (a) MCHS/S and (b) MoS₂/MCHS/S electrodes.³⁵

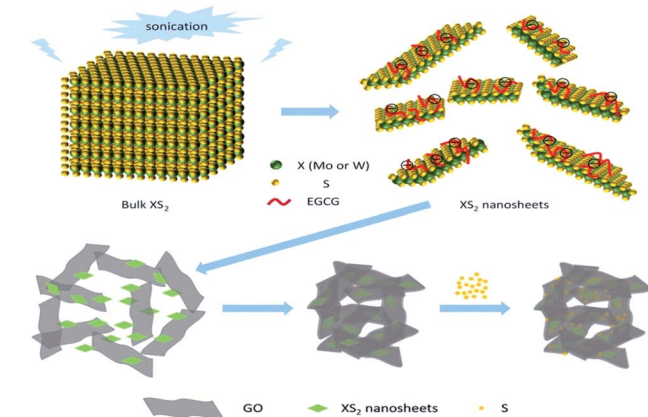


Fig. 9 Proposed adsorption mechanism of polysulfides for XS₂ (Mo or W).³⁶



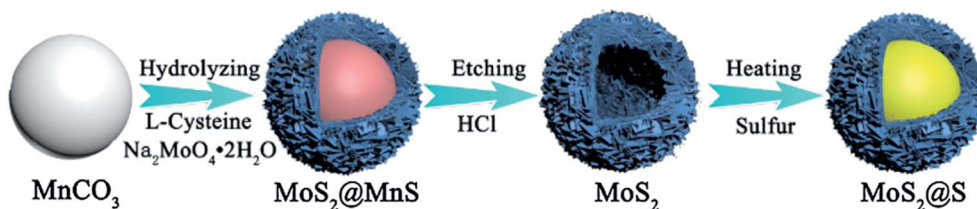


Fig. 10 Schematic of the synthesis route of the core-shell structured $\text{MoS}_2\text{@S}$ spherical cathode.⁴⁸

Other researchers have also^{49–53} devoted their attention to the application of core-shell structured MoS_2 nanocomposites. The double-layer core-shell structure has good prospects. This special structure can effectively alleviate the shuttle effect of batteries. On the other hand, it can improve the sulfur loading rate and buffer the volume expansion of sulfur during the charging and discharging processes. However, the sulfur load is hard to improve, because the infiltration of sulfur is often not sufficient and uniform. And in the process of experiments, superior formation conditions of the core-shell structure need to be explored when the repeatability is not high.

Flower-like nanomaterials have a large surface area because of their unique and complex morphology. Therefore, the application of flower-like nanomaterials in the cathode of Li-S batteries can effectively improve the loading rate of sulfur and the capacity of the batteries. Tang⁵⁴ synthesized MoS_2 nano-flowers consisting of many irregular MoS_2 nanosheets with an average diameter of about 1–2 μm by a facile CTAB-assisted hydrothermal method at 180 $^\circ\text{C}$ for 24 h. Zhang⁵⁵ successfully synthesized high-purity MoS_2 nanoflowers by a hydrothermal method. The particle diameter is around 300 nm, consisting of tens of hundreds of MoS_2 petals, and the thickness of each layered petal is about 10 nm. Through gradient experiments, it

was found that silicotungstic acid played an important role in the formation of the nano-flower MoS_2 . Xiong⁵⁶ fabricated hierarchical porous MoS_2/C flower-like microspheres as shown in Fig. 12. The initial discharge capacity of the porous MoS_2/C flower-like microsphere electrode was 1125.9 mA h g^{-1} . The discharge capacity remained at 916.6 mA h g^{-1} after 400 cycles at 200 mA g^{-1} . This is attributed to the unique porous composite structure of MoS_2/C effectively improving the contact area between the active substances and electrolytes. This also provides more channels for the rapid transmission of electrons and ions during charging and discharging, contributing to a fast kinetic reaction and effectively improving the electrochemical performance of the batteries.

Flower-like nanomaterials have been studied a lot among all kinds of battery materials, because the flower structure has a large specific surface area, which can effectively improve the loading of active materials. Compared with the core-shell structure, the synthesis process is relatively mature, and has been widely studied.^{57,58}

Therefore, different structures of MoS_2 have great impacts on the electrochemical properties of materials. In the current research, three-dimensional MoS_2 is widely researched as the cathode material of Li-S batteries, while the research of two-dimensional MoS_2 is mostly conducted in the diaphragm. Few research studies have paid attention to the application of one-

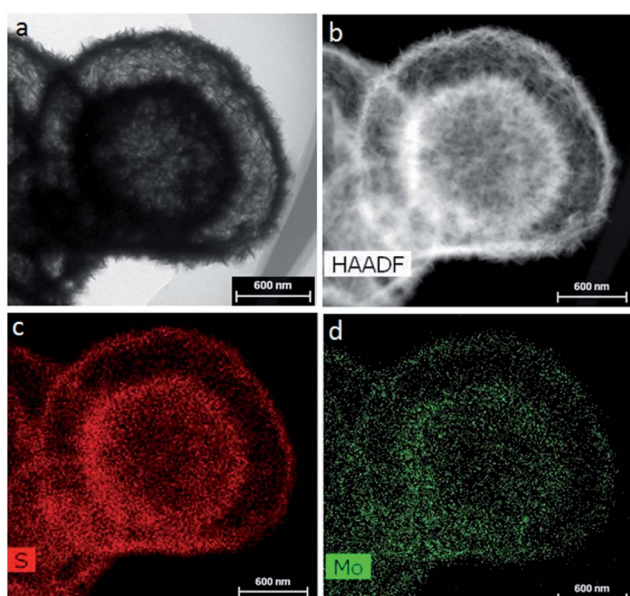


Fig. 11 (a) TEM image, (b) HAADF image, and (c) S and (d) Mo element mapping of the MoS_2 shells.⁴⁸

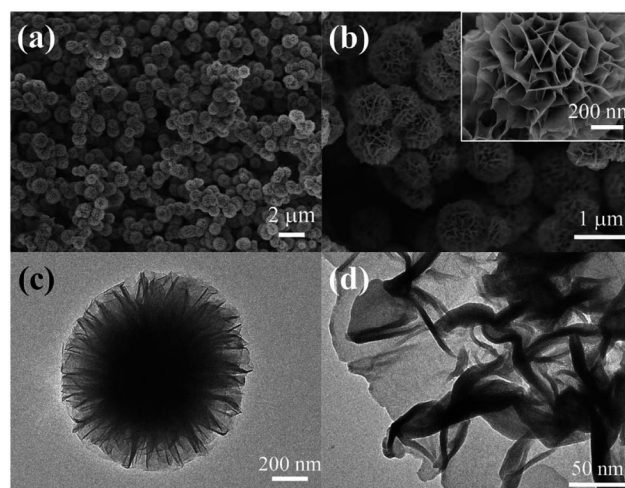


Fig. 12 Morphological and structural characterization of the MoS_2/C flower-like microspheres: (a and b) FESEM images with low and high magnification, respectively; (c and d) TEM images with low and high magnification, respectively.⁵⁶



dimensional MoS₂ in Li-S batteries, which is worth exploring. Nano-mesoporous materials have the advantages of high specific surface area, well-ordered channels, high porosity and good thermal stability. As a battery material, they can retain high porosity and uniform aperture distribution on adjusting the size of the material. So the design of mesoporous MoS₂ nanomaterials can improve the reversibility, rate performance of discharge and cycling life of electrode materials.^{59–62}

3.2 Preparation and properties of MoS₂/carbon composite cathode materials

In spite of many advantages, MoS₂ has another serious disadvantage: poor conductivity which cannot guarantee rapid electron transfer in the process of electrode reaction. Therefore, simple structure design of MoS₂ is not enough for high-rate performance. At present, conductive nanoporous MoS₂ cathode materials with excellent electrochemical properties have been put forward, such as MoS₂/carbon nanocomposites.^{63,64} Carbon materials that have an interconnected conductive network structure can effectively improve the conductivity and dynamic performance of electrodes.⁶⁵ It has been found that the strong chemical and electronic coupling between MoS₂ nanoparticles and graphene nanosheets could allow rapid electron transportation through the conductive graphene substrate.^{66,67}

At present, the synthesis methods of MoS₂/carbon composites in Li-S batteries are mainly based on chemical methods. They include vapor phase synthesis, like chemical vapor deposition, and liquid phase methods, such as hydrothermal methods, solvothermal methods, template methods, thermal decomposition and precipitation methods, *etc.*

3.2.1 Chemical vapor deposition. Chemical vapor deposition (CVD) is a direct synthesis method to obtain a uniform MoS₂ coating on targeted carbon substrates. Namjo *et al.*⁶⁸ obtained a uniform MoS₂ coating on the surface of porous carbon structures with nano-sized pores by chemical vapor deposition. Mugyeom *et al.*⁶⁹ synthesized MoS₂-SRGO composites by one-pot deposition of MoO₃ on SRGO and simultaneous reduction of GO to SRGO in supercritical methanol followed by sulfuration. The obtained MoS₂-SRGO composites contain an 11–14 layer crystalline MoS₂ phase.

However, the deposition temperature of CVD is relatively high, generally at 900–1200 °C, which is not conducive to the preparation of inorganic materials. In recent years, with the improvement of industrial production requirements, the process and equipment of CVD have been continuously improved. Not only are a variety of new heating sources used, but also auxiliary methods such as plasma, laser and electron beam are used to reduce the reaction temperature, making its application scope wider.^{70,71}

3.2.2 Hydrothermal methods. Hydrothermal methods are a common method for material preparation. Ren⁷² prepared multi-dimensional N-doped porous carbon/MoS₂/CNT nanostructures by a facile hydrothermal process. The synergistic action of polar MoS₂ and porous carbon imbedded with electroconductive acid-CNTs could construct a conductive network for

the rapid transfer of ions/electrons. As the cathode of Li-S batteries, N-doped porous carbon/MoS₂/CNT nanostructures deliver a high discharge capacity of 1313.4 mA h g⁻¹ at 0.1C and good cycling stability with an average capacity fade of 0.059% per cycle after 500 cycles at 1.0C. This can significantly strengthen the chemical attraction with polysulfides. Chen⁷³ prepared graphene-like-MoS₂/graphene (GL-MoS₂/G) composites by a hydrothermal method assisted with cetylammmonium bromide cationic surfactant and subsequent heat treatment. You⁷⁴ prepared a three-dimensional porous MoS₂/rGO foam based sulfur cathode by a facile hydrothermal method. Few-layer MoS₂ nanosheets with mixed 1T and 2H phases were developed on reduced graphene oxide, forming a continuous 3D porous network.

Solvothermal reactions are a development of hydrothermal reactions, where the reaction occurs in an organic solvent or non-aqueous solvent (such as organic amine, alcohol, ammonia, carbon tetrachloride or benzene, *etc.*).

Huo⁷⁵ prepared S/N co-doped reduced graphene oxide modified with MoS₂ by a one-pot solvothermal method with L-cysteine mixed in ethylene glycol. The specific surface area of this compound gel was estimated to be 151.41 m² g⁻¹. Its large specific surface area can promote the contact between the electrode and electrolyte, and the porous structure provides transport channels for electrons and ions. Electrochemical tests revealed that the capacity retention of the electrode was 91.32% after 500 cycles. The size and morphology of the phase particles can also be controlled by a solvothermal method, and the product also has good dispersion.

Hydrothermal methods can directly obtain powders with high purity, good dispersity and good crystal shape, with no need for burning treatment at high temperature, and the preparation process is relatively simple and the production cost is relatively low.⁷⁶ However, solvothermal reactions are not as safe as hydrothermal reactions according to practical experience. So it would be better to avoid reactions that produce large quantities of gases and heat in solvothermal reactions.

3.2.3 Template methods. Template methods are a very important technique to synthesize nanocomposites. Jiang⁷⁷ synthesized nitrogen-doped hollow mesoporous carbon spheres (NMCS) using SiO₂ as a template. Wang⁷⁸ synthesized TiO₂ nanotubes using MnO₂ nanowires as templates and coated them with nitrogen-doped carbon (NC). Ultra-thin MoS₂ nanosheets were grown on them by a hydrothermal method to obtain layered nanostructures of TiO₂@NC@MoS₂. Yin⁵⁰ firstly prepared MoS₂ and carbon on the surface of SiO₂ nanoparticles as a sacrificial template by a sol-gel method with CTAB. Then, MoS₂/carbon hollow microspheres wrapped with petaloid MoS₂ lamellae and amorphous carbon were prepared by alkali liquor etching of the silica microsphere matrix. The average diameter of the MoS₂/C hollow microspheres was approximately 200–300 nm. As the cathode material of a lithium battery, the first charge-discharge capacity was more than 1400 mA h g⁻¹ at a current density of 100 mA g⁻¹. This technique has the following advantages: simple experimental device, high flexibility, accurate control (size, morphology and structure), and



effective prevention of agglomeration. Therefore, it has attracted wide attention.⁷⁹

3.2.4 Thermal decomposition methods. Li⁸⁰ successfully studied MoS₂-decorated coaxial nanocable carbon aerogel composites (MoS₂/CNCA) by phenolic reaction and treatment at high temperature in a sulfur atmosphere. The MoS₂-decorated carbon aerogel (CA) with carbon nanotubes as fine wires presented a narrow distribution of pore size, an interconnected structure and high conductance. The discharge capacity was 1314 mA h g⁻¹ at 0.2C with the capacity retention of 81% after 200 cycles. These improved results can be attributed to MoS₂ as a network entangled structure. However, the reaction is usually endothermic as heat is required to break chemical bonds in the compound. If decomposition is sufficiently exothermic, it can easily lead to thermal runaway and possibly an explosion.

In summary, hydrothermal methods and template methods are widely applied at present in the synthesis of Li-S battery cathode materials. Hydrothermal methods can synthesize nanomaterials in different dimensions in one step, such as nanotube structures, two-dimensional nanosheet structures, three-dimensional nanoflower-like structures, and hierarchical porous structures. The template method is more conducive to synthesizing core-shell structures, and it provides a good idea for solving the shuttle effect of Li-S batteries. In addition to the above methods, physical methods such as stripping and vacuum condensation, and chemical methods such as precipitation are also commonly used to prepare nanomaterials. However, these methods are less used to prepare MoS₂ cathode composites for Li-S batteries.

3.3 Preparation and properties of MoS₂/metal oxide composite cathode materials

Metal oxides, which have chemical bonds or electrostatic adsorption with polysulfides, can effectively inhibit the shuttling of polysulfides and improve the charge-discharge performance of materials as cathode materials of Li-S batteries. Zhang⁸¹ synthesized MoS₂/SnO₂ nanocomposites by a two-step hydrothermal method, and SnO₂ was uniformly loaded on the surface of the MoS₂ nanosheets. After loading SnO₂ nanoparticles, the diffusion of lithium polysulfides was greatly inhibited, and the conductivity of the material was also improved by embedding Mo atoms. Xu⁸² first prepared TiO₂@PNT coaxial nano-materials by a sol-gel method. Porous TiO₂ nanotubes were obtained by roasting the PNT template in air. Furthermore, MoS₂ nanosheet@TiO₂ nanotube structures were successfully prepared by a solvothermal method. Porous TiO₂ nanotubes as supporting materials slow down the agglomeration of MoS₂ and make it distribute more uniformly. This intelligent design has remarkable lithium storage performance.

The use of metal oxides in cathode materials of Li-S batteries is of great significance. However, excessive introduction of metal oxides will affect the overall energy density of the batteries because of the high density of metal oxide. Moreover, their conductivity cannot meet the needs of cathode materials. Therefore, there are few studies on the application of MoS₂ and

metal oxides in Li-S battery cathode materials, and most of the current studies are on lithium-ion battery electrode materials.

4. Conclusions

As the cathode material of Li-S batteries, MoS₂ can accelerate the redox reaction kinetics during the discharge/charge process through strong adsorption of polysulfides, fast electron transfer and catalysis for fast redox. It has great potential advantages for Li-S batteries.

(1) Strong adsorption of polysulfide lithium: as the cathode material of Li-S batteries, MoS₂ has a great advantage in reducing the "shuttle effect" that has gravely hindered their commercialization. MoS₂ has strong adsorption for sulfur-containing groups, thus preventing polysulfides from dissolving. Thus, it can ensure better cycling stability over several thousands of charge/discharge cycles.

(2) Graphene-like two-dimensional layered structure: MoS₂ is a kind of typical graphene-like two-dimensional layered transition metal sulfide. Each layer of Mo is sandwiched between two layers of S atoms, and the layers are connected by weak van der Waals forces. This special structure makes the interaction forces inside the layer strong, while the interactions between layers are relatively weak, and this makes it easy for external substances to be embedded, especially those having a good match with graphene.

(3) Good storage capacity: MoS₂ has a high theoretical storage capacity of 670 mA h g⁻¹ when it reacts with Li⁺, which is much higher than that of graphene (372 mA h g⁻¹). The Mo atom has an oxidation state from 2 valence to 6 valence. These characteristics determine its high theoretical lithium storage capacity. It can effectively solve the insulating nature and lower electronic and ionic conductivity of sulfur.

Many methods have been developed for the synthesis of MoS₂ nanocompounds, and hydrothermal methods and template methods are widely applied at present. Hydrothermal methods can synthesize nanomaterials in different dimensions in one step, such as nanotube structures, two-dimensional nanosheet structures, three-dimensional nanoflower-like structures, and hierarchical porous structures. Template methods are more conducive to synthesizing core-shell structures, and provide a good idea for solving the shuttle effect of Li-S batteries. The progress of these methods has made great contributions to the development of Li-S batteries.

Conflicts of interest

There are no conflicts to declare.

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