A Review on the Status and Challenges of Electrocatalysts in Lithium-Sulfur Batteries

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Abstract

Lithium-sulfur (Li-S) batteries, which have a high theoretical specific capacity (1,675 mA h g^{-1} of S) and a high energy density (2,600 Wh kg^{-1} of S), have received a great deal of attention in recent years. Intense research efforts have been made to solve the outstanding issues in Li-S batteries. Various catalysts with high activity for stabilizing the lithium-polysulfide shuttle process and thus improving the electrochemical performance of Li-S batteries are reviewed here. Challenges and prospects for designing highly efficient catalysts for Li-S batteries are discussed.

Keywords: Lithium sulfur batteries; catalytic effect; host materials; lithium polysulfides; shuttle effect

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1. Introduction

The spread of electric vehicles and portable electronic devices is spurring the demand for energy-storage devices with long-cycle life and high-energy density [1-6]. Lithium-sulfur (Li-S) batteries have been considered as a promising candidate for conventional energy-storage devices, due to their advantages, such as high theoretical specific capacity (1,675 mAh g^{-1} of S) [7-10], high theoretical energy density (~ 2,600 Wh kg^{-1} of S) [11-14], environmental friendliness, and low cost [15]. However, the practical application of Li-S batteries is still challenged by several drawbacks [16-19]. These include the large volume expansion of sulfur, poor electronic and ionic conductivity of lithium sulfide (Li_2S) and sulfur, and sluggish kinetics of lithium polysulfide (LiPS) redox during their conversion reaction [20-25]. In addition, the dissolution and migration of the intermediate LiPSs result in a loss of the active material and shuttling of LiPSs between the anode and cathode, which has been regarded as one of the crucial issues hindering the practical application of Li-S batteries [26-29].

In order to improve the conductivity of the sulfur cathode, many conductive hosts have been developed, such as porous carbon [30], carbon nanotubes [31], graphene [32], and conductive polymers [33]. However, due to the weak interaction between nonpolar carbon-based materials and highly-polar LiPS species, the carbon-based materials can only provide a weak confinement towards LiPSs, which further diffuse into the electrolyte, and thus result in capacity decay and poor rate capability [34]. In this regard, it is important to improve the interaction between the LiPSs and the cathode-host. Recently, research on heteroatom-doped carbon-based materials, such as nitrogen-

mesoporous carbon [35], sulfur-graphene [36], and nitrogen-functionalized carbon nanotubes [37] have shown great potential in immobilizing LiPSs, owing to the strong anchoring sites provided by the heteroatom doping. In addition, the introduction of polar materials into carbon-based materials, such as metal oxide [38], metal sulfides [39], metal carbides [40], metal nitrides [41], and metal organic frameworks [14,42,43] has also been developed to address the aforementioned issues and enhance cycle life because of their strong interaction with LiPSs.

However, the shuttle effect in Li-S batteries still needs a fundamental breakthrough to be completely overcome since the physical or chemical confinement of LiPSs only solves the issues on a superficial level. In a typical reaction of the Li-S battery, sulfur (cyclo-S_8) reacts with Li ion to transform into high-order LiPSs (Li_2S_n, $6 < n \leq 8$) to lower-order LiPSs (Li_2S_n, $2 < n \leq 6$) [3,44,45] to eventually Li_2S during the discharge process. The intermediate LiPSs easily dissolve in the liquid electrolyte and migrate between the cathode and anode, resulting in a "shuttle effect". It is the main cause of low Coulombic efficiency in Li-S batteries. Finally, insoluble and insulating Li_2S/Li_2S_2 is formed, which may further decrease the kinetics of LiPSs redox. In the charge process, Li_2S/Li_2S_2 is transformed to S_8 with the formation of intermediate LiPSs [46]. Based on the above discussion, the "shuttle effect" can be alleviated in two promising ways. One is effective confinement of the LiPSs in the cathode hosts and the other is the acceleration of LiPSs redox kinetics. In recent research, it has been proven that a lot of polar hosts, such as metal oxide, metal sulfides, metal carbides, metal nitrides, metal phosphides, and some metal-free hosts can significantly improve the cycling

performance of Li-S batteries owing to their strong affinity towards LiPSs and high catalytic activity for LiPSs redox as shown in Fig. 1. The work provides a promising direction to alleviating the LiPS shuttling for Li-S batteries.

In this review, we first present the recent advances in sulfur cathode-hosts with high catalytic ability in three parts. The first part is mainly on the metal-free hosts for sulfur, such as nitrogen-doped carbon, nitrogen and sulfur dual-doped carbon, black phosphorus, boron nitride, and carbon nitride. In order to further modulate the affinity towards LiPSs and catalytic ability for LiPS redox, the second part focuses on various polar compounds, such as metal oxides, sulfides, nitrides, phosphide, carbides, and metal-organic frameworks, which have emerged as highly efficient hosts for Li-S batteries. The third part focuses on heterostructured hosts based on the surface and interface design, such as TiO_2–TiN, MoN-VN, and VO_2–VN. These well-designed heterostructures can not only improve chemical interaction with LiPSs but also accelerate the surface kinetics for LiPSs redox. Finally, we present our perspective on the future development of electrocatalysts for Li-S batteries.

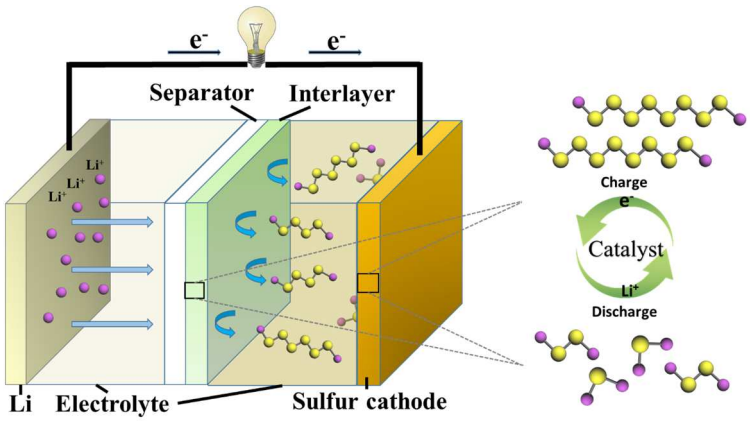

Fig. 1 Illustration of the catalytic effects in Li–S batteries.

2. Metal-free catalysts for Li-S batteries

In 2009, the Nazar group first reported the highly ordered mesoporous carbon as the sulfur host, which can greatly enhance the cyclic performance and specific capacity of Li-S batteries by physical immobilization of LiPSs [47]. After that, various conductive metal-free hosts, such as carbon nanotubes [31,48,49], mesoporous carbon [50-52], graphene and polymers [32,53-57], have been developed to improve the conductivity of the cathode and confine the LiPSs by physical interaction. In order to enhance the interaction between the metal-free hosts and LiPSs, a number of heteroatom-doped carbon-based materials, such as N-doped porous carbon, N-doped carbon nanotubes, N-doped graphene, and sulfur-doped graphene were developed. Recently, some heteroatom-doped carbon-based materials and some other metal-free hosts have been demonstrated that possess both strong chemical affinity towards LiPSs and high catalytic activity for LiPSs redox. In this part, we will review several typical metal-free catalysts (*e.g.*, N-doped carbon, N- and S-doped carbon, black phosphorus, boron nitride, and carbon nitride) to illustrate the potential of metal-free hosts for Li-S batteries.

2.1 Heteroatom-doped carbonaceous materials

Recently, heteroatoms were introduced into carbon-based materials, which can effectively trap the LiPSs due to the strong chemical interaction between the anchoring sites of heteroatom-doping and LiPSs [36,58,59]. Importantly, Chen et al. introduced a conductive nitrogen-doped carbon host [35]. Through a combined *in-situ* Raman spectroscopy and density functional theory (DFT) analysis, the complicated chemistry on the sulfur cathode-host surface was revealed (Fig. 2). It was demonstrated that the

nitrogen-doped carbon host could work as a conductive Lewis-base catalyst host to facilitate the oxidization of Li_2S_6 to Li_2S_8 and to S_8. Therefore, the sulfur utilization and cycling performance could be greatly enhanced. It has been reported that nitrogen and sulfur co-doped carbon could significantly enhance the catalytic activity for the oxygen reduction reaction [60]. Inspired by this work, Nazar's group reported a nitrogen and sulfur co-doped carbon as the sulfur host, which can greatly improve electrical conductivity, enhance affinity towards LiPSs, and favor high-rate kinetics [61]. These improvements are further demonstrated by a combined study of ab-initio theoretical calculations and X-ray photoelectron spectroscopy (XPS). When the co-doped carbon was employed as a sulfur matrix, the cathode delivered a high capacity of 1,370 mA h g^{-1}.

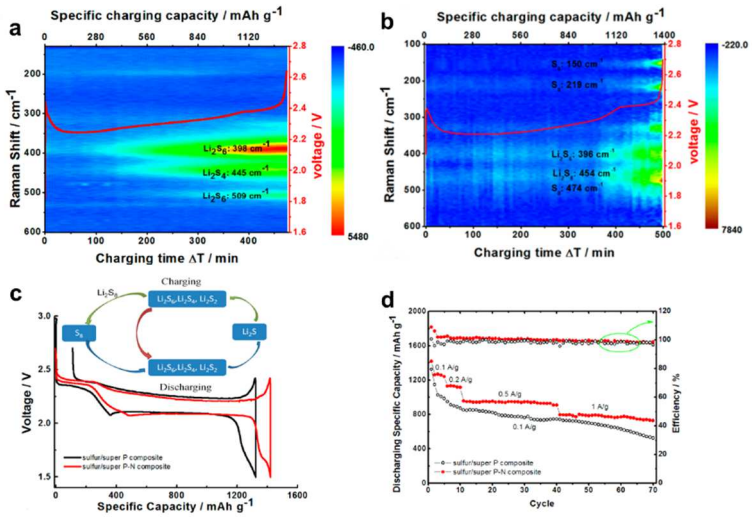

Fig. 2 Time sequence of Raman spectra during charging the processes of (a) sulfur/super P composite and (b) sulfur/super P–N composite. (c) Comparative analysis of the initial discharge-charge curves of super-P carbon with or without N-doping. (d) Electrochemical performance of sulfur/super P–N composite. Reproduced with permission [35]. Copyright 2015, American Chemical Society.

2.2 Black phosphorous

Black phosphorous (BP), which is an allotrope of phosphorous with high thermodynamic stability, has high electronic conductivity, an exceptionally high room-temperature hole mobility, low density, a high Li-ion diffusion constant, and high binding energies towards sulfur. These excellent properties indicate the potential application of BP as host in Li-S batteries [62]. The Cui group employed BP to modify the separator to confine and activate the soluble LiPSs in Li–S batteries [63]. When the BP-modified separator was used in Li-S batteries, the sulfur cathode with a high sulfur content of 80% showed improved specific capacity and cyclability. Li et al. demonstrated few-layer phosphorene (FLP) nanosheets as a polysulfide immobilizer and catalyst for Li-S batteries [64]. With the help of FLP in the cathode, the cycle life of Li-S batteries was greatly enhanced with a capacity decay rate of 0.053% per cycle. The addition of phosphorene greatly lowered the polarization and accelerated the redox kinetics of LiPSs, and thus enhanced the electrochemical performance. Lau and co-workers employed BP quantum dots as highly efficient electrocatalysts for the LiPS redox reaction [62]. The edges of the BP quantum dots provide abundant catalytically-active sites, resulting in high catalytic activity towards LiPSs redox reaction. The presence of BP quantum dots accelerated the reaction kinetics and improved the chemical interaction towards LiPSs (Fig. 3), which resulted in excellent cycling performance with a low capacity-fading rate (0.027% per cycle over 1000 cycles) and

high areal capacities. These findings demonstrate the application of BP catalysts for high-energy Li-S batteries.

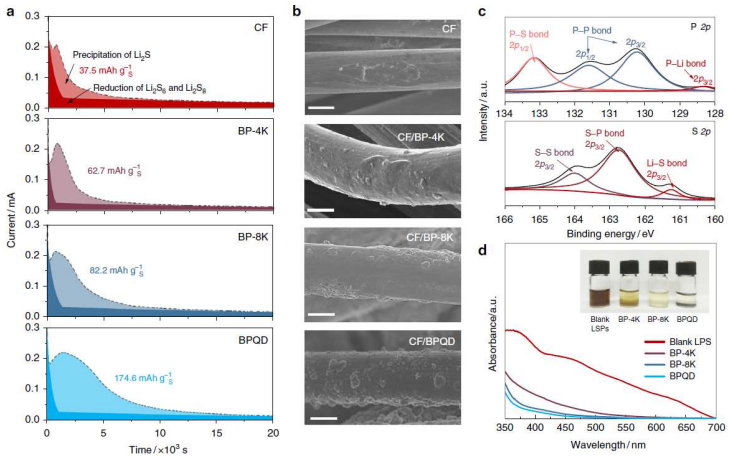

Fig. 3 Black phosphorus flakes for lithium polysufide conversion and adsorption. (a) Potentiostatic discharge curves of Li_2S_8-tetraglyme solution on different hosts. (b) SEM images indicating the precipitation of Li_2S on different hosts as implied by (c) XPS spectra for P 2p and S 2p of the BP flakes adsorbed with LiPSs and (d) ultraviolet–visible (UV–vis) spectra of LiPS with different-sized BP flakes. Reproduced with permission [62]. Copyright 2018, Nature Publishing Group.

2.3 Boron nitride

Boron nitride (BN) nanosheets, consisting of a few layers of alternating boron and nitrogen atoms in a hexagonal arrangement, have been widely employed in composite reinforcement, field nanoemitters, and nanoelectronics owing to their high resistance to oxidation, electrical insulation, good chemical stability, and high thermal conductivity [65]. Ying and co-workers developed a functionalized BN nanosheets/graphene interlayer for Li-S batteries [66], as shown in Fig. 4. Owing to the ultralight and thin

interlayer, the cathode showed significantly improved cycle life over 1,000 cycles with a low capacity decay rate of 0.0037% per cycle. Deng et al. developed a graphene/BN composite with high catalytic activity for LiPSs conversion in Li-S batteries in a wide range of temperatures [67]. Benefitting from the excellent catalytic capability of BN, the graphene/BN-sulfur cathode showed excellent cycle life in the wide operating temperature range of -40 to 70 °C. It was able to exhibit a capacity of 888 mA h g^{-1} at 2C rate over 300 cycles at 70 °C, and a capacity of > 650 mA h g^{-1} at -40 °C.

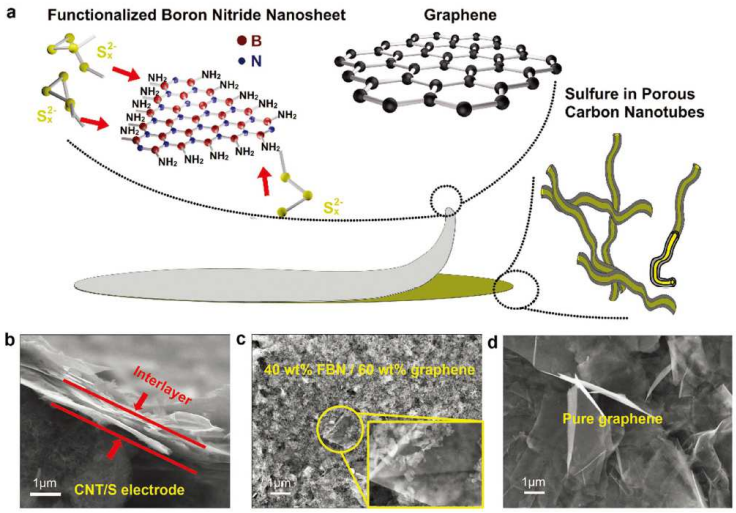

Fig. 4 (a) Schematic illustration of a Li–S cell with FBN/G interlayer. (b) The cross sectional SEM image of FBN/G interlayer and cathode. (c) The top-surface morphologies of FBN/G interlayer. (d) The top-surface morphologies of pure graphene interlayer. Reproduced with permission [66]. Copyright 2017, Wiley.

2.4 Carbon nitride

Due to its facile synthesis procedure, unique electronic structure, and chemical stability, carbon nitride (C_3N_4) is attractive in the application of energy storage materials. Li and co-workers demonstrated that C_3N_4 has strong affinity towards LiPSs

and can reduce the kinetic barrier of the LiPS redox reaction [68], as shown in Fig. 5a - c. When C_3N_4 serves as the sulfur host in Li-S batteries, the cathode exhibited high capacity and a low capacity-fading rate of 0.037% per cycle. A 3D-porous sulfur/graphene@graphitic-C_3N_4 (S/GCN) hybrid sponge was prepared as the cathode through a microemulsion-assisted assembly method [69]. The macroporous GCN with a large number of N atoms ensure abundant anchoring sites for LiPSs, which allows for the realization of a "physical-chemical" dual-immobilization of LiPSs. S/GCN presents a sharp and intense peak at 2.1 V in the differential capacity (dQ/dV) plots, indicating a facile electrochemical reduction process and fast kinetics.

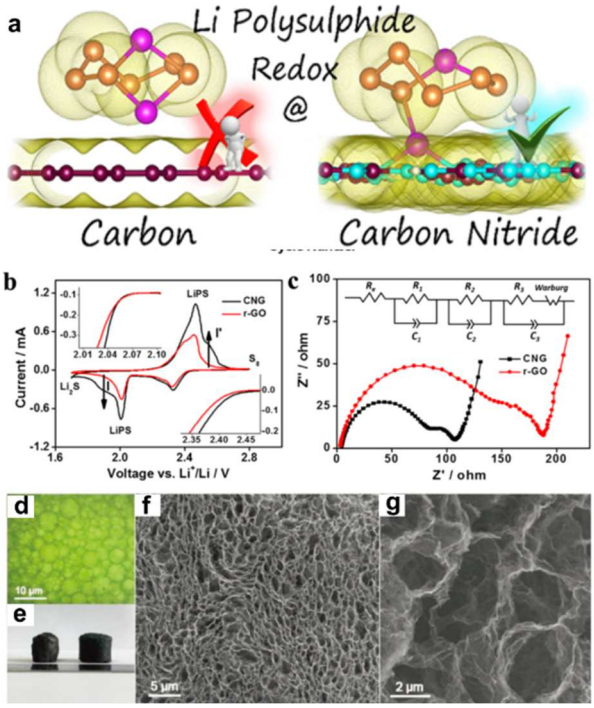

Fig. 5 (a) Schematic demonstration of the improved LiPSs redox reaction kinetics by C_3N_4. (b) CVs and onset region of the discharge peaks of GCN and r-GO. (c) EIS Nyquist plots of GCN and r-GO. Reproduced with permission [68]. Copyright 2016, American Chemical Society. (d) Optical microscope images of the emulsion droplet. (e) Photo image of the G-sponge (left) and the S/GCN hybrid sponge (right). (f, g)

Cross-sectional SEM images of S/GCN. Reproduced with permission [69]. Copyright 2018, Wiley.

3. Metal-based catalysts for Li-S batteries

Metal-based catalysts are the largest family of materials for electrocatalysis owing to their intriguing structural and electronic properties, which have been widely employed for energy-conversion devices. Recent work show that some of these metal-based catalysts also exhibit strong affinity towards LiPSs and high catalytic activity for LiPSs redox reaction, which can effectively alleviate the "shuttle effect" in Li-S batteries. In this section, some of the metal-based catalysts applied in Li-S batteries are reviewed.

3.1 Metal

Typically, platinum (Pt) is one of the most important electrocatalysts and has also been widely known as the most efficient catalyst in a number of electrochemical energy conversion systems [70]. Arava et al. first designed a current collector coated with Pt electrocatalyst for Li-S batteries, which demonstrated that high surface area is necessary to ensure efficient utilization of catalysts [71]. Therefore, they further investigated the catalytic effect of Pt for the LiPSs conversion by investigating the structural and electrochemical advantages of Pt/graphene host in Li-S batteries [72]. The graphene layers with a uniformly dispersed Pt catalyst nanoparticles enabled a 40% improvement in the specific capacity compared to that of pristine graphene and allowed enhanced cycle life over 100 cycles, with a high Coulombic efficiency of 99.3%.

Further, the improved exchange current density of Pt/graphene during the charge and discharge process confirmed the acceleration in LiPSs redox reaction rate (Fig. 6).

Dong et al. demonstrated the excellent catalytic activity of transition metals, such as cobalt by designing a 3D-porous N-doped graphitic carbon–cobalt (Co–N-GC) composite as the sulfur cathode-host [73]. The Co catalyst can not only help the LiPSs deposit back to soluble long-chain LiPSs but also catalyze the conversion of long-chain LiPSs to Li_2S_2/Li_2S, thus improving the reaction kinetics. In addition, the doped nitrogen could also facilitate the oxidation of Li_2S_6 to Li_2S_8 and to S_8, thus resulting in an enhanced specific capacity and rate performance. Therefore, even at a high rate of 1C, it could still deliver a capacity of 1,150 mA h g^{-1} initially and retained a capacity of 625 mA h g^{-1} after prolonged 500 cycles. Qiu et al. fabricated cobalt-embedded nitrogen-doped hollow carbon nanorods (Co@NHCRs) as the sulfur hosts [11]. The Co@NHCRs incorporated sulfur cathode achieved a high reversible capacity of 971 mA h g^{-1} at 0.5C rate, good cycling stability with a good capacity retention rate of 73% after 100 cycles, and good rate performance with a specific capacity of 747 mA h g^{-1} at 1C rate. In particular, we recently prepared a Li_2S@C–Co–N cathode by loading ultrafine Li_2S nanoparticles into graphitic carbon dual-doped with cobalt and nitrogen (C–Co–N), which further confirmed the catalytic effect of Co [74], as shown in Fig. 6d. Because of the synergistic effects of C–Co–N, the obtained Li_2S@C–Co–N composite delivered a high reversible capacity of 1,155 mA h g^{-1} of Li_2S in the first cycle and 929 mA h g^{-1} of Li_2S after 300 cycles corresponding to a capacity fading of 0.06% per cycle. It also showed excellent rate performance, with a capacity of 604 mA

h g^{-1} of Li_2S at the high rate of 4C. These results confirm the important role of metal catalysts in Li-S batteries, which can significantly mitigate the "shuttle effect" due to their highly catalytic capability for LiPSs redox reaction.

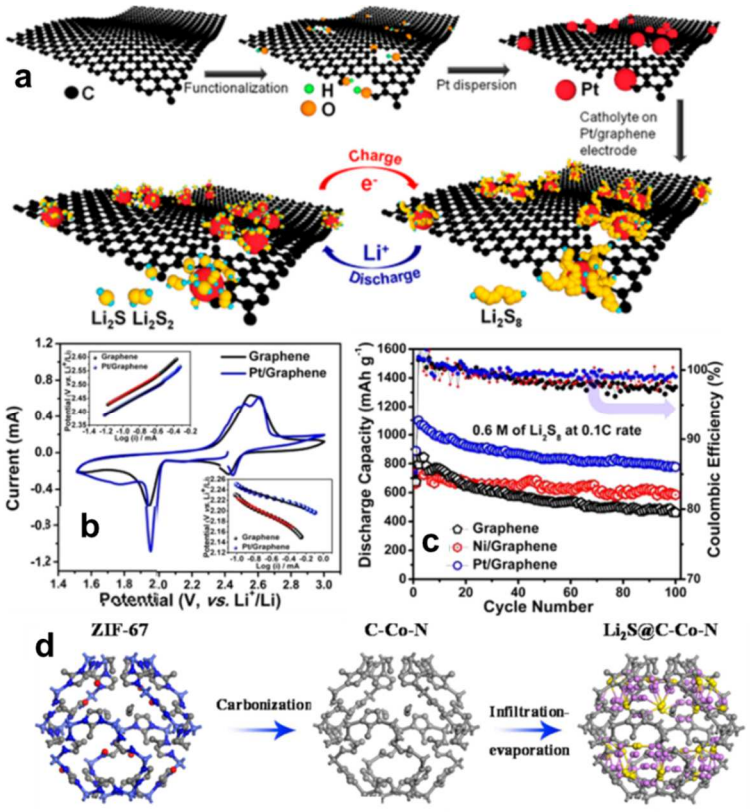

Fig. 6 (a) Schematic preparation of the Pt/graphene nanocomposite and its interaction with LiPSs during the charge/discharge process. (b) CVs of graphene and Pt/graphene electrodes (inset: Tafel plots for corresponding oxidation and reduction reactions). (c) Cyclic performance of pristine and Pt/graphene electrodes. Reproduced with permission [72]. Copyright 2015, American Chemical Society. (d) Schematic illustration of the preparation of Li_2S@C–Co–N composite. Reproduced with permission [74]. Copyright 2016, American Chemical Society.

3.2 Metal oxide

Although metal catalysts exhibit excellent catalytic activity for the LiPS conversion reaction, the use of costly noble metals and toxic heavy metals still limit their practical application. In this regard, low-cost metal oxides have attracted intense attention as catalysts for the LiPSs redox reaction. In this part, we will review several typical metal-oxide catalysts, such as the Ti_4O_7, MnO_2, Fe_2O_3, VO_2, MoO_3, WO_{3-x}, and CeO_2, to demonstrate their potential for enabling high efficiency Li-S batteries.

Pang et al. presented a Magneli phase Ti_4O_7 with high surface area as the sulfur host, which exhibits a high metallic conductivity of 2×10^3 S cm^{-1} at room temperature and strong affinity towards LiPSs [75]. The LiPS adsorption studies, XPS, and X-ray absorption near-edge spectroscopy (XANES) reveal that the surface interactions play a very important role in the dissolution and deposition of LiPSs. In addition, the presence of Ti_4O_7 is favorable for the reduction of LiPSs to Li_2S and allows for enhanced electron-transfer kinetics. In a Li-S battery, the Ti_4O_7/S cathodes deliver a high capacity of 1,070 mA h g^{-1} and show stable cyclic performance at a high rate for 500 cycles. Using MnO_2 as a catalyst in Li-S batteries was also reported by the Nazar group [76]. They designed a highly efficient catalyst δ -MnO_2 for Li-S batteries and proposed a new chemical strategy to entrap LiPSs within the cathode. Thiosulfate groups are first formed by the reaction between LiPSs species and ultra-thin MnO_2 nanosheets. Upon the proceeding of the reduction reaction, these groups can serve as a redox shuttle to trap soluble long-chain LiPSs and transform them into insoluble short-chain LiPSs. XPS results reveal the presence of thiosulfate (167.2 eV) and polythionate (168.2 eV)

during the conversion, showing evidence for the catalytic effect of MnO_2 for LiPSs transformation. The sulfur/MnO_2 cathode with 75 wt% sulfur content delivers a high capacity of 1,300 mA h g^{-1} of S, with a decay rate of 0.036% per cycle over 2,000 cycles.

Zheng et al. designed a three-dimensional hierarchical porous graphene with uniformly dispersed α- Fe_2O_3 nanoparticles (Fe-PGM) as the sulfur matrix for Li-S batteries [77]. They illustrated that the α-Fe_2O_3 nanoparticles not only have strong interactions with the LiPSs, but also promote their transformation, which plays an important role in the development of practically useable Li-S batteries. Therefore, the Fe-PGM-S cathode provides a high capacity of 565 mA h g^{-1} with a low capacity fade rate of 0.049% per cycle over 1,000 cycles at 5C rate. Song et al. prepared VO_2 nanobelts as cathode-matrix additives for the graphene-based sulfur electrode (Fig. 7) [78]. The VO_2 nanobelts enable strong chemical confinement of LiPSs and remarkable improvement in the sulfur redox kinetics. The VO_2/G/S electrode delivers a discharge capacity of 1,405 mA h g^{-1} initially at a current rate of 0.2C rate , as well as enhanced rate performance, with a capacity of ~ 830 mA h g^{-1} at 2C rate. Anderson and co-workers fabricated a separator modified by molybdenum trioxide (MoO_3) nanobelts [79]. The MoO_3 layer exhibits strong affinity towards LiPSs and promotes the redox reaction of LiPS conversion, which can help keep the LiPSs within the cathode region and thus mitigate the “shuttle effect”. As shown in Fig. 7f, the cyclic voltammograms (CV) of symmetrical Li_2S_6–Li_2S_6 cells with MoO_3 show a great increase in the current density compared with CNTs, indicating that MoO_3 can improve the electrochemical reaction kinetics of LiPSs. In addition, the second reduction peak in the CV profiles of

Li-S cells with MoO_3 shows a positive shift, as shown in Fig. 7g, further confirming the catalytic capability of MoO_3.

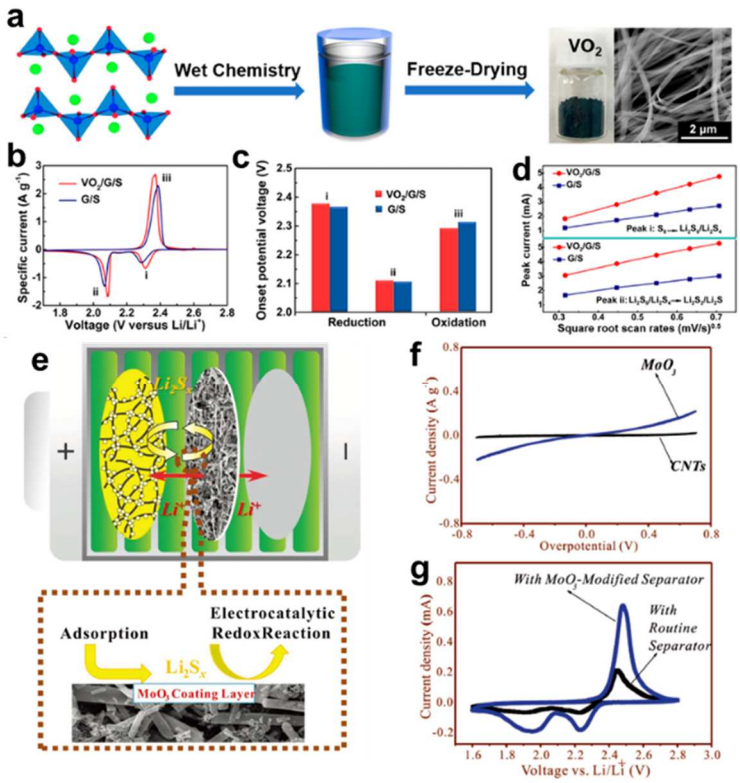

Fig. 7 (a) Scheme of the VO_2 preparation. (b) CV curves of VO_2/G/S and G/S cathodes. (c) Corresponding reduction and oxidation onset potentials for the VO_2/G/S and G/S electrodes. (d) The Li-ion diffusion properties of the cathodes at various potential scan rates. Reproduced with permission [78]. Copyright 2018, American Chemical Society. (e) Schematic illustration of the cells with CNT/S cathode and MoO_3 modified separator. (f) Polarization profiles of the symmetric cells and (g) CV curves of Li-S batteries with the pristine and MoO_3-modified separator. Reproduced with permission [79]. Copyright 2018, Wiley.

Lee and co-workers developed oxygen-deficient tungsten oxide (WO_{3-x}) as an effective bidirectional electrocatalyst for the LiPSs conversion reaction, which helps illustrate that oxygen deficiency in transition-metal oxides is beneficial for their catalytic capability [80]. The UV–vis spectra of the solution around the sulfur cathode with WO_{3-x} and WO_3 catalysts reveals that the oxygen deficiency in the WO_{3-x} surface can facilely react with the LiPSs. Such accelerated LiPS redox reaction can alleviate the accumulation of LiPSs in the sulfur cathode and suppress active material loss. Consequently, the S/WO_{3-x} cathode is able to show good cycling stability with a low capacity fade rate of 0.13% per cycle at 0.5C rate. Jin and co-workers implanted cerium oxide (CeO_2) nanocrystals uniformly into porous nitrogen-rich carbon (MMNC) nanospheres, which were employed as the sulfur host [81]. The introduction of polar and electrocatalytically-active CeO_2 in MMNC can effectively mitigate LiPSs dissolution and further promote LiPS redox reaction. The synergistic effects of CeO_2/MMNC result in high reversible capacities (1,066 mA h g^{-1} at 0.2C rate after 200 cycles) and high cycling stability (a low capacity decay rate of 0.024% per cycle over 1,000 cycles).

The application of a metal-oxide host with high catalytic activity for Li–S batteries is still under investigation. For now, a number of metal oxides, such as V_2O_5 [82], SiO_2 [83], SnO_2 [84], TiO_2 [85], ZrO_2 [86], ZnO [87], MgO [88], Nd_2O_3 [89], Al_2O_3 [90], CoO [91], and $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [92] have been employed as the LiPS adsorbent because of their strong chemical interaction towards LiPSs. However, the catalytic capability of

these metal oxides still needs to be investigated deeply, so that the utilization of sulfur and the problem of LiPS shuttling can be fundamentally solved.

3.3 Metal sulfide

Metal sulfides, which are abundantly available resources on earth, have been investigated intensively as the effective catalysts in solar cells and other energy storage systems [93]. Motived by these studies, metal sulfides were considered as attractive catalysts for Li-S batteries. There are several advantages for using metal sulfides as catalysts in Li-S batteries. First is their excellent stability towards sulfur chemistries. Second is their strong sulfiphilic property towards LiPSs. Third is their low lithiation potential vs Li/Li^+, which helps avoid overlap with the working potential range in Li-S batteries. Finally, most of the metal sulfides are metallic or semi-metallic, which is favorable for electron transfer. Recently, various metal sulfides, such as CoS_2 [94], CoS[95], Co_3S_4 [96], Co_9S_8 [97,98], WS_2 [99], MoS_2 [100], NiS [101], ZnS [102], SnS_2 [103], $NiCo_2S_4$ [104], and $FeCo_2S_4$ [105], have been used as effective catalysts in Li-S batteries. In this part, we will review the progress that has been made in using metal sulfides as highly efficient catalysts for Li-S batteries.

Cobalt disulfide (CoS_2) is an earth-abundant mineral exhibiting pyrite-type crystal structure. The Zhang group incorporated CoS_2 into graphene/sulfur cathodes (S/CoS_2+G) [94]. The incorporation of CoS_2 can effectively promote the LiPSs redox reaction owing to its strong chemical interaction with LiPSs. Enhanced LiPSs redox

kinetics were confirmed by electrochemical evidence. The increased current density, decreased polarization, and improved energy efficiency of CoS_2/graphene (CoS_2/G) compared to G directly reflect the accelerated kinetics of the LiPS conversion reaction, as shown in Fig. 8a,b. Thus, the S/CoS_2+G cathodes can achieve excellent cyclic performance with a sulfur content of 75 wt.%, and a low capacity fade rate of 0.034% per cycle over 2,000 cycles.

Pu et al. prepared multifunctional Co_3S_4 nanotubes by hydrothermal reaction as a highly efficient sulfur cathode-host (Fig. 8c) [96]. The obtained Co_3S_4 nanotubes have high electronic conductivity and strong chemical affinity towards LiPSs. As shown in Fig. 8d, e, a symmetric cell using Co_3S_4 nanotubes with and without Li_2S_6 electrolyte was used to obtain the chronoamperometry and CV curves. Both the Co_3S_4 and acetylene black (AB) with Li_2S_6-containing electrolyte show increased current density in chronoamperometry curves, indicating that the current responses are derived from lithiation/de-lithiation reactions instead of double-layer capacitance. The CV curves shown in Fig. 8f indicate that the current response improved in the presence of Co_3S_4 nanotubes, demonstrating that the Co_3S_4 nanotubes accelerate the kinetics of lithiation/delithiation reactions of LiPSs. An optimized Co_3S_4@S nanotube electrode delivers a capacity of 1267 mA h g^{-1} at 0.05C rate and shows a low capacity-decay rate of 0.041% per cycle at 5C rate over 1,000 cycles.

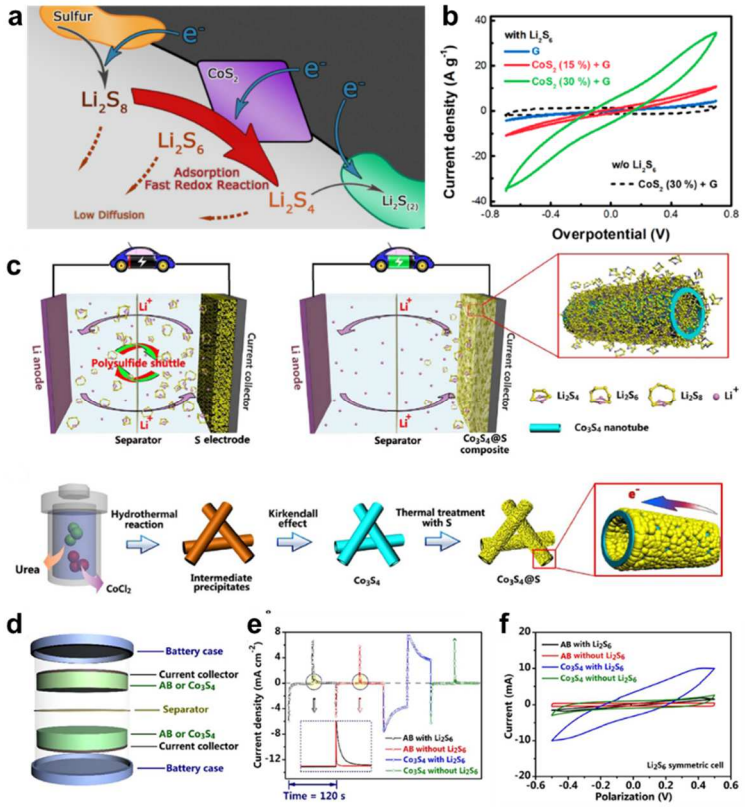

Fig. 8 (a) Scheme of the discharge process in CoS_2-incorporated carbon/sulfur cathode. (b) Polarization profiles of symmetric Li_2S_6 cells. Reproduced with permission [94]. Copyright 2016, American Chemical Society. (c) Scheme of a Li-S battery with "shuttle effect" and a Co_3S_4@S nanotube composite cathode to mitigate the LiPS shuttling. (d) Scheme of a symmetric cell. (e) Chronoamperometric and (f) CV profiles of the Co_3S_4 and AB symmetric cells. Reproduced with permission [96]. Copyright 2016, Elsevier.

Our group developed a metal-organic framework (MOF)-derived Co_9S_8 nanowall array directly grown on the commercial Celgard separator (Co_9S_8-Celgard) through a facile liquid-reaction approach [106]. Here, the Co_9S_8 nanowall array functions as an efficient multifunctional polar barrier for LiPSs in Li-S batteries. The Co_9S_8-Celgard separator has a large surface area, high conductivity, and particularly strong LiPSs-

confining ability through both chemical and physical interactions. The cells with Co_9S_8-Celgard deliver a high capacity of 530 mA h g^{-1} at 1C rate even after an impressive 1,000 cycles, with a capacity fading of only 0.039% per cycle, indicating the potential application in long cycle life Li-S batteries.

Pang et al. reported the polar Co_9S_8/carbon hollow nanopolyhedra with high conductivity as sulfur matrix in Li-S batteries [97]. The embedded Co_9S_8 nanocrystals with their highly polar and quasi-metallic properties can ensure strong interactions with LiPSs, and thus restricting their shuttling. Importantly, the Co_9S_8/C shells allow enhanced redox reaction kinetics and thus improve the rate capability. The hollow architecture rich with plentiful void spaces allows for high sulfur loading by physical confinement. Such a three-dimensional structure manifests an improved cyclic stability, with a low capacity fade rate of < 0.045% per cycle over 1,500 cycles at 0.5C rate. The Arava group successfully demonstrated that electrocatalytic WS_2 nanosheets can help alleviate LiPS shuttling in Li-S cells [99]. There are several advantages of this catalytic strategy in Li–S batteries: (i) the lithium-ion transfer will not be hindered as there is no physical encapsulation of LiPSs; (ii) the WS_2 host is economical, which results in low cost of the Li-S batteries. The reversible catalytic processes of physico-chemical conversion of LiPSs at the electrode/electrolyte interface is revealed by a combination of microscopic and spectroscopic studies. The catalytically-active edge sites of WS_2 play an important role for stabilizing electrochemical performance in Li-S batteries. As a result, the WS_2-S electrode delivered a specific capacity of 590 mA h g^{-1} with a high Coulombic efficiency (99%) over 350 cycles.

Lee and co-workers demonstrated that MoS_{2-x}/reduced graphene oxide (MoS_{2-x}/rGO) is able to accelerate the LiPS conversion rate to enhance electrochemical performance of Li-S batteries (Fig. 9a) [100]. The sulfur deficiencies on the surface of MoS_{2-x}/rGO play a vital role during the LiPSs redox reaction, which is confirmed by microstructural analysis of the cathode material. The accelerated redox reaction of LiPSs can mitigate its accumulation in the sulfur cathode and thus alleviate the loss of active material (Fig. 9b). Therefore, the sulfur cathode with a small amount of MoS_{2-x}/rGO provided a high capacity of 826.5 mA h g^{-1} at a high rate of 8C and exhibited improved cyclic stability with a low decay rate of 0.083% per cycle over 600 cycles. These results evidence the catalytic effect of MoS_{2-x}/rGO in accelerating LiPSs redox reaction kinetics in Li-S batteries.

Our group designed a novel freestanding three-dimensional graphene/1T MoS_2 (3DG/TM) composite to enhance Li-S battery performance and demonstrate its electrocatalysis mechanism (Fig. 9c) [107]. In this well-designed architecture, 3DG/TM is employed as a highly efficient catalyst for the transformation of LiPSs. The few-layered 2D-MoS_2 nanosheets directly grown on a porous 3D graphene framework ensures rich active sites and thus guarantees sufficient catalytic activity for the conversion of LiPSs. The highly conductive graphene and 1T MoS_2 network allow for fast electron transfer. The porous structure is favorable for electrolyte penetration and Li-ion transportation. Benefitting from these synergistic effects, the cells with 3DG/TM delivered a high reversible specific capacity (1,181 mA h g^{-1}) and an excellent cycling stability with a low capacity fade rate of 0.08% per cycle over 500 cycles (Fig. 9d).

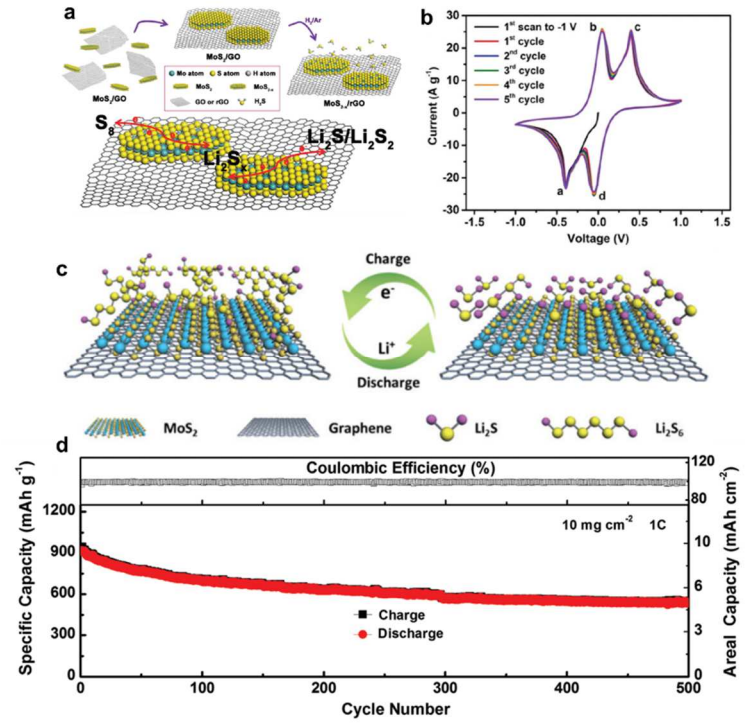

Fig. 9 (a) Schematic illustration of the preparation of MoS_{2-x}/rGO composite and the conversion of Li_2S_x on the MoS_{2-x}/rGO surface. (b) CVs of the MoS_{2-x}/rGO symmetric cell. Reproduced with permission [100]. Copyright 2017, Royal Society of Chemistry. (c) The conversion of LiPSs on a graphene surface with 1T MoS_2. (d) Cycling performance of 3DG/TM with Li_2S_6 catholyte. Reproduced with permission [107]. Copyright 2019, Royal Society of Chemistry.

Gao et al. designed cobalt-doped SnS_2 anchored on N-doped carbon nanotubes (NCNT@Co-SnS_2) as the cathode-host in Li-S batteries, which serves as a LiPS shield and an electrocatalyst [103]. XANES analysis helped demonstrate that the cobalt-doped SnS_2 serves as an efficient catalyst by promoting the conversion reaction for LiPSs. In addition, Co-doped SnS_2 shows enhanced chemical affinity towards LiPSs compared to SnS_2. Hence, the S/NCNT@Co-SnS_2 cell showed excellent electrochemical

performance, providing an initial specific capacity of 1,337 mA h g^{-1} and retaining a capacity of 1,004 mA h g^{-1} after 100 cycles. The Cui group systematically investigated a series of metal sulfides to determine the key factors for Li_2S oxidation and LiPS adsorption capability in Li–S batteries [108]. A combination of first-principles calculations and experimental results illustrate that strong interactions between LiPSs and metal sulfides and the energy barrier of Li_2S oxidation is related to the interaction between isolated Li ions and the sulfur atom in sulfides.

Lu et al. prepared a $NiCo_2S_4$@CNTs/S cathode for Li-S batteries through a facile hydrothermal reaction [104]. The bimetal sulfides ($NiCo_2S_4$) show strong affinity towards LiPSs, effectively mitigating the LiPS shuttling. As a result, the $NiCo_2S_4$@CNTs/S electrode provided a capacity of 788 mA h g^{-1} at 0.5C rate, 758 mA h g^{-1} at 2C rate, and a low capacity fade rate of 0.0489% per cycle at 0.6C rate over 1,000 cycles. Xu and co-workers designed a flexible sulfur cathode-host material composed of $FeCo_2S_4$ nanotube arrays grown on carbon cloth [105]. The $FeCo_2S_4$ nanotube arrays can not only promote electron and Li-ion transfer, but also suppress the dissolution of LiPSs through their strong chemical interactions. Importantly, the $FeCo_2S_4$ nanotube arrays also show high catalytic capability for improving the reaction kinetics of LiPS conversion. Therefore, the $FeCo_2S_4$/CC@S cathode provided a high specific capacity of 1,384 mA h g^{-1} at 0.1C rate and a stable Coulombic efficiency of about 98%.

3.4 Metal nitrides

In order to find an efficient and low cost catalyst as an alternative to noble metals, metal nitrides have attracted immense attention because of their long record in various catalytic applications [109]. In particular, various metal nitrides have emerged as highly efficient electrocatalysts for HER, ORR, OER, as well as methanol oxidation reaction (MOR). The high catalytic activity of metal nitrides derives from their unique electronic structure, which ensures appropriate adsorption between the surface of nitrides and protons during the catalytic process. In addition, most metal nitrides possess high electronic conductivity in the metallic range, which is beneficial for electron transfer during the catalytic process. In this context, some metal nitrides, such as vanadium nitride (VN) [110], cobalt nitride (Co_4N) [111], and molybdenum nitride (Mo_2N) [112], have been employed as electrocatalysts in Li-S batteries. In this part, we will review the progress made on the catalytic effect of metal nitrides in Li-S batteries.

Deng et al. prepared Co_4N mesoporous spheres composed of nanosheets through a facile method [111]. The obtained Co_4N shows strong affinity, fast trapping, and absorbing capability with LiPSs and exhibits high catalytic activity for the LiPS conversion reaction. These excellent properties indicate that Co_4N can be an ideal host for sulfur active material. The sulfur cathode in the presence of Co_4N shows excellent electrochemical properties, with a high capacity of 1,659 mA h g^{-1} at 0.1C rate, a long cycle life of 300 cycles at 5C rate, and a high capacity of 1,259 mA h g^{-1} even with a high sulfur content of 94.88%.

Xia and co-workers reported an easy combined method to prepare novel porous carbon fibers/vanadium nitride array (PCF/VN) composite matrix for the accommodation of sulfur [110]. As shown in Fig. 10, through a facile chemical etching process combined with a solvothermal–supercritical fluid method, a large amount of active sulfur is accommodated in the PCF/VN host and a physical-chemical dual-confinement towards LiPSs is achieved, effectively mitigating the shuttle effect. Owing to its unique structure and dual-trapping effect, the obtained PCF/VN/S electrode shows a high specific capacity of 1,310 mA h g^{-1} at 0.1C rate, a long cycle life of over 250 cycles, and improved rate performance.

Sun et al. developed a conductive porous vanadium nitride nanoribbon/graphene (VN/G) composite as catholyte host for Li-S batteries [41]. VN/G provides strong chemical affinity towards LiPSs and accelerated LiPS conversion reaction kinetics. Such strong interaction was further revealed through experimental and theoretical analysis. Because of the highly conductive vanadium nitride, the cathode shows improved redox reaction kinetics and lower polarization compared to that of a bare reduced-graphene cathode. The VN/G could deliver an initial capacity of 1,471 mA h g^{-1} and retain a capacity of 1,252 mA h g^{-1} after 100 cycles, demonstrating the promising application of the conductive electrocatalyst in Li-S batteries.

Jiang et al. proposed mesoporous, conductive Mo_2N as the sulfur cathode-host in Li-S batteries [112]. The mesoporous Mo_2N possesses a high surface area of 121 m^2 g^{-1} which provides a surface rich with polar sites for efficiently binding LiPSs. Mo_2N with a conductivity of 1×10^5 S m^{-1} facilitates facile electron transfer and thus

accelerates the redox reaction of LiPSs. Impressively, the obtained Mo_2N/S cathode delivered a high capacity of 995 mA h g^{-1} and good cycling capability with a capacity retention of 91.9% after 100 cycles.

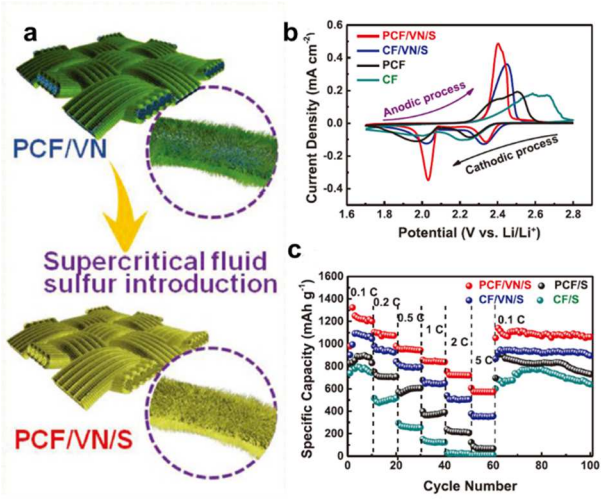

Fig. 10 (a) Scheme of the preparation of PCF/VN/S. (b) CV profiles of the various cathodes. (c) Rate performance of the four electrodes. Reproduced with permission [110]. Copyright 2018, Wiley.

3.5 Metal phosphide

Concurrent with the development of metal chalcogenides, carbides, sulfides, and nitrides for catalytic purposes, metal phosphides are being considered as typical representatives of the burgeoning field of non-noble metal electrocatalysts. In particular, the investigation of metal phosphides as catalysts for the LiPSs redox reaction in Li-S batteries is still in a very early phase.

The Wang group reported a new multifunctional interlayer constructed with molybdenum diphosphide (MoP_2) nanoparticles and a carbon nanotube (CNT) film in Li-S batteries [113]. Here, MoP_2 serves as both the catalyst and LiPS adsorbent, which

helps promote the LiPS conversion reaction during the cycling process and capture the LiPSs within the cathode region. As shown in Fig. 11a-g, the *in-situ* Raman spectroscopy results confirm that most liquid LiPSs were immobilized in the cathode side. The intermediate products in the cathode region were mainly Li_2S_4 and Li_2S_2, indicating that long-chain LiPSs were successfully reduced into short-chain LiPSs. The *in-situ* Raman analysis confirms that MoP_2 plays a catalytic role during cycling, which is key to enhancing the cycle life of Li-S batteries. Therefore, the cells with the MoP_2/CNT interlayer delivered a capacity of 905 mA h g^{-1} after 100 cycles at 0.2C rate with a capacity decay rate of 0.152% per cycle.

Yang and co-workers demonstrated that iron phosphide (FeP) nanocrystals could be used as an ideal catalyst for high-rate, ultra-stable Li-S batteries [114]. Density functional theory (DFT) calculations suggest that FeP has strong chemical affinity towards LiPSs (Fig. 11h-i). In addition, the FeP nanocrystals possessed high catalytic capability to promote the LiPS redox reactions and decrease the Li_2S nucleation energy (Fig. 11k-m). This shows that the FeP nanocrystals could effectively alleviate LiPSs dissolution and facilitate the LiPS conversion reaction through their intrinsic LiPS affinity and catalytic activity. Therefore, the cells with the presence of FeP nanocrystals displayed ultra-stable cycling performance with a low capacity decay rate of 0.04% per cycle and good rate capability, with a reversible capacity of 613 mA h g^{-1} at 3C rate.

Zhong et al. proposed a LiPS-binding mechanism mediated through the surface oxidation layers of transition-metal phosphide and chalcogenide materials [115]. Owing to the natural oxidation (forming Co–O–P-like species) in CoP nanoparticles,

the surface Co sites are activated for interacting with LiPSs through Co-S bonding, and LiPSs can be strongly adsorbed by CoP nanoparticles. The oxidation layer ensures strong confinement of LiPSs and the inner core is useful for conducting electrons. Thus, CoP nanoparticles are an attractive candidate for enhancing and stabilizing electrochemical performance of Li-S batteries. As a result, the modified cathode with a high sulfur areal loading of 7 mg cm^{-2} could deliver a high areal capacity of 5.6 mA h cm^{-2} with good stability over 200 cycles.

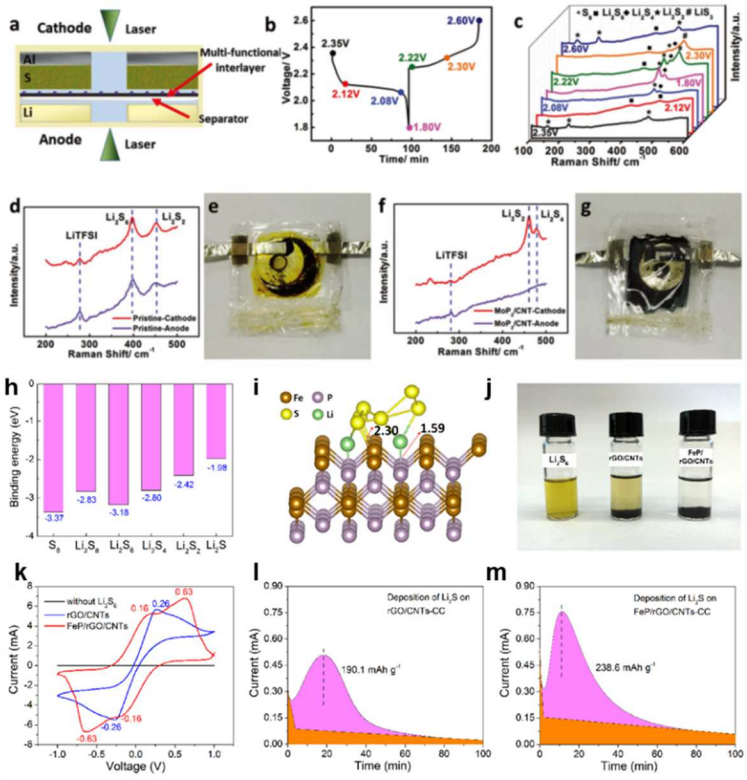

Fig. 11 (a) Schematic illustration of the in-situ Raman measurements. (b) Voltage curve of the initial discharge/charge process of the Li–S pouch cell. (c) Raman spectra of the Li–S cell with the MoP_2/CNT interlayer at different discharge/charge voltages as indicated in (b). Raman spectra and digital photographs of the Li–S cell with (d,e) the pristine separator and (f,g) the CNT/MoP_2 interlayer. Reproduced with permission [113]. Copyright 2018, Wiley. (h) Theoretical calculation of binding energies between

LiPSs and FeP. (i) Geometry of Li_2S_6 binding to the (111) plane of FeP. (j) LiPS adsorption capability study of FeP/rGO/CNTs. (k) CV profiles of symmetric cells. Potentiostatic discharge profiles of Li_2S_8 solution at 2.07 V on the (l) rGO/CNTs-CC host and (m) FeP/rGO/CNTs-CC host. Reproduced with permission [114]. Copyright 2018, Elsevier.

3.6 Metal carbides and Metal boride

Most metal carbides and borides possess certain attractive properties, such as high stability, good corrosion resistance, high mechanical strength, high melting point, *etc*., which have led to intense attention in recent years in the context of their potential application as electrocatalysts [116].

The Yu group reported a unique electrocatalyst of metal carbide nanoparticles decorated on carbon nanofibers (MC NPs-CNFs) [40]. When the MC NPs-CNFs were employed in Li-S batteries, the cathodes could exhibit high rate capability, low hysteresis, and good cycling stability. A combination of experimental results and DFT calculations reveals that the surface of MC NPs provides moderate chemical affinity towards LiPSs, which is favorable for the adsorption and containment of LiPSs in the cathode region. In addition, the catalytic properties of MC NPs are also proven by CV analysis. With these merits, the cathode based on W_2C NPs-CNFs showed a high reversible capacity of 1,200 mA h g^{-1} at 0.2C rate, and long cycling stability with a capacity fade rate of 0.06% per cycle over 500 cycles.

The Nazar group proposed a lightweight MgB_2 as a metallic sulfur cathode-host, which ensures both good electronic conduction and strong LiPS confinement [117].

They demonstrated that their borides were unique in that both B- and Mg-terminated surfaces bond with the S_x^{2-} anions (not Li^+) and thus improve electron transfer to the active S_x^{2-} ions. This surface-mediated LiPS conversion reaction leads to an improved exchange current density compared to MgO and bare carbon. The cells with MgB_2 show good electrochemical performance with stable cycling at a high sulfur loading of 9.3 mg cm^{-2}.

4. **Heterostructural catalysts for Li-S batteries**

Heterostructural sulfur cathode-hosts constructed by novel surface and interface design of various inorganic materials have attracted great attention in the field of Li-S batteries. A new and general LiPS-binding mechanism can be realized in heterostructured sulfur hosts, such as TiO_2–TiN [118], VO_2–VN [119], MoN-VN [120], and Co_9S_8/CoO [121], through improved chemical interaction with LiPSs and enhanced interfacial LiPS redox kinetics, which result in enhanced electrochemical performance in Li-S batteries.

The Yang group designed a twinborn TiO_2–TiN heterostructure as a highly efficient catalyst for Li-S batteries, which possesses the dual advantages of highly adsorptive TiO_2 and highly conductive TiN [118]. TiO_2 shows strong interaction with LiPSs while TiN accelerates LiPS conversion reaction kinetics during cycling. With such efficient LiPS trapping and redox conversion, the TiO_2–TiN heterostructure can act as a highly efficient barrier for LiPSs when coated on the separator. The cells with

TiO_2–TiN interlayer could exhibit long cycling stability, with a capacity retention of 73% at 1C rate over 2,000 cycles.

Song et al. reported a VO_2–VN binary matrix which exhibits the advantages of ultrafast anchoring (VO_2) with good electronic conductivity (VN) to realize effective confinement and transformation of LiPSs (Fig. 12) [119]. Those synchronous merits can effectively mitigate LiPS shuttling, accelerate the conversion kinetics, and thus enhance the performance of Li-S batteries. Therefore, the sulfur electrode with VO_2–VN/graphene matrix shows good rate performance with a capacity of 935 mA h g^{-1} at 2C rate and long cycling stability with a low capacity fade rate of 0.06% per cycle over 800 cycles.

The Qiao group designed and prepared a 2D heterostructured MoN-VN composite as the sulfur host to confine LiPSs and to obtain atomic-level insights into LiPS adsorption behavior [120]. The DFT results show that the electronic structure of MoN is doped with V on the surface, leading to improved LiPS adsorption. Furthermore, a combination of NEXAFS and *in situ* synchrotron X-ray diffraction (*in situ* synchrotron XRD) further demonstrates that MoN-VN can improve the sulfur utilization efficiency as the sulfur host compared with bare MoN. Thus, the MoN-VN modified sulfur cathode could achieve a high discharge capacity of 708 mA h g^{-1} at 2C rate with a low capacity fading rate of 0.068% per cycle over 500 cycles.

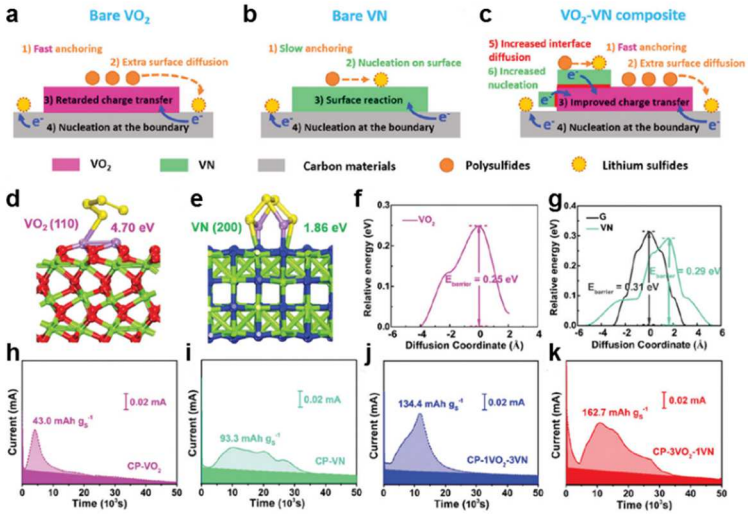

Fig. 12 (a – c) Schematic illustrations of LiPS trappping, surface diffusion, and redox processes on VO_2, VN and VO_2 - VN binary host surfaces. (d and e) Optimized geometries of Li_2S_4 on VO_2(110) and VN(200) surfaces. (f) Energy curves for Li_2S_4 diffusing along the [-111] direction of the VO_2(110) surface. (g) Energy curves of Li-ion diffusion on VN(200) and graphene surfaces. (h–k) Potentiostatic discharge curves of a Li_2S_8/tetraglyme solution. Reproduced with permission [119]. Copyright 2018, Royal Society of Chemistry.

5. Conclusions and Perspectives

Alleviating the inherent "shuttle effect" has become a key research topic in Li-S batteries. In particular, the sluggish kinetics during their redox reactions cause serious challenges in attaining the cycle life and rate performance required for commercial applications. In this regard, it is still necessary to design a sulfur host with strong affinity towards LiPSs and high catalytic capability, which can not only chemically confine LiPSs, but also promote the LiPS redox reaction kinetics. Recent advances in the use of cathode-host materials with high catalytic activity for LiPS conversion in

advanced Li–S batteries, including both metal-free and metal-based materials, are reviewed here. Although a lot of achievements in realizing host materials with high catalytic activity in Li-S batteries have been realized, several challenges still remain.

- Given the large family of catalysts available for use in Li-S batteries and their unique chemical/physical/electrochemical catalytic properties compared to other applications (such as ORR, OER), there is still a large room to be explored for further development.
- Mechanistic studies on the fundamental aspects of such catalytic activities are in urgent demand.
- *In situ* characterization methods are required to better understand the catalytic effect in Li-S batteries.
- Towards the practical application of Li–S batteries, large-scale controllable synthesis of catalysts and abundance of the raw materials should be considered for economic relevance.

In summary, the progress in designing host materials with high catalytic capabilities has paved a new direction towards high-performance Li-S batteries. The catalytic effect has been proved to play an important role in mitigating LiPS shuttling. Through searching for more highly efficient catalysts, the performance of Li-S batteries is expected to be further improved. In addition, it is expected that the progress on catalysts in Li-S batteries can serve as a guide for Li-Se batteries, Li-Te batteries, and other related energy storage systems.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering under award number DE-SC0005397.

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Graphical abstract

A Review on the Status and Challenges of Electrocatalysts in Lithium-Sulfur Batteries

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