

Host Materials Anchoring Polysulfides in Li-S Batteries Reviewed

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Abstract

Lithium-sulfur batteries (Li-S) have become a viable alternative to future energy storage devices. The electrochemical reaction based on lithium and sulfur promises an extraordinary theoretical energy density, which is far higher than current commercialized Li-ion batteries. However, the principal disadvantage impeding the success of Li-S batteries lies in the severe leakage and migration of soluble lithium polysulfide intermediates out of cathodes upon cycling. The loss of active sulfur species incurs significant capacity decay and poor battery lifespans. Considerable efforts have been devoted to developing various sulfur host materials that can effectively anchor lithium polysulfides. Herein, a comprehensive review is presented to provide recent advances in sulfur host materials. On the basis of the electrochemistry of Li-S batteries, the strategies for anchoring polysulfides are systematically categorized into physical confinement and chemical bonding. The structural merits of various sulfur host materials are highlighted and the interaction mechanisms with sulfur species are discussed in detail, which provides valuable insights into the rational design and engineering of advanced sulfur host materials facilitating the commercialization of Li-S batteries. Future challenges and promising research prospects for sulfur host materials are proposed at the end of the review.

1. Introduction

Electrical energy conversion and storage is becoming one of the increasingly major concerns in future low carbon society. The depletion of fossil fuels and oils, as well as the revival of electric vehicles, has motivated scientists to develop sustainable electrical energy storage systems.^[1-6] Over the past three decades, rechargeable lithium-ion (Li-ion) batteries have gained in popularity due to their large energy storage, low self-discharge, and stable cycling performance, significantly advancing the development of energy storage technologies.^[7-9] However, current commercialized Li-ion batteries using conventional insertion cathode materials, such as LiCoO_2 and LiFePO_4 , have reached an energy density of around 300 Wh kg⁻¹

¹, which is expected not to lead to a considerable improvement in the near future owing to battery technologies and their theoretical limits. According to the commercialization goal of the United States Advanced Battery Consortium (USABC), such an energy density cannot accomplish a 500 km travel range based on a single charge. The exploration of novel battery systems, showing a higher energy density and longer cycle life, would be a viable alternative to conventional Li-ion systems.

Firstly proposed in the early 1960s, lithium-sulfur (Li-S) batteries have received a great deal of attention.^[10-13] Owing to the overwhelming theoretical specific energy of 2600 Wh kg⁻¹ and impressive specific capacity of 1675 mAh g⁻¹, respectively, Li-S batteries hold a promising opportunity to achieve a quantum leap in energy storage, addressing current challenges. Since then, Li-S batteries have been recognized as an attractive option among the most potential energy storage devices for practical applications. More importantly, sulfur is naturally abundant, cost-effective, and eco-friendly, thus boosting the potential for commercialization of Li-S batteries.

Despite these prominent merits in energy density and cost, several problems have restricted the development of Li-S batteries for commercialization.^[14-16] The first issue is that elemental sulfur and its final discharge species Li₂S_n ($1 \leq n \leq 2$) are poor conductors, leading to large electrochemical polarizations and battery impedances. Another obstacle is diffusion and migration of sulfur intermediates into the electrolyte upon charging and discharging. These long-chain lithium polysulfide intermediates can be transported to the anodes, react with metallic lithium, and form short-chain lithium polysulfides. This so-called shuttle effect incurs the severe losses of electroactive substances in cathodes. The third problem lies in the volumetric variation of sulfur cathodes upon cycling. The lithiation and delithiation process pulverizes the cathode and detaches the active mass from conductive substrates. Among those problems, the dissolution of lithium polysulfides into the electrolyte is most notorious and

intractable. It severely decreases the utilization of sulfur cathodes, resulting in fast capacity degradation, low Coulombic efficiency, and eventual battery failure.

Over the past few years, considerable endeavors to alleviate the detrimental shuttle issue have been devoted, including cathode functionalization,^[17-22] separator modification,^[23-26] and electrolyte tailoring.^[27-29] The design and engineering of sulfur host materials confining active sulfur intermediates have been proven to be a successful approach to improving the capacity and cycling stability of sulfur cathodes. Various sulfur host materials possessing desirable structures have been developed to confine sulfur species through spatial inhibition and chemical anchoring.^[30-32] Despite numerous perspectives to solve the shuttle issue, very few reviews have been published, systematically discussing the various anchoring strategies for polysulfides to improve the performance of Li-S batteries.

This review specifically focuses on various sulfur host materials that are able to anchor polysulfides in Li-S batteries. By interpreting the underlying anchoring mechanisms of polysulfides, the review is expected to provide a comprehensive and detailed insight into the function and role of sulfur host materials. The operation and reaction mechanism of Li-S batteries are firstly elucidated. Furthermore, the anchoring strategies of host materials towards sulfur species are systematically discussed on the basis of physical confinement and chemical bonding. Then three classes of sulfur host materials, *i.e.* nanostructured carbon, polymers, and metal compounds, are presented to highlight the breakthroughs in sulfur cathodes. Finally, perspectives on future challenges and promising directions of sulfur hosts are proposed, providing more insight into the design and engineering of cathode materials, which may consequently boost the future development of advanced Li-S batteries. Since this review aims for sulfur host materials, modified separators and interlayers will not be discussed here. For the convenience of the reader, a list of abbreviations is presented at the end of the paper.

2. Electrochemistry of Li-S batteries

As illustrated in **Figure 1a**, the configuration of Li-S batteries involves a metallic lithium anode and an elemental sulfur cathode immersed in an organic electrolyte. Elemental sulfur reacts with lithium converting to lithium sulfide (Li_2S) during discharging and Li_2S decomposes into Li and S during charging. The overall electrochemical charge transfer reaction at the cathode can be represented by Equation (1).



This two-electron (per S atom) redox process offers a considerable theoretical capacity of sulfur cathodes, which is almost ten times higher than that of the present commercial Li-ion cathode materials.^[33] In comparison with conventional metal oxide cathode materials undergoing insertion reactions with lithium, sulfur involves numerous structural changes and complicated reactions due to the multistep electrochemical process occurring upon cycling. The soluble lithium polysulfide intermediates (Li_2S_n , $4 \leq n \leq 8$) and insoluble $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ discharge products have a major impact on the electrochemistry of Li-S batteries.^[34, 35]

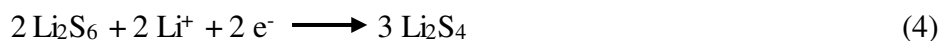
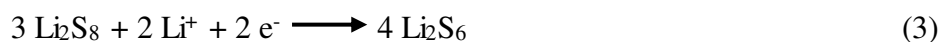
A typical charge (green curve) and discharge voltage (red curve) profile of a Li-S battery is shown in **Figure 1b**. On the basis of the phase transitions of sulfur species, four stages can be distinguished in the discharge process:

Stage I: The reduction from solid sulfur into highly soluble long-chain Li_2S_8 , corresponding to a solid-liquid two-phase reaction in Equation (2).^[36]



A small sloping plateau emerges during discharging at a relatively high voltage of approximately 2.3 V. Due to the continuous dissolution of Li_2S_8 into the electrolyte, the cathode becomes porous, resulting in the volumetric contraction of the cathode.

Stage II: A two-step reduction process of Li_2S_8 into soluble Li_2S_4 , involving a liquid-liquid single-phase reaction, according to Equation (3) and (4).



During this stage, the concentration and viscosity of soluble polysulfides gradually rise. A small voltage peak emerges at the end of this discharge stage, which results from a higher overpotential caused by the high electrolyte viscosity due to polysulfide dissolution.^[37] Stage I and II contribute to the one fourth (419 mAh g^{-1}) of the overall theoretical specific capacity, corresponding to the acceptance of 0.5 electron per sulfur atom.^[38]

Stage III: Soluble Li_2S_4 is reduced to insoluble Li_2S_2 and Li_2S species. This stage involves liquid-solid conversions in Equation (5) and (6), resulting in gradually decreased redox kinetics.



These reduction reactions take place simultaneously and compete with each other at the long lower voltage plateau of about 2.1 V.

Stage IV: The last stage relates to the further reduction of Li_2S_2 to Li_2S , which suffers high polarization and slow kinetics due to the solid-solid transformation reaction, according to Equation (7).



Note that Stage IV considerably depends on Stage III, in which the competition reactions occur. The sloping plateau, characteristic for Stage IV, becomes short or even disappears when the dominant reaction in Stage III is equation (6). Stage III and IV contribute to the three fourths (1256 mAh g^{-1}) of the overall theoretical specific capacity, corresponding to the acceptance of additional 1.5 electrons per sulfur atom.^[39]

Upon the reversible charging process, the solid Li_2S and Li_2S_2 species are oxidized to various soluble polysulfides, which are finally converted into elemental sulfur (green voltage curve in **Figure 1b**). Another peak appears during the initial stage of the solid-liquid phase transition from Li_2S_2 and Li_2S into soluble polysulfides. This potential barrier mainly arises from the phase nucleation of polysulfides.^[40]

Overall, from the electrochemical reaction of Li-S batteries discussed above, the dissolution and diffusion of polysulfides have a substantially detrimental effect on the electrochemical performance of Li-S batteries. Practically, due to the shelf-discharge of cathodes and the shuttle effect of polysulfides, sulfur cathodes therefore suffer heavy capacity degradation. Various strategies to effectively anchor polysulfides within the cathode have proven to be successful for the design of high-performance Li-S batteries.

3. Strategies for anchoring polysulfides

The design and fabrication of various sulfur host materials that can encapsulate and anchor polysulfides have been extensively reported. Specifically, the current investigations can mainly be classified into two strategies: physical confinement and chemical binding. Here, systematic and comprehensive analyses and discussions on physical confinement and chemical binding for Li-S batteries are presented in the following context.

3.1. Physical confinement

Physical confinement is a common and facile strategy to anchor polysulfides, which aims to spatially confine polysulfides inside sulfur cathodes. The focus of this strategy lies in the structural design of sulfur host materials. Generally, an ideal sulfur host should be able to become an efficient physical barrier that impedes polysulfide migration into the electrolyte. Based on this principle, the structure of sulfur hosts can mainly be divided into two classes: (1) porous structures and (2) shelled/layered structures.

The diffusion of soluble polysulfides can be physically confined either by porous materials or by external barrier coatings. Materials which either are porous or can be readily tailored into shelled/layered structures are perceived as efficient sulfur host materials. Among these, carbon-based materials, possessing a large specific surface area, tunable structures, and excellent conductivity, have been considered as one of the ideal candidates to physically confine

polysulfides.^[41-43] Various carbon-based materials, including porous carbon, graphene, and carbon nanotubes (CNTs), have been extensively employed as sulfur hosts to enhance the electrical conductivity of electrodes as well as to inhibit the diffusion of polysulfides outside the cathodes.

3.1.1. Porous structures

Due to the porosity and large specific surface area, porous structures are able to effectively accommodate sulfur particles and confine sulfur species into the porous configurations. Consequently, a higher sulfur loading can be achieved and the volume variation during the cycling process can additionally be mitigated. The pore walls act as physical barriers and the charge transfer reaction of the encapsulated sulfur occurs within the pores, preventing the diffusion of polysulfides. The initial research using mesoporous carbon materials in sulfur cathodes was conducted by Wang *et al.*^[44,45] The authors employed active carbon with the main pore size of 2.5 nm to mix with sulfur. During a thermal treatment, sulfur converted into liquid and moved into the mesopores of the active carbon. Owing to the physical confinement of polysulfides into the mesopores, the initial specific capacity of the composite cathodes reached 800 mAh g⁻¹. A stable capacity of about 440 mAh g⁻¹ was maintained with high sulfur utilization of 90% upon cycling. From that moment on, various porous structures, such as porous carbon,^[46, 47] porous carbon fibers,^[48, 49] and porous organic polymers,^[50] have been proposed to confine sulfur species.

Porous carbon-based structures can be fabricated from various precursors. Using a hard template from self-stacked water-soluble NaCl and Na₂S crystals, Li *et al.* synthesized three-dimensional (3D) porous graphitic carbon (PGC).^[51] As shown in **Figure 2a**, the authors initially fabricated a 3D glucose-coated hybrid material by freeze-drying. Then a thermal treatment transformed the glucose into PGC. Sulfur nanoparticles were *in situ* formed in PGC due to the reaction between Na₂S and Fe(NO₃)₃. The prepared sulfur composite cathode,

designated as 3D S@PGC, achieved tunable sulfur contents with a maximum of 90 wt.% by altering the ratio of Na₂S and glucose. This *in-situ* approach resulted in the covalent bonding of sulfur at the surface of PGC. Due to these covalent bonds, hierarchically porous networks, and homogeneous sulfur nanoparticles, the 3D S@PGC composite cathodes exhibited substantially enhanced cycle life and excellent rate capabilities.

Metal-organic frameworks (MOFs) have been considered as promising precursors to fabricate carbon materials with tunable porous morphologies. Xi *et al.* selected four kinds of zinc metal-centered MOFs to produce hierarchically porous carbon structures since zinc was readily eliminated as metallic vapor during high-temperature pyrolysis.^[52] Four MOFs were pyrolyzed under Ar atmosphere to produce hierarchically porous carbons. The authors demonstrated that the porosity of the pyrolyzed MOFs depended linearly on the Zn/C ratio of the precursors. As sulfur host materials, their pore volumes and pore size distribution had distinct effects on the initial storage capacities and cycling stabilities of Li-S batteries. Micropores benefited a prolonged cycle life by effectively confining polysulfides, while mesopores enabled a higher initial capacity by facilitating the Li⁺ transfer.

Inorganic compounds can also be tailored to porous structures as sulfur hosts. Sun *et al.* synthesized a porous VN nanoribbon/graphene (VN/G) hybrid with high conductivity (**Figure 2b**).^[53] Two steps were conducted to synthesize this porous VN/G composite material. Firstly, a hydrothermal method converted graphene oxide (GO) and NH₄VO₃ precursors into a vanadium oxide/graphene (VO_x/G) hydrogel. This process resulted in the *in-situ* formation of VO_x on GO and the simultaneous formation of a 3D foam. Then the VO_x/G hydrogel was immersed in deionized water followed by freeze-drying to form a VO_x/G macrostructure. The freestanding VN/G composite material was obtained after annealing in an NH₃ atmosphere. The Li₂S₆ catholyte was directly added to the VN/G host. The 3D free-standing graphene network facilitated the charge transfer and benefited the electrolyte absorption. The VN nanoribbons contained a large number of mesopores, allowing fast ionic transportation and strong adsorption

of polysulfides. As a result, the VN/G cathode exhibited a high initial capacity of 1471 mAh g⁻¹ at 0.2 C and mitigated polarization (**Figure 2c**).

3.1.2. Shelled/layered structures

Coating a shell or layer on the surface of sulfur particles can also impede their diffusion spatially. These shelled/layered structures can adequately suppress the undesirable shuttle effect. Sulfur cathodes with core-shell structures show superior electrochemical performance, where the sulfur core is coated with shells composed of carbon or other homogenous materials. For example, Wu *et al.* developed a unique coating structure via the layer-by-layer (LBL) assembly. As illustrated in **Figure 2d**, the authors employed graphene sheets (GS) as the outer shell and polyelectrolyte multilayers (PEMs) as an inner shell to encapsulate the hollow carbon spheres/sulfur composites (HCS/S).^[54] The LBL shells have multiple advantages. The inner PEMs restrained the movement of polysulfides via electrostatic repulsion. The outer GS stabilized the PEMs and accelerated the charge transfer by providing sufficient electron pathways. The beneficial effects of the LBL shells contributed to the HCS/S-LBL cathode with an enhanced storage capacity of over 200 cycles at 1 A g⁻¹ (**Figure 2e**). Other types of core-shell structures, including the inorganic compound shells^[55, 56] and multiple shells,^[32, 57] have also been proven to effectively confine polysulfides.

However, the lithiation of sulfur cores is accompanied by a large volume expansion, which causes the protective shells to crack and fracture. The design of sulfur yolk-shell structures can be a good alternative.^[58, 59] The major advantage of the yolk-shell structures lies in the presence of the gap between yolks and shells. The additional voids allow the large volumetric variation of sulfur during cycling, thus enabling the integral shell structures. Based on this strategy, a sulfur-polyaniline (S-Pani) yolk-shell nanoarchitecture has been designed as sulfur cathodes for Li-S batteries by Zhou *et al.*^[60] A facile fabrication approach was employed to obtain S-Pani yolk-shell composites. Uniform sulfur nanoparticles were initially synthesized by a chemical

reaction. Subsequently, polyaniline was coated on sulfur nanoparticles to achieve an S-Pani core-shell composite. Thermal treatment at 180 °C under argon resulted in the *in-situ* vulcanization of polyaniline, forming the S-Pani yolk-shell structures. In contrast to the S-Pani core-shell composites, the yolk-shell counterpart exhibited significantly enhanced cycling stabilities.

Coating a barrier layer on sulfur cathodes is another structural design to inhibit the diffusion of polysulfides upon cycling. By this method, a tiny amount of coating can significantly enhance the active sulfur utilization. Using atomic layer deposition (ALD), Yu *et al.* deposited TiO₂ layers on nitrogen-doped graphene/sulfur electrodes adding only negligible additional weight.^[61] The deposited TiO₂ layers immobilized the soluble polysulfide species and prevented a severe loss of sulfur upon cycling. The resulting sulfur cathodes exhibited improved cycling stability. In addition, the deposition of Al₂O₃ coatings has also been proven effective to confine polysulfides.^[62, 63]

Sulfur can also be encapsulated within the layers of two-dimensional (2D) materials. 2D materials with a large specific area can intrinsically act as the barrier layer to confine sulfur particles. Moreover, these layers can also provide excellent conductive pathways for charge transfer. A case in point is the sulfur cathodes designed by Chen *et al.*^[64] The authors combined reduced graphene oxide (rGO) with poly(anthraquinonyl sulfide) (PAQS) to assemble a freestanding composite thin film as sulfur cathodes. As shown in **Figure 2f**, a sulfur-amine chemical process enabled nanoscale sulfur particles to grow in rGO suspensions (S@rGO). Then the addition of PAQS gave rise to the adsorptive interaction with S@rGO. Vacuum filtration achieved the assembly of freestanding stacked films (S:rGO:PAQS). In this structure, rGO restricted the shuttle effect of polysulfides and alleviated the volume variation of sulfur cathodes. PAQS provided favorable ionic conduction pathways and also inhibited the polysulfide shuttling. The resulting sulfur composite cathodes maintained a steady storage capacity of 615 mAh g⁻¹ at 8 C (**Figure 2g**). Besides, 2D inorganic compounds composed of

such as nanosheets^[65, 66] and nanoflakes^[67, 68] can serve as an effective barrier layer to confine active sulfur species.

In conclusion, both porous and shelled/layered structures can function as effective sulfur host materials. Their large surface area enables efficient physical confinement and therefore sulfur particles are spatially restricted into the cathode. Various of these developed host materials are carefully analyzed and summarized in this review with the focus on the advantages of physical confinement of polysulfides. The comprehensive and systematic discussion is beneficial for the reader to gain a better understanding of the design of the various available sulfur host materials.

3.2. Chemical bonding

Considering the polarity of polysulfides, it is desirable to employ materials that can form strong chemical bonding with polysulfides as sulfur hosts.^[69] The strong chemical interaction between sulfur host materials and polysulfides can substantially enhance the anchoring of polysulfides, hence inhibiting their movement and diffusion into the electrolyte. Generally, the chemical bonding between sulfur hosts and polysulfides can be achieved by four approaches: (1) polar-polar interactions; (2) Lewis acid-base interactions; (3) redox interactions; (4) covalent binding interactions. In order to attain optimum chemical bonding, materials should be designed in such a way to provide sufficient bonding sites, which are able to generate chemical interactions with polysulfides. Therefore, structures with a large specific surface area and pore volume are considered to be ideal sulfur host materials. Various materials, including metal oxides, heteroatom doped carbon, and MOFs have been investigated to explore their chemical binding with polysulfides, as will be outlined below.

3.2.1. Polar-polar interactions

The asymmetry of polysulfides endows them with polarity, so polar materials can anchor polar polysulfides by polar-polar interactions. Materials with strong polarity have the potential as

good sulfur hosts. Due to the intrinsic polarity, metal compounds can be directly applied as host material. There have been many studies that demonstrate their superiority in confining polysulfides.^[11, 70] On the other hand, some of the metal compounds exhibit relatively poor conductivity, which is detrimental to the redox kinetics of sulfur cathodes. Highly conductive carbon materials are therefore often added to improve Li-S batteries.

By modifying the carbon surface with heteroatoms (*e.g.* oxygen and nitrogen), non-polar carbon materials can be converted to polar materials. These heteroatoms can chemically anchor polysulfides by forming polar interactions. Concerning the abundant oxygen-containing polar groups of GO, Ji *et al.* initially demonstrated that the functional groups on GO exhibited enhanced chemical bonding to sulfur via theoretical calculation and X-ray absorption spectroscopy.^[71] Doping not only increases the polarity of carbon-based materials but also enhances the conductivity. Many studies have confirmed that nitrogen,^[72, 73] phosphorus,^[74] and multiple doping elements^[75, 76] create abundant active sites at carbon, effectively enabling chemical anchoring of sulfur species. These doped carbon precursors can be graphene, CNTs, porous carbon, and carbon nanospheres. Although some of the research did not definitely indicate polar-polar interactions, the corresponding theoretical calculations and experimental analyses revealed the presence of electron transfer between polar carbon hosts and sulfur species.^[71, 77]

Metal oxides have been widely reported to confine polysulfides by polar-polar interactions. The strong polarity allows them to form metal-sulfur bonds or oxygen-lithium bonds. The Nazar group initially employed Magnéli phase (Ti_4O_7) to chemically bind polysulfides.^[78] Ti_4O_7 containing polar O-Ti-O units has a strong affinity for polysulfides (**Figure 3a**). Combining the visual adsorption investigations with X-ray photoelectron spectroscopic (XPS) and X-ray absorption near-edge structure (XANES) studies, the authors confirmed the strong metal oxide-polysulfide chemical interactions. As a result, $\text{Ti}_4\text{O}_7/\text{S}$ cathodes achieved a durable cycling stability for 500 cycles at 2 C (**Figure 3b**). Other oxides including TiO_2 , Co_3O_4 , and Fe_3O_4 have

been developed to anchor polysulfides.^[57, 79, 80] Their high polarity can generate strong polar-polar interactions with polysulfides. Also, many studies have employed sulfides, such as Co₉S₈, MoS₂, and TiS₂ to chemically bond polysulfides.^[81-83] The charge transfer and configuration distortion caused by polar-polar interactions were validated by both theoretical calculations and experimental results. Besides, some polar nitrides and carbides have also been demonstrated to form polar-polar interactions with polysulfides.^[84, 85]

3.2.2. Lewis acid-base interactions

Since polysulfide anions own occupied orbitals with lone electron pairs, they can be considered as a Lewis base. Lewis acids, containing unoccupied orbitals, can accept the lone pair of electrons of Lewis bases to form coordinate bonds. Therefore, a chemical species with the property of a Lewis acid is capable of anchoring polysulfides by Lewis acid-base interactions. It has been demonstrated that the metal ions in MOFs and MXenes can accept a lone pair of electrons from polysulfides. As sulfur hosts, MOFs and MXenes can therefore significantly suppress the dissolution of polysulfides from the cathode.

Zheng *et al.* initially investigated the Lewis acid-base interactions between MOFs and polysulfide anions in detail.^[86] A new Ni-based MOF host (Ni-MOF) was synthesized to impregnate sulfur. Electrochemical studies revealed that the Ni-MOF/S cathode exhibited considerably increased cycling stability than other MOF/S cathodes. The authors expected that apart from the pore effects of MOFs, other factors might also affect the behavior of sulfur cathodes.

First-principles calculations were initially introduced to analyze the interactions between Li₂S_x ($2 \leq x \leq 8$) and Ni-MOF. The calculated binding energies increased with the chain length of polysulfides. Accordingly, the Ni 2p XPS spectra of MOF/S shifted to lower binding energies, confirming the interaction between nickel cations and polysulfide anions. The authors further synthesized Co-MOF by substituting nickel with cobalt to study the interaction mechanisms

between polysulfide anions and metal cations. Compared to Ni-MOF/S, the Co-MOF/S cathode indicated an inferior cycling performance and lower binding energies between Co-MOF and polysulfides, which means a weaker coordination between the cobalt cations and polysulfide anions. These results were consistent with the Irving-Williams Series, in which the stability constant of the Ni(II) complex is higher than that of the Co(II) counterpart.

From then on, various MOFs with open metal sites have been reported as Lewis acid to anchor polysulfides. The Lewis acid-base interactions between MXenes and polysulfide anions were firstly proposed by Nazar *et al.*^[87] The authors found the surface Ti atoms of Ti₂C had unoccupied orbitals to bind with polysulfide anions forming strong Ti-S bonds. This interaction resulted in the suppression of the polysulfide diffusion. A more detailed discussion on MXenes as Lewis acid will proceed in the section of metal compound hosts.

3.2.3. Redox interactions

When an electrode material is above the redox potential window of polysulfides, the polysulfides can be oxidized to generate thiosulfate/polythionate species anchored at the material surface. This reaction significantly inhibits the loss of polysulfides and boosts the electrochemical performance of sulfur cathodes. This novel anchoring mechanism was initially proposed by the Nazar group.^[88] MnO₂ nanosheets were chosen as prototype to investigate their interactions with polysulfides. Based on XPS analyses, they proposed that the insoluble thiosulfate species are responsible for mediating the polysulfide conversion in a two-step redox process. Polysulfides initially produced at the discharging stage reacted with MnO₂ to form thiosulfate groups. With the reaction proceeding, the fresh polysulfides then reacted with the thiosulfate groups to generate polythionate complexes and shorter-chain polysulfides. The relatively poor solubility of the polythionate complex considerably suppressed the shuttle issue of polysulfides. This conversion proceeded gradually until the discharging process was finished. Meanwhile, MnO₂ was reduced to Mn²⁺. The resulting S/MnO₂ cathode with 75 wt.% sulfur

loading delivered a 0.036% capacity fading per cycle during 2000 cycles at 2 C. Their further studies demonstrated that this mechanism could also be responsible for the superior cell performance with GO hosts. In their follow-up work, Nazar *et al.* concluded that materials having a redox potential window of 2.4-3.05 V (*e.g.* VO₂) were able to trigger this reaction mechanism to chemically anchor polysulfides.^[89] Besides, they also revealed that the formation of thiosulfate was responsible for the interaction between Titanium-based MXene phases and polysulfides.^[90] The terminal hydroxyl groups of MXenes reacted with polysulfides to form thiosulfate species. Together with the resulting Ti-S bonding based on Lewis acid-base interactions, these dual anchoring effects substantially inhibited the loss of sulfur species, leading to the increased cycle life of sulfur cathodes.

In view of the complex multistep reactions and sluggish redox kinetics, accelerating the conversion of sulfur species is beneficial to the mitigation of polysulfide losses. Electrocatalysis may play a major role in regulating the redox conversion rate. Many reports have demonstrated that host materials have catalytic properties, accelerating the conversion of soluble polysulfides, the deposition of solid lithium sulfides, and the oxidation of Li₂S during charging and discharging. The electrocatalysis of the polysulfide transformation was initially proposed by Al Salem *et al.*^[91] These authors chose graphene to support Pt nanoparticles to increase the surface areas and the number of catalytic sites, as schematically shown in **Figure 3c**. The superior catalytic effect of Pt/graphene composites significantly reduced the overpotential of the oxidation and reduction peaks observed in cyclic voltammetry (CV) compared to pristine graphene. Moreover, the enhanced exchange current densities during (dis)charging clearly showed that Pt/graphene accelerated the conversion reactions of polysulfides. Benefiting from these merits, Pt/graphene cathodes revealed a 40% increase in capacity over pristine graphene (**Figure 3d**). The XPS spectra also confirmed the existence of Pt²⁺ species during discharging, indicating the redox interactions with polysulfides. A decrease in Pt²⁺ intensity during charging further revealed the reversibility of the redox interactions. Electrocatalysis therefore offers new

routes to anchor and effectively convert sulfur species, leading to a better performance of Li-S batteries.

The anchoring and conversion approaches have further been developed by Yuan *et al.* They incorporated sulfiphilic CoS₂ into carbon/sulfur cathodes to promote the redox reactions of polysulfides (**Figure 3e**).^[30] Owing to the strong chemical affinity with polysulfides, CoS₂ effectively increased the sulfur utilization. This has been confirmed by the CV of symmetrical Li₂S₆ cells, in which the current densities significantly increased with a rise in the CoS₂ weight ratio. The enhanced current density resulted from the accelerated reaction kinetics of polysulfides. Consequently, a CoS₂/graphene composite host with 15% CoS₂ weight ratio (CoS₂ (15%) + G) exhibited an optimal capacity of 1368 mAh g⁻¹ (**Figure 3f**).

During the charging process, catalyzing the oxidation of solid Li₂S can mitigate the reaction overpotential and thus contribute to better redox kinetics. The Cui group found a series of metal sulfides showing catalytic effects for the decomposition of Li₂S to sulfur upon charging.^[92] The decomposition process was perceived as one Li₂S molecule converting into one LiS cluster and one Li⁺. They concluded that the decomposition of Li₂S correlated with the binding of sulfur atoms in sulfides to isolated lithium ions. The strong interactions gave rise to lower overpotentials, which was the principal reason for a reduced decomposition barrier, while the weak interactions of carbon materials towards lithium ions incurred a high activation energy barrier.

3.2.4. Covalent binding interactions

Sulfur covalently binding at the surface of carbon and polymer materials is an effective approach to eliminate the dissolution of soluble polysulfides during cycling. In this case, sulfur exists in the form of short sulfur chains to form covalent bonds with carbon atoms, *e.g.* C-S and C=S. Various carbons and polymers can covalently bind with sulfur by sulfurization at elevated temperatures. The resulting sulfurized compounds are promising cathode materials.^[93] Because

of covalent binding interactions, sulfur is fully anchored at the host material, achieving a solid-to-solid transformation between covalent sulfur chains and lithium sulfides during the discharging and charging process. The covalently bound sulfur produces a distinctly different electrochemical characteristic of Li-S batteries. Traditional composites, integrating sulfur and hosts, present two cathodic peaks and two discharge plateaus in their CV and voltage profiles, respectively. This reaction process results from the conversion of sulfur to polysulfides and solid lithium sulfides. In contrast, sulfurized compounds typically exhibit solely one cathodic CV peak and one sloping discharge plateau at 1.9 V, indicating a solid-to-solid phase transformation.^[94, 95] Moreover, because of the complete elimination of polysulfides upon cycling, carbonate electrolytes can be beneficially applied in combination with sulfurized compounds.

The content of sulfur in sulfurized compounds depends on the types of host material and sulfurization temperature. Hosts with abundant surface functional groups, such as hydroxyl and carbonyl, are capable of reacting with sulfur forming covalently bound sulfur. Surface functionalized carbon and polymers, like polyacrylonitrile (PAN) and polyaniline, are desirable precursors for sulfurization. The sulfurization temperature varies from the boiling point of sulfur up to 600 °C. For example, Frey *et al.* synthesized a sulfurized material from polymethyl methacrylate (PMMA) and PAN via facile thermal conversion.^[96] A 550 °C heating treatment for 3 h resulted in sulfur covalently bound to PAN. The obtained sulfurized PAN (SPAN) exhibited a high sulfur content of 46 wt.%. Generally, a high sulfurization temperature contributes to a shorter sulfur chain, implying a lower sulfur content and specific storage capacity. On the other hand, the sulfur distribution will be more homogeneous, so an improved cycling stability can be expected. Overall, the present sulfur content in sulfurized compounds is not as high as in sulfur/host composites. By covalent binding interactions, the dissolution issue of polysulfides can be fully suppressed. Sulfurized compounds provide therefore an interesting alternative to construct reliable Li-S batteries.

Generally, the four interactions discussed above do not exist separately between host materials and sulfur species. A sulfur host may have multiple interactions. For example, MXenes anchor polysulfides through both Lewis acid-base and redox interactions. Based on different characterization methods and detailed analyses, it has been concluded that one sulfur host may offer distinct interaction mechanisms. Despite the insufficient understanding, it has been firmly demonstrated that these interactions improve the polysulfide anchoring effectively and consequently boost the utilization of sulfur species, which leads to a significant improvement of the electrochemical performance of sulfur cathodes. The concluded four interactions cover the main mechanisms of chemical bonding to polysulfides. Together with the two host structures for physical confinement, a systematic and comprehensive perspective on strategies for anchoring polysulfides is therefore offered, which provides a better insight and outlook on sulfur host materials.

4. Nanostructured carbon hosts

Nanostructured carbon materials have been considered to be effective sulfur hosts because of the good mechanical stability, excellent conductivity, natural abundance, and high specific surface area. Polysulfides are prone to be confined within the carbon matrix to inhibit their diffusion into the electrolyte, resulting in enhanced electrochemical performance of sulfur cathodes. Nanostructured carbon materials employed as sulfur hosts can be divided into five categories: (1) porous carbon; (2) graphene; (3) carbon nanotubes and fibers; (4) heteroatom-doped carbon; (5) carbon nitride.

4.1. Porous carbon

Porous carbon materials generally can be used as a framework to host active sulfur species, where polysulfides are mainly encapsulated in the pores. Owing to the excellent conductivity, large specific surface area, and adequate pore volume, porous carbon can substantially improve

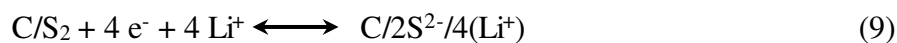
the conductivity of sulfur cathodes. Also, the porous structure effectively anchors polysulfides and accommodates the volume variation of cathodes upon cycling.^[97-99] According to the variation in pore size, porous carbon is mainly categorized into three different types, where the pore diameter (d) is leading: (1) microporous carbon ($d < 2$ nm); (2) mesoporous carbon (2 nm $< d < 50$ nm); and (3) macroporous carbon ($d > 50$ nm). Many efforts have been devoted to developing porous carbon materials with various morphologies and structures as sulfur host in recent years.^[51, 100-102]

4.1.1. Microporous carbon

Microporous carbon (MPC) structures are widely perceived as a good sulfur host that can homogeneously anchor sulfur intermediates. Considering the reduced dimension of micropores, sulfur molecules tend to be anchored into the carbon matrix in the form of small S_{2-4} molecules instead of the larger S_8 molecules.^[103-105] This leads to a deviating discharging profile which is significantly different from that of the reduction of S_8 molecules into dissolved polysulfides. The sulfur shuttle problem can therefore be avoided. Tailoring S_8 into small allotropes, Xin *et al.* realized a new strategy to confine metastable S_{2-4} molecules (S_2 , S_3 , and S_4) into the internal voids of a conductive MPC matrix.^[103] Multi-walled CNTs coated with a MPC layer were designed for sulfur accommodation. As shown in **Figure 4a**, the obtained CNT@MPC revealed a coaxial structure with a CNT core and a MPC sheath. The micropore size of MPC was about 0.5 nm. Since the size of large S_{5-8} molecules exceeded that of MPC, only small chain-like S_{2-4} molecules smaller than 0.5 nm can be accommodated in the micropores of MPC. The voltage profile of S/(CNT@MPC) in **Figure 4b** shows a single long sloping discharge plateau at about 1.7 V. The confined small S_{2-4} molecules avoids the detrimental conversion between S_8 and S_4^{2-} upon (dis)charging, and limits the overall process to a direct solid-solid reaction, according to Equation (8).



In another report, microporous carbon with subnano-internal voids was synthesized as a sulfur host, where short-chain S_2 species were successfully confined inside the pores.^[104] The subnano-entrapped S_2 cathodes revealed a unique electrochemical mechanism which may correspond to the coupling between the charge-sharing $C/2S^{2-}$ matrix and Li ions, according to Equation (9).



In a carbonate electrolyte, a novel solid electrolyte interphase (SEI) comprising thiocarbonates was formed during the initial cycle at the composite cathode surface. Both the subnano-confinement and the SEI, covering the surface, effectively prevented the shuttling of S_2 species. The SEI-coated C/S cathode showed a high storage capacity even after 4000 cycles with very low capacity losses. Furthermore, Zhu *et al.* employed a novel ultra-microporous carbon (UMC) to encapsulate small S_{2-4} molecules.^[105] The UMC was designed and prepared from polyvinylidene fluoride (PVDF) by a facile pyrolysis process. The micropores with a homogeneous size of 0.55 nm enabled UMC to exclusively trap smaller S_{2-4} molecules. Therefore, the corresponding discharge process only showed the direct reduction of S_{2-4} to Li_2S . The shuttle effect caused by dissolved polysulfides was fundamentally avoided. The merits of UMC hosts were demonstrated by the prolonged cycling stability, in which only about 0.03% capacity loss per cycle occurred in the first 1000 cycles at 1 C-rate.

Conclusively, the electrochemical performance of sulfur molecules encapsulated in micropores have been significantly changed due to the pore size effect of the host material. However, the intrinsic drawback of low sulfur loading still restricts the widespread application of microporous carbon materials. The low sulfur content loaded inside the micropores inevitably results in rather low energy densities of complete Li-S batteries, impeding further practical applications of microporous carbon host materials.

4.1.2. Mesoporous carbon

To accommodate as much as sulfur in host materials, various mesoporous carbon materials have been extensively developed. A series of breakthroughs have been achieved by the Nazar group. They encapsulated sulfur into a highly ordered mesoporous carbon (CMK-3) host with channel voids of 3 to 4 nm.^[17] The synthesized CMK-3 host was composed of a combination of hollow carbon rods of 6.5 nm thickness separated by channel voids in 3 to 4 nm width. The mixture of elemental sulfur and CMK-3 was heated at 155 °C, consequently the liquid sulfur could easily diffuse into the mesopores making use of capillary forces. A 70 wt.% sulfur content was achieved with the as-prepared composite cathode, leading to a favorable capacity of 1005 mAh g⁻¹ in the first cycle. A further modification was conducted with a polyethylene glycol (PEG) coating. The PEG-modified composite cathode revealed an increase in initial capacity of 1320 mAh g⁻¹. The confinement of sulfur species inside the mesopores ensured fast reaction kinetics and the cathode capacity could be adequately exploited. From then on, many mesoporous carbon host materials have been developed to anchor the sulfur species and significantly boosted the advancement of the use of sulfur cathodes.

In subsequent investigations, Schuster *et al.* synthesized unique nanoscale spherical ordered mesoporous carbons (OMC) with extremely high bimodal porosities.^[106] The spherical OMC revealed a homogeneous particle size with a diameter of about 300 nm. The applied silica etching process generated hierarchical mesopores with 6 and 3.1 nm in size. The resulting composite cathodes with 49.7 wt.% sulfur content combined an initial capacity of 1200 mAh g⁻¹ at 1 C with a favorable cycle life. Analyzing nanosize and bulk carbon, the authors concluded that the nanoscale morphology of mesoporous carbon was responsible for the excellent electrochemical properties of Li-S cells.

Park *et al.* synthesized ordered mesoporous carbon nanosheets (OMCNS) with honeycomb-like structures to load sulfur.^[107] An acidic etching process of the self-assembled carbon nanosheets and iron oxide hybrid produced the 2D OMCNS. OMCNS displayed homogeneous 20 nm long mesoporous tight-packed cells, between which gaps existed of about 4 nm wide.

The ordered mesoporous cubes with numerous voids mitigated the volumetric expansion of the cathode material and also anchored the polysulfides upon cycling, thereby effectively suppressing the shuttle effect and offering a stable cycle life performance. The OMCNS-S cathodes combine an initial storage capacity of 1238 mAh g⁻¹ at 0.1 C with an impressive capacity fading of only 0.081% per cycle maintained for 500 cycles.

Due to the complex fabrication process of the mesoporous carbon materials, their large-scale application for Li-S batteries is, however, heavily hampered. The synthesis of mesoporous carbons involves a series of complex steps, such as a high-temperature process, pretreatment, and etching of templates. This approach makes the practical production of these materials rather cost-ineffective.

4.1.3. Hollow carbon

Hollow carbons have a macropore structure and adequate internal cavities, which can maximize the energy density of Li-S batteries. Hollow carbon materials have therefore been widely investigated as sulfur hosts. Early research on hollow carbon tends to employ the pure carbon structure to confine sulfur. Recently, combining other elements or components with hollow carbon has become a common approach. These introduced components not only enhances the conductivity of cathodes but also benefit polysulfide adsorption.

Considering the advantages of the highly controllable morphology of organic frameworks, Li *et al.* prepared porphyrin organic framework hollow spheres (POF-HS) using polystyrene (PS) microspheres as template.^[108] The as-synthesized POF-HS exhibited a hollow spherical morphology with inner diameter and thickness of 500 and 40 nm, respectively (**Figure 4c**). Due to the favorable polarity and hollow structures, POF-HS adequately alleviated the polysulfide shuttling via the dual functions of physical confinement and chemical adsorption. The POF-HS/S electrode combined a steady capacity of 773 mAh g⁻¹ after 200 cycles with a stable Coulombic efficiency of close to 100% (**Figure 4d**), implying a substantial inhibition of

polysulfide shuttling. The excellent reaction kinetics of the composite cathode was also demonstrated at high rates. A favorable storage capacity of 800 mAh g⁻¹ was attained at 4.0 C (Figure 4e).

More recently, Zhong *et al.* reported a novel porous carbon with macrocellular structures.^[46] The authors were inspired by the instantaneous puffing to produce popcorn. The rice was directly puffed into a highly porous macrocellular structure by an *in situ* pressure-releasing approach. Specifically, the pristine rice with a dense structure was loaded into a heated pressure vessel. Under the internal vapor pressure, the rice starch became unstable and gradually expanded. The inner starch had a volume enlargement of about 20 times when the outer pressure was released by opening the sealed vessel. The puffed rice derived carbon (PRC) was achieved through facile carbonization. The prepared PRC possessed a 3D microcellular porosity generated by interconnected secondary carbon sheets with a large pore size of 100 μm. Ni nanoparticles were further embedded in the PRC. A PRC/Ni composite was achieved with both high conductivity and a large surface area. The designed PRC/Ni/S cathode exhibited a high reversible capacity of 1257 mAh g⁻¹ at 0.2 C and achieved a 65% capacity retention after 500 cycles. It was concluded that the excellent properties resulted from the improved conductivity and increased polysulfide adsorption of the PRC/Ni structure.

4.1.4. Hierarchical porous carbon

Hierarchical porous carbon, combining different types of pore sizes, such as micropores, mesopores, and even macropores, has also drawn extensive attention. Pores with different sizes have distinct roles in the electrochemical performance. Macroporous structures are typically used to accommodate and encapsulate enough sulfur to obtain Li-S batteries with desirable energy densities. Mesoporous structures are also beneficial to electrolyte access for good charge transfer kinetics. Resulting from their specific spatial confinement and an abundance of adsorption sites, micropores can confine sulfur species and mitigate the shuttle effect. The

design and fabrication of sulfur hosts, combining various pore structures, will therefore contribute to desirable sulfur cathodes.

Various approaches have recently been proposed to design hierarchical porous carbon for improving Li-S batteries.^[47, 102, 109, 110] For instance, Pei *et al.* designed a unique 2D yolk-shell carbon nanostructure to build a self-supporting cathode.^[111] This yolk-shell nanostructure consisted of highly dispersible graphene encapsulated in hollow mesoporous carbon nanosheets (G@HMCN). As illustrated in **Figure 4f**, G@HMCN revealed a clear void space between the core and the shell. A free-standing and flexible G@HMCN/S-G hybrid paper cathode was obtained by vacuum filtration of the aqueous dispersion containing G@HMCN/S and graphene. The authors investigated three G@HMCN/S-G cathodes with different sulfur loading (2.0, 3.5, and 5.0 mg cm⁻²). From the cycling performance shown in **Figure 4g**, all of them revealed high sulfur utilization at 0.2 C. Also, three G@HMCN/S-G cathodes exhibited good rate capability even up to 4 C (**Figure 4h**). Moreover, a higher sulfur loading was reached at 10 mg cm⁻², giving rise to an increase in areal storage capacity to 11.4 mAh cm⁻². This research demonstrated that self-supporting structures can effectively mitigate capacity degradation and offer insights into the application of Li-S batteries with high energy density.

4.2. Graphene

Graphene, composed of a few layers of graphite atoms, is a 2D carbon material with fascinating electrical and mechanical characteristics. The excellent conductivity and large specific surface area make graphene a highly promising sulfur host material.^[112] Various methods have been developed to synthesize and modify graphene and its derivatives to improve the electrical conductivity and confinement of polysulfides.

In order to localize active sulfur species at the cathode side, Zhou *et al.* designed a novel sulfur cathode where pure sulfur was sandwiched between two graphene layers.^[113] The active sulfur material was coated with a graphene membrane at one side, which was used as a current

collector. A commercial separator was covering another graphene membrane. The sulfur composite electrode wrapped by these two graphene membranes enabled fast charge transfer pathways, mitigated the volumetric expansion of sulfur, and alleviated the shuttle issue. This sandwich electrode structure contributed to Li-S batteries with higher energy density. Recently, Li-S batteries with high volumetric energy densities were achieved by Li *et al.*, using dense graphene monolith (GM) to host the Li_2S_6 catholyte.^[114] The authors produced “ink-bottle-like” (IB) pores in GM through a phosphoric acidic activation process. The final IBGM structure was obtained by capillary evaporation-induced drying (CEID). Because of the narrow neck and wide-body pore configuration, polysulfides were readily confined in IBGM. Consequently, a composite cathode loading of 5.6 mg cm^{-2} sulfur (54% loading) revealed a high volumetric capacity of 653 mAh cm^{-3} . Furthermore, a $100 \text{ }\mu\text{m}$ thick cathode exhibited an extraordinary volumetric energy density of up to 408 Wh L^{-1} .

The functionalization of graphene gives rise to a change in molecular structure, which not only enhances the affinity of polysulfides but also accelerates the charge transfer kinetics. For example, by employing a template-free thermally induced expansion approach, Song *et al.* prepared nitrogen-doped graphene (NG) sheets with highly crumpled structures, which displayed a large surface area and a considerably high pore volume.^[115] The interweaving of the NG sheets offered many nitrogen-containing active sites, which allowed strong polysulfide adsorption and high sulfur content in the NG host. The obtained NG-S composite cathode with 80 wt.% sulfur loading showed an initial storage capacity of 1227 mAh g^{-1} and durable cycling stability. Meanwhile, cathodes with 5 mg cm^{-2} sulfur loading showed an areal storage capacity of 5 mAh cm^{-2} . The abundant porosities, interwoven structures, and favorable polysulfide adsorption resulting from the NG sheets, contributed to the excellent electrochemical performance.

Duan *et al.* synthesized N-doped graphene (rNGO) with a 3D porous framework structure via an *in situ* hollow cathode discharge plasma (HCD) approach.^[116] As illustrated in **Figure**

5a, a GO suspension was freeze-dried to generate uniform 3D GO frameworks. With an argon and nitrogen flow treatment, these frameworks underwent synchronous reduction and N-doping by HCD, resulting in high-quality 3D rNGO. The rNGO/S composite was obtained by infiltrating the S/CS₂ solution into rNGO. Compared to the rGO/S composite cathode, rNGO/S exhibited better rate capability at various current densities (**Figure 5b**). Moreover, rNGO/S maintained a higher capacity retention than rGO/S at 1 C, achieving a steady capacity of 578 mAh g⁻¹ after 1000 cycles (**Figure 5c**). This rNGO framework increased the charge transfer kinetics and offered highly effective interactions between nitrogen atoms and polysulfides, which minimized the polysulfide shuttling in the rNGO/S composite cathode.

Reduced graphene oxide (rGO) can offer sufficient electrode conductivity and maintain certain polarity that facilitated to confine polysulfides. Therefore, it has been considered as good sulfur hosts. Wang *et al.* proposed a facile approach employing amino-functionalized rGO to covalently stabilize active sulfur species.^[117] Ethylenediamine (EDA) was chosen for functionalization since it offered a strong affinity of lithium sulfides and effectively prevented the loss of active mass. Density functional theory (DFT) calculations revealed high binding energies of EDA-functionalized rGO (EFG) towards lithium sulfides. The synthesized EFG-S cathode combined a steady capacity retention of up to 80% at 0.5 C within 350 cycles with excellent rate capabilities.

The combination of rGO and graphene foam (GF) has been reported by Hu *et al.* as sulfur host.^[118] Highly conductive GF prepared via chemical vapor deposition (CVD) acted as a substrate to assemble conductive rGO aerogels. The as-obtained 3D GF-rGO hybrid material revealed a hierarchically interconnected structure, which successfully increased the contents and areal sulfur loading in the cathode. The hierarchical network helped retain the electrolyte and effectively alleviated the volume variation of sulfur cathodes during cycling. Benefiting from the integrated merits of favorable conductivity and high host porosity, the high loading GF-rGO/S cathodes exhibited a high areal capacity of more than 10 mAh cm⁻² with good

capacity retention of over 350 cycles. Another research involved hydrothermally reduced graphene oxide (rGO) as a conductive matrix to efficiently wrap submicrometer sized sulfur particles.^[119] Thiosulfate was reduced by concentrated HCl to form sulfur particles homogeneously distributed on rGO with the addition of polyvinylpyrrolidone (PVP). Evaluated as sulfur cathodes, this composite electrode displayed a reversible capacity of over 900 mAh g⁻¹ at 0.2 C and more than 650 mAh g⁻¹ after 100 cycles.

Graphene combined with other types of carbons, *e.g.* CNTs, is also a promising approach to form effective host materials for sulfur composite cathodes.^[120-123] Zhang *et al.* employed a facile pyrolysis approach to integrate graphene nanosheets (GN) with CNTs to a unique 3D GN-CNT matrix.^[124] CNTs were *in situ* grown on GN and revealed strong covalent bonding to GN. As shown in **Figure 5d**, even with the ultrasonic treatment, CNTs still adhere well to GN. The grown CNTs revealed an external and inner diameter of 38 and 32 nm, respectively (**Figure 5e**). The CNT density and length could be easily regulated. This 3D GN-CNT matrix had two advantages: (1) the open and porous structure offered rapid charge transfer pathways and accelerated electrolyte penetration; (2) abundant nitrogen, oxygen dopants, and cobalt nanoparticles, existing in the GN-CNT matrix, were beneficial to the immobilization of active sulfur species via chemical interaction. The resulting S/GN-CNT composite cathodes exhibited effective sulfur utilization and high capacity for more than 500 cycles. Both at 0.5 and 1 C, the cathodes revealed only a slow capacity fading (**Figure 5f**).

Another similar research was presented by Yang *et al.* Nitrogen-doped CNTs (NCNTs) were *in situ* grown on graphene via a nickel-catalyzed thermolysis method, synthesizing a NCNT-G composite.^[125] The grown NCNTs indicated good chemical bonding to graphene, in which NCNTs were regularly distributed. The graphene sheets facilitated an efficient charge transfer network. In addition, the highly doped NCNTs enhanced the chemical anchoring of polysulfides. The NCNTs in combination with graphene inhibited the polysulfide shuttle effect and guaranteed a high sulfur utilization. The obtained NCNT-G/S electrode showed a highly steady

storage capacity of 1484 mAh g⁻¹ at 0.1 C. Even at 1 C, it still maintained 400 cycles with a capacity fading as low as 0.06% per cycle.

4.3. Carbon nanotubes and nanofibers

Due to their high aspect ratio and excellent conductivity, CNTs and carbon nanofibers can provide a high surface area for anchoring active sulfur species and create better conductive networks in the electrodes. The one-dimensional configuration substantially enhances the electron conduction between current collectors and sulfur species. In addition, their outstanding mechanical properties are capable of mitigating the volume variation of sulfur cathodes upon cycling. These merits allow them to design and fabricate highly flexible and freestanding sulfur composite cathodes.

4.3.1. Carbon nanotubes

Integrating CNTs with sulfur as cathodes has been considered as a promising method for better Li-S batteries.^[126-128] A typical approach is to heat the mixture of sublimed sulfur and CNTs under optimized conditions, preparing sulfur composite cathodes. However, the mixing and heating method has an implicit drawback for CNTs. The inhomogeneous dispersion of sulfur particles might incur low utilization of cathode materials and inferior cycling stability.

Inspired by the sulfur solubility in CS₂, Guo *et al.* proposed a novel approach to impregnate disordered CNTs (DCNTs) with sulfur.^[129] The dissolved sulfur in CS₂ was uniformly impregnated into the DCNT arrays. The sulfur-impregnated DCNTs (SDCNTs) were subsequently heated in a vacuum-sealed quartz tube at optimized temperatures. This method had two advantages: (1) the high-temperature heating facilitated the vaporized sulfur incorporation into DCNTs, in which the liquid electrolyte penetration was prevented; (2) S₈ molecules were broken into smaller S₆ or S₂ molecules, enabling the formation of sulfur-carbon bonds. A new charging-discharging mechanism emerged, which did not involve anymore the

soluble polysulfide intermediates from the Li-S₈ reaction. The voltage curves of SDCNT obtained with the high-temperature treatment revealed that both the conversion of sulfur to S₆²⁻ and the reduction of S₆²⁻ to S₄²⁻ have almost disappeared. The CV observation also indicated a new charge transfer mechanism as represented by a new cathodic peak. The heat treatment had a critical impact on the electrochemistry of SDCNT cathodes. A 500 °C heating allowed the SDCNT cathodes to show a high capacity retention of up to 72.9% over 100 cycles at 0.25 C.

Given the excellent conductivity of CNTs, it is expected to achieve high-rate sulfur cathodes. A super-aligned CNT (SACNT) matrix has been employed to anchor sulfur nanocrystals.^[130] The SACNT exhibited a large aspect ratio of about 10⁴ and intense intermolecular interactions between tubes and bundles. As illustrated in **Figure 6a** the SACNT bundles were impregnated with a sulfur-ethanol solution. The ultrasonic dispersion induced swelling of these bundles to a continuous 3D network with highly open and porous structures. With the dropwise addition of deionized water, sulfur nanoparticles deposited uniformly on SACNT, forming a nano S-SACNT composite as a flexible and binder-free electrode after drying. Such nano S-SACNT electrodes delivered a capacity of 1071 mAh g⁻¹ in the first cycle at 1 C. The corresponding capacity retention was as high as 85% over 100 cycles with nearly 100% Coulombic efficiency (**Figure 6b**). Compared to the rigid sulfur host materials, the flexible nano SACNT enabled a more accessible network for adequate electrolyte infiltration and fast charge transfer, giving rise to the excellent electrochemical performance. The 85% capacity retention at a high current density enabled Li-S batteries with high power density.

An increase in sulfur content of the electrodes is obviously beneficial for the energy density. Aligned CNTs have therefore been employed as sulfur host by Cheng *et al.*^[131] The authors developed a scalable, facile, and one-step ball milling strategy to fabricate the CNT/sulfur composite cathodes. Sulfur was well confined in the aligned CNTs with interconnected conductive networks. Such a strategy considerably increased the tap density of composite cathodes, implying enhanced specific capacity and energy density. The composite cathode

reached 90 wt.% sulfur loading with a high tap density, delivering favorable storage capacities based on the whole electrode mass. The significantly increased sulfur content was proven to be a promising alternative for aligned CNTs to practical applications. A facile bottom-up strategy has been proposed by the Zhang group to design a hierarchically freestanding CNT-S paper cathode.^[132] Specifically, 15 nm wide multi-walled CNTs (MWCNTs) with 10-50 μm long were chosen to host sulfur because of the short-range conductivity. Moreover, the authors also used vertically aligned CNTs (VACNTs) more than 1000 μm long to provide long-range conductivity. The hierarchically conductive CNT networks were able to reach ultrahigh sulfur-loading up to 17.3 mg cm^{-2} through piling three CNT-S papers. This stacked cathode revealed an areal capacity of 15.1 mAh cm^{-2} . The bottom-up electrode design offered a good alternative to efficiently load active sulfur species for practical applications.

More recently, based on theoretical considerations, Fang *et al.* indicated that CNTs with smaller diameter revealed a high conductivity efficiency because of the shorter electron transfer distance. The authors designed a lightweight single-wall CNT (SWCNT) network with interconnected structures to host sulfur.^[133] This freestanding network achieved flexible film cathodes composed of almost pure sulfur (APS), in which the sulfur content was as high as 95 wt.% (**Figure 6c**). The interwoven SWCNT network contributed to accelerated pathways for charge transport and also allowed polysulfides confined within the cathode. Consequently, the areal sulfur loading of electrodes substantially increased to 7.2 mg cm^{-2} through a simple stacking. A high areal storage capacity of nearly 9 mAh cm^{-2} was attained with a favorable cycle life (**Figure 6d**).

Functional modifications of CNTs are attractive strategies to boost the utilization of sulfur. CNTs with amine functionalization has been demonstrated to effectively promote the polysulfide immobilization. For instance, Ma *et al.* designed and synthesized a hybrid sulfur host consisting of CNTs covalently linked to polyethylenimine (PEI) polymers with abundant amine groups.^[134] As determined by DFT analyses and spectroscopic measurements, the amine

groups in the PEI chain revealed strong and covalent-like bonds with polysulfides. The authors further analyzed the polysulfide dissolution kinetics in the tetraglyme solvent by measuring the time-dependent concentration. CNT-PEI substantially decreased the dissolution rate of polysulfides into the electrolyte. Associated with the interconnected conductive CNT substrate, the composite cathodes with 70 wt.% sulfur maintained a capacity of 750 mAh g⁻¹ after 300 cycles at 0.5 C.

Another aminated carbon nanotubes network for sulfur host had also been employed recently. Yan *et al.* used ethylenediamine (EDA) to modify CNTs networks and then covered these with polyaniline, forming a 3D ferroconcrete-like architecture (P@E-CNT).^[135] The prepared P@E-CNT/S composite preserved the initial morphology (**Figure 6e**). The EDA moieties were very effective to anchor the polar discharge products at nonpolar carbon, hence efficiently preventing polysulfides from dissolving into the electrolyte. The polyaniline layers provided a favorable blocking effect on restraining polysulfides within cathodes. The authors analyzed the chemical adsorption of E-CNT towards sulfur species by DFT calculations. E-CNT revealed a strong binding energy of 1.95 eV towards Li₂S with the smallest steric hindrance, which was much stronger than pristine CNTs. The resulting P@E-CNT/S cathode exhibited a capacity of 1215 mAh g⁻¹ in the first cycle at 0.2 C. A reversible storage capacity up to 975 mAh g⁻¹ was attained after 200 cycles (**Figure 6f**). Overall, modifying nonpolar CNTs with polar components to chemically anchor sulfur species offers a desirable approach to improve Li-S batteries.

4.3.2. Carbon nanofibers

The morphology and conductivity of carbon nanofibers (CNFs) are similar to those of CNTs, while CNFs possess a significantly larger diameter. Therefore, CNFs with hollow structures possess larger inner space to accommodate sulfur, which is beneficial to the polysulfide confinement.

Research on CNFs as a sulfur host has been reported to boost the performance of Li-S batteries.^[49, 136, 137] For instance, the early exploration by Cui and co-workers was to encapsulate sulfur in hollow carbon nanofiber arrays.^[138] Synthesized by thermal carbonization of polystyrene on anodic aluminum oxide (AAO) templates, CNFs with high aspect ratio provided a high-quality matrix for anchoring polysulfides. Sulfur was effectively confined in the interior of CNFs, limiting the direct exposure to the electrolyte only through the two open ends. The developed hollow carbon nanofiber-encapsulated sulfur cathodes achieved high capacities for more than 150 cycles at 0.2 C. In their follow-up study, hollow CNFs modified with an amphiphilic surface were introduced to improve the cycling performance.^[139] The amphiphilic surface rendered strong chemical bonding between polar polysulfides and the nonpolar carbon, effectively stabilizing the discharge products. This modification strategy enabled sulfur cathodes a capacity up to 1180 mAh g⁻¹ at 0.2 C and maintained an 80% storage capacity after 300 cycles at 0.5 C.

Due to the open end morphology of CNFs, the electrolyte is inevitably in contact with active sulfur species during cycling, leading to dissolution and diffusion of polysulfides out of the cathode. Designing hollow carbon nanofibers (HCFs) with closed ends would therefore be an interesting solution for this drawback. Zhang *et al.* reported a sulfur host of HCFs with closed ends and dynamically adjustable pore sizes.^[140] By etching the SiO₂ layer at the surface of HCFs, the carbon network gradually stacked together and the initial mesopores in the walls were retracted to micropores. Such dynamically adjustable pore sizes eliminated the excessive exposure of sulfur species to the electrolyte and the closed structure further blocked the polysulfide dissolution from both ends. The as-prepared S@HCF cathodes exhibited an adequate sulfur utilization of up to 98%, excellent rate capabilities at high current densities, and a high capacity of 847 mAh g⁻¹ at 2.0 C after 300 cycles with a low capacity fading of 0.055% per cycle.

The insulating nature of sulfur impedes the rate capability of sulfur cathodes. Several studies have developed CNFs with various structures to enhance the rate performance. For example, the Manthiram group synthesized multichannel carbon nanofibers (MCNF) by simple single-nozzle co-electrospinning and a KOH activation reaction (**Figure 7a**).^[141] The obtained MCNF, comprising parallel mesoporous channels with interconnected microporous structures, was demonstrated to be a favorable sulfur reservoir (**Figure 7b**). By the KOH activation process, the produced MCNF (a-MCNF) revealed nanoscale pores and oxygen-containing groups, further enhancing the anchoring of sulfur at the carbon nanofibers. The S-a-MCNF composite cathode was loaded with 2.2 mg cm⁻² sulfur and showed outstanding rate capabilities. Even at 5 C, an 847 mAh g⁻¹ storage capacity was still attained (**Figure 7c**). The improvement of the rate capability was attributed to two elements: (1) mesoporous multi-channels facilitated the electrolyte to penetrate the carbon nanofibers and shortened the charge transfer pathways; (2) sulfur species were well dispersed in the micropores with the assistance of the oxygen-containing groups, resulting in firm adsorption of sulfur particles onto the carbon nanofibers.

In order to achieve a high areal capacity for practical applications, Yun *et al.* reported an interwoven CNF matrix as sulfur host to anchor the polysulfides.^[142] Polyacrylonitrile was chosen as the precursor to produce the electrospun CNFs. The interwoven CNF structures created cross-junctions via interconnected networks. As shown in **Figure 7d**, sulfur particles were intertwined between the nanofibers by impregnating the heat-treated CNF sheets with 1-methyl-2-pyrrolidone and the sublimed sulfur mixture. This simple design achieved tunable sulfur loading in CNFs. On the basis of the viscosity of polysulfides, the entanglement of interwoven CNF matrices effectively adsorbed polysulfides via cohesive forces. The obtained CNF-S cathodes loaded with 4.4, 6.0, and 10.5 mg cm⁻² exhibited favorable storage capacities and cycling stabilities (**Figure 7e, f**). Another example involves the preparation of hierarchically porous carbon nanofiber (HPCNF) via a simple electrospinning approach to achieve a freestanding cathode with high sulfur loading.^[143] The HPCNF structure possessed

macropores surrounded by micro/mesopores near the edges. The macropores accommodated a large number of sulfur species and the denser micro/mesoporous structures impeded the sulfur losses during cycling. The hierarchical architecture allowed the sulfur loading of more than 12 mg cm⁻² and significantly utilized sulfur species up to 80% with an 11.3 mAh cm⁻² areal capacity.

Because of the nonpolar nature, CNFs have relatively weak chemical interaction with polar polysulfides. Increasing the polarity of CNFs is a promising approach to chemically anchor sulfur species. This can be achieved by doping or composition to modify the CNFs.^[144, 145] For instance, Li *et al.* integrated nickel nanoparticles with N-doped porous carbon nanofibers as sulfur host.^[146] The synthesized composite host efficiently encapsulated sulfur in the network. The porous structures benefited the spatial confinement of polysulfides and shortened the charge transport pathways. Moreover, the Ni nanoparticles and nitrogen doping enhanced the chemical anchoring of polysulfides, causing favorable redox kinetics. The composite cathodes exhibited good capacities with low polarization at various current densities. At 0.2 C, a high capacity up to 1320 mAh·g⁻¹ was attained.

Other approaches include the combination of the merits of CNFs and CNTs to reach advanced sulfur hosts.^[147, 148] For instance, Zhang *et al.* integrated porous carbon nanofibers with CNTs to fabricate free-standing PCNF/CNT films.^[149] Such a carbon structure presented a 3D interconnected network, offering a high sulfur loading, good electrolyte penetration, and the mitigation of volume variation of cathodes. The nitrogen and oxygen doping further improved the chemical anchoring of polysulfides. The resulting S/PCNF/CNT film cathodes revealed favorable cycling stabilities and rate capabilities with 3.9 mg cm⁻² sulfur loading. Moreover, a multi-layer stacked electrode reached a 12 mg cm⁻² sulfur loading, exhibiting an areal capacity of nearly 11 mAh cm⁻² after 50 cycles.

4.4. Heteroatom-doped carbon

Nanostructured carbon with heteroatom doping can anchor sulfur species by chemical bonding, which will boost the suppression of the shuttle effect. Heteroatom doping has been introduced to various carbon precursors, such as graphene,^[115, 150] CNTs,^[73, 151] and porous carbon.^[152] Among them, nitrogen doping has been proven as a promising approach. For example, a novel nitrogen and oxygen dual-doped nonporous carbonaceous material (NONPCM) was synthesized by Mi *et al.* to improve sulfur cathodes.^[153] The polar NONPCM possessed abundant active sites to chemically confine sulfur species. XPS analyses and DFT calculations revealed that the presence of Li-N bonds significantly inhibited the polysulfide dissolution and enhanced the utilization of sulfur species. NONPCM loaded with 70 wt.% sulfur exhibited a stable capacity up to 540 mAh g⁻¹ at nearly 1 C after 300 cycles. Lu *et al.* designed a new dodecylamine micelle-induced nitrogen-doped carbon comb (NCC) as sulfur host.^[154] This nitrogen-doped NCC substantially increased the conductivity of cathodes and introduced the chemical anchoring towards polysulfides, effectively suppressing the losses of sulfur species upon cycling. As a result, NCC with a high loading of sulfur achieved an impressive cycling lifespan and rate performance. Besides, Chen *et al.* grew ZIF *in situ* on graphene nanosheets and then converted these into nitrogen-doped porous carbon (NPC/G) by carbonization.^[72] The doped nitrogen enabled the successful immobilization of polysulfides by chemical adsorption. The composite cathode achieved 1372 mAh g⁻¹ in capacity at a moderate current.

Apart from nitrogen doping, phosphorus,^[76, 155] boron,^[151, 156] and sulfur doping^[150, 157, 158] are also advantageous to the polysulfide confinement. Wang *et al.* proposed a facile approach to fabricate double-shelled N and P doped carbon spheres (NPDSCS), which showed good trapping for polysulfides via strong chemical affinity.^[75] XPS analyses of NPDSCS-S composite cathodes revealed the formation of P-S and P-Li bonds after cycling. DFT calculations demonstrated that the binding energies of polysulfides significantly increased with the introduction of P-doping. These results validated the strong chemical interactions between NPDSCS and polysulfides. At 0.1 C, a 1326 mAh g⁻¹ capacity was achieved based on an

NPDS-CS cathode loading of 72.4 wt.% sulfur. A boron-doped porous carbon sphere/graphene hybrid (BPCS-G) was developed by Ai *et al.*^[159] With a high boron dopant content up to 6.51 wt.%, BPCS-G exhibited favorable polysulfide adsorption. The effectiveness of chemical binding polysulfides with BPCS-G was confirmed by DFT calculations. Consequently, the corresponding BPCS-G/S cathode combined a high capacity at 0.02 C with a prolonged cycling life at 0.5 C over 500 cycles with 0.05% capacity fading per cycle.

4.5. Carbon nitride

Carbon nitride (C_3N_4) is a type of compounds composed of continuous tri-s-triazine or triazine building blocks with a high ratio of nitrogen to carbon. C_3N_4 compounds have been extensively developed and investigated for energy storage and catalysis.^[160] Due to the abundant polar functional groups, C_3N_4 can offer a number of anchoring sites (*e.g.* pyridinic N) to confine polysulfides by chemical interactions. On the other hand, the poor conductivity of C_3N_4 is detrimental to the charge transfer kinetics of sulfur cathodes. Integrating other highly conductive materials with C_3N_4 is a favorable approach to improve the utilization of sulfur species. The Nazar group initially demonstrated that a light-weight nanoporous graphitic C_3N_4 (g- C_3N_4) had superior polysulfide adsorptivity.^[161] As sulfur host, g- C_3N_4 ensured an ultra low capacity loss of 0.04% per cycle during long-term cycling (1500 cycles) at 0.5 C.

In their follow-up research, they employed alternately stacked g- C_3N_4 and graphene to construct a stable cathode with high sulfur content.^[162] As shown in **Figure 7g**, a hybridization process formed an integrated sulfur host. Sulfur was then loaded into the host via self-assembly and sulfur diffusion. With a cross-linked elastomeric binder carboxymethyl cellulose (CMC), a crack-free and compact electrode with 14.9 mg cm⁻² sulfur loading has been obtained by traditional slurry processing. Such an integrated sulfur host enabled desirable conductivity and polysulfide anchoring, which was verified by DFT calculations and potentiostatic titration. The cross-linked CMC binder was beneficial to particle adhesion and electron transport. This

comprehensive strategy enabled the electrode with an ultralow electrolyte/sulfur ratio of 3.5:1 ($\mu\text{L}:\text{mg}$). An initial areal capacity of nearly 15 mAh cm^{-2} was attained (**Figure 7h**). The combination of a superior graphene conductivity network and chemical adsorption of g- C_3N_4 towards polysulfides played a major role in the performance enhancement of these sulfur cathodes.

In addition to the strong affinity with polysulfides, C_3N_4 also showed a favorable influence on the charge transfer kinetics. On the basis of theoretical calculations, Liang *et al.* confirmed the presence of electrostatically-induced strong interaction between polysulfides and polymeric C_3N_4 (p- C_3N_4).^[163] They fabricated a p- C_3N_4 /graphene hybrid material to directly host the Li_2S_6 catholyte. Compared to pure graphene, p- C_3N_4 /graphene contributed to good polysulfide redox stability and considerably good charge transfer kinetics. Such an effect was ascribed to the strong affinity of p- C_3N_4 which changed the steric and bonding configurations of polysulfides.

Gong *et al.* proposed a self-assembly method to prepare a nanocomposite composed of 3D porous C_3N_4 nanosheets and rGO (PCN@rGO).^[164] The PCN has numerous polar sites, allowing chemically immobilization of polysulfides, and rGO facilitated fast electron transfer. The resulting sulfur composite electrode delivered a capacity of about 1000 mAh g^{-1} at 0.5 C, which was more or less stable up till 800 cycles. Another work involving the integration of g- C_3N_4 and porous graphene was presented by Wang and coworkers.^[165] The authors introduced g- C_3N_4 into a 3D hierarchically porous graphene structure. The formed g- C_3N_4 nanosheets in the graphene network catalyzed fast polysulfide conversion, effectively enhancing the sulfur utilization. Further integration of C_3N_4 with graphene or CNTs has also been developed.^[166, 167]

Considering the intrinsic advantages and current achievements, nanostructured carbon host materials have tremendous potential for practical applications in Li-S batteries. On the basis of these advances, nanostructured carbon host materials used in Li-S batteries are listed in **Table 1**, presenting the latest studies of host structures and battery performance parameters for comparison.

5. Polymer hosts

Polymers have long been considered as promising sulfur host materials, since they have the following advantages for sulfur cathodes: (1) favorable conductivity benefits the charge transfer kinetics of sulfur cathodes; (2) abundant functional groups can chemically confine active sulfur species; (3) mechanical flexibility affords the volume variation of sulfur cathodes during cycling; (4) facile synthesis conditions allow fast incorporation of sulfur. A number of studies demonstrated that polymer-sulfur composites were formed by various approaches such as coating, encapsulation, and vulcanization.

The Cui group has conducted thorough research into polymer coatings to improve sulfur cathodes.^[168-170] They investigated sulfur cathodes fabricated from different polymer-coated hollow sulfur nanospheres. The results revealed that the polymer shells were able to physically confine polysulfides. The chemically bound Li_xS ($1 \leq x \leq 2$) to the heteroatoms from polymers substantially boosted the cycle life of sulfur cathodes. Lim *et al.* employed a facile surface-induced cross-linking polymerization strategy to coat a polymer on sulfur cathodes.^[171] The cross-linked polymer layer was chemically anchored to the sulfur electrode by coordinated Cu ions. Such an electrode maintained an interesting storage capacity of nearly 700 mAh g⁻¹ for 100 cycles at high currents.

Jia *et al.* synthesized Fe-doped macroporous conjugated polymers with Fe-doping as sulfur host.^[172] As illustrated in **Figure 8a**, poly(3-hexylthiophene) (P3HT) was *in situ* grown on RGO sheets. Then a gelation process in p-xylene followed by freeze-drying formed macroporous conjugated polymers (RGO-g-P3HT). The macroporous RGO-g-P3HT hosts possessed a high pore volume up to 34 cm³ g⁻¹ with tunable porosities, ensuring excellent encapsulation of sulfur. DFT calculations demonstrated the enhanced interaction between the P3HT frameworks and polysulfides with the incorporation of Fe (**Figure 8b**). The sulfur composite cathode with Fe-doping exhibited enhanced capacities and cycling stabilities, indicating that Fe-doping

accelerated the charge transfer kinetics of sulfur cathodes and hence inhibited the shuttle problem of polysulfides.

The main-chain imidazolium-based ionic polymer (ImIP) has also been introduced as sulfur host materials by Cheng *et al.*^[173] It was demonstrated to be efficient for anchoring polysulfides. Due to the electrostatic interactions between polysulfides and ImIP, the polysulfide shuttling was significantly inhibited and the charge transport was also accelerated. Such a novel anchoring approach of polysulfides allowed sulfur cathodes with good reversible capacities and durable cycle life.

By means of vulcanization, Park and co-workers synthesized sulfur-rich polymers with 3D interconnected networks as cathode active materials.^[174] The authors proposed a soft template preparation, starting from porous trithiocyanuric acid (TTCA) crystals. The TTCA template was initially vulcanized at 160 °C in a sealed vessel to encapsulate sulfur in the pores. A thermal treatment at 245 °C resulted in the sulfur ring-opening and subsequent polymerization at the thiol surfaces, generating 3D interconnected sulfur-rich polymers. This vulcanization approach was facile to synthesize organosulfur compounds with tunable morphology. The cathodes with sulfur-rich polymers achieved a high storage capacity of 850 mAh g⁻¹ with 83% capacity retention after 450 cycles. A strong rate capability was attained at 5 C with a reversible capacity of up to 730 mAh g⁻¹. The enhanced performance was obtained from the complete anchoring of polysulfide intermediates onto the vulcanized polymers and the fast charge transport facilitated by the amine groups of TTCA frameworks. In their follow-up research, sulfur-rich polymers synthesized from different functional linkers were reported.^[175] The authors prepared these sulfur-rich polymers from four ligands with quinone and triazine structures. The results revealed that the tetra(allyloxy)-1,4-benzoquinone (TABQ) ligand (**Figure 8c**) allowed the sulfur cathode to significantly increase the conductivity by about 450 times. Furthermore, the corresponding redox kinetics also enhanced twofold. Benefiting from these improvements, the prepared poly(S-TABQ) cathodes exhibited an excellent capacity of 1346 mAh g⁻¹ in the first

cycle and maintained steady for over 100 cycles at 0.1 C (**Figure 8d**). Even at an ultrahigh 10 C-rate, poly(S-TABQ) still reached 833 mAh g⁻¹ in capacity. The introduction of TABQ resulted in a homogeneous sulfur distribution and facilitated charge transport in the sulfur-rich polymers frameworks. Associated with the polar anchoring of TABQ, poly(S-TABQ) attained a considerable increase in electrochemical performance.

Vulcanization or sulfurization results in the covalent binding of sulfur onto the polymer surface via C-S bonds, which might change the (dis)charging mechanism of sulfur cathodes. Some of the studies confirmed that sulfurized polymers by the high-temperature process showed only a single sloping voltage plateau near 2 V with a significant voltage hysteresis.^[95, 176, 177] This is mainly because short sulfur chains are generated at high temperatures, eliminating the conversion from S₈ molecules to soluble long-chain polysulfide intermediates during cycling. For instance, Liu *et al.* employed SBA-15 with ordered mesoporous structures as a template to prepare mesoporous sulfurized polyacrylonitrile (MSPAN).^[178] As schematically shown in **Figure 8e**, an *in situ* polymerization process produced the SBA-PAN composite. Followed by direct sulfurization, sulfur was incorporated into PAN. The resulting MSPAN composite was achieved by the HF etching to remove the SBA-15 template. MSPAN with highly ordered mesopores revealed a large surface area, hence improving the electrolyte impregnation and charge transport. MSPAN cathodes displayed a distinct reaction mechanism in the CV curves, only revealing a broad cathodic peak below 2.0 V. This CV result indicates that no polysulfides were produced since active sulfur species mainly existed in the form of S₃ or S₂ chains covalently bound to the PAN backbone. Besides, Tsao *et al.* coated sulfur by aniline polymerization.^[179] The obtained sulfur@polyaniline (S@P) then convert into vulcanized polymers (S@h-P) via a facile thermal treatment. S@h-P exhibited cross-linked networks with abundant covalently bound sulfur. Due to the complete elimination of the polysulfide shuttling, the S@h-P cathode exhibited satisfactory cycling stabilities and desirable rate performance.

Overall, polymers applied as host materials can confine sulfur species via three different approaches: (1) similar to carbon-based materials, the facile tuning of structures allows polymers as desirable barriers to physically block polysulfides; (2) the presence of abundant surface groups further enhances the polysulfide anchoring via chemical anchoring; (3) the covalent bonding of polymers gives rise to a distinct anchoring mechanism of sulfur species from other confinement approaches. The intrinsic merits of polymer materials considerably broaden the design and understanding of sulfur host electrodes. A summary of performance parameters for polymer host materials used in Li-S batteries is listed in **Table 2**.

6. Metal compound hosts

Various polar metal compounds possess strong chemical interactions with polysulfides. Compared with non-polar carbon, such polar host materials reveal much stronger chemical anchoring of polysulfides. They can mitigate the polysulfide loss and improve sulfur utilization. On the other hand, the poor conductivity of some metal compounds restricts the rate capability of these sulfur cathodes. Metal compounds are therefore often combined with highly conductive carbon materials.

6.1. Metal oxides

Extensive investigations have been carried out to explore the chemical anchoring of metal oxides towards polysulfides. Metal oxides have a strong polar surface due to the presence of oxygen anions. As a result of the abundant polar active sites for the polysulfide adsorption, polar metal oxide hosts substantially promote the electrochemistry of sulfur cathodes.

6.1.1. Titanium-based oxides

The use of titanium dioxide (TiO_2) as sulfur host has been extensively reported. The early work has been investigated by Seh *et al.*, employing TiO_2 as shells to alleviate the cathode volume

swelling caused by the lithiation process.^[180] The authors covered a sulfur core with TiO₂ layers to form a yolk-shell structure, which successfully maintained the integral shell upon cycling for inhibiting the polysulfide dissolution. Various TiO₂ morphologies have been developed to confine polysulfides, such as spheres, nanotubes, and nanosheets.

Using the electrospinning technique with subsequent heat treatment, Qian *et al.* prepared mesoporous TiO₂ nanotubes (MTDNTs) as sulfur hosts.^[181] The MTDNTs with anatase mischcrystal structures combined a hollow morphology with a high surface area of about 100 m² g⁻¹. Sulfur was encapsulated in MTDNTs by mixing MTDNTs with a sulfur/CS₂ solution to get MTDNT/S composites. TEM and SEM analyses indicated the uniform distribution of sulfur in the mesopores of the as-prepared MTDNT walls. Combined with the fast Li⁺ transfer facilitated by the hollow structure, the MTDNT/S composite cathodes exhibited desirable cycling stabilities and good rate performance. Even at 8 C, the reversible capacity still reached 610 mAh g⁻¹. Ni *et al.* introduced mesoporous hollow TiO₂ microboxes to improve Li-S batteries.^[182] CaTiO₃ precursors were employed to synthesize the TiO₂ microboxes by a two-step solvothermal reaction. The authors validated that the TiO₂/S composite with 70 wt.% sulfur showed the optimal electrochemical performance. Ultraviolet-visible spectroscopy (UV-vis) analyses of Li₂S₄ revealed an efficient polysulfide anchoring by TiO₂ microboxes. More recently, Wang *et al.* investigated oxygen-deficient TiO₂ as novel sulfur host.^[183] Based on experimental observations and DFT calculations, they found that the oxygen vacancies boosted the polysulfide adsorption by TiO₂, reducing the shuttle effect. In addition, the oxygen vacancies accelerated the charge transfer at the vacancy-enriched electrode surface, hence catalyzing the electrochemical conversion of active sulfur species. The TiO₂/S composite cathode delivered high capacities, outstanding rate capabilities, and desirable cycling stabilities.

Combining carbon with TiO₂ in sulfur cathodes is beneficial to the electrochemical charge transfer kinetics.^[79, 184] Yu *et al.* deposited atomic TiO₂ layers on a sulfur cathode constructed from nitrogen-doped graphene (NG).^[61] The performance of these composite cathodes was

substantially enhanced due to the on-site polysulfide absorption of TiO_2 and the accelerated charge transfer. The TiO_2 layers in combination with NG offer combined effects: increasing the conductivity of cathodes and alleviating the polysulfide migration. An initial capacity of 1069 mAh g^{-1} at 1 C was reached and showed a capacity retention up to 86% over 500 cycles.

$\text{C@TiO}_2\text{@C}$ hollow microspheres with sandwich structures have been designed as sulfur host to physically and chemically confine polysulfides.^[185] As illustrated in **Figure 9a**, TiO_2 layers were initially coated on polystyrene (PS) microspheres using a sol-gel process. PS@TiO_2 was further covered with a layer of homogenous polydopamine (PDA). Upon carbonization, the final sandwich hollow microspheres were obtained. The TiO_2 layers enabled effective chemical anchoring for polysulfides, while the two carbon shells allowed adequate charge transport pathways and also acted as physical barriers to spatially restrain the movement of polysulfides. Moreover, the hollow cavity structure (**Figure 9b**) alleviated the volumetric change of sulfur cathodes during (de)lithiation. Such a designed $\text{C@TiO}_2\text{@C-S}$ host material achieved a high sulfur loading of 76.4 wt.%, delivering a high storage capacity of more than 1200 mAh g^{-1} at 0.2 C (**Figure 9c**). In addition, TiO_2 nanoparticles were also introduced into a porous carbon matrix. A 3D ordered macro/mesoporous carbon (3DOMC) was in this way designed by Liang *et al.* to be a support of TiO_2 .^[186] The $\text{TiO}_2/3\text{DOMC}$ exhibited a desirable specific surface area with a large pore volume, indicating a high sulfur loading of more than 73 wt.%. The incorporation of TiO_2 nanoparticles successfully inhibited the polysulfide shuttling by their strong electrostatic interaction with polysulfides.

In view of the regular oxygen vacancies in the lattice, the Ti_4O_7 Magnéli phase has been proven highly electronic conductive. The strong adsorption of polysulfides associated with a high conductivity allows Ti_4O_7 to be an effective sulfur host.^[78, 187, 188] Wei *et al.* prepared mesoporous Magnéli Ti_4O_7 microspheres by an *in situ* carbonization process to improve the performance of sulfur cathodes.^[189] These synthesized Ti_4O_7 microspheres revealed interconnected mesopores with large surface area and pore volume. XPS characterization

indicated that the Ti_4O_7 surface formed Ti-S bonding with polysulfides, which enhanced the chemical anchoring with active species. Consequently, the high conductivity of the Magnéli microspheres in combination with the favorable polysulfide anchoring contributed to an improved utilization of these composite cathodes. A high initial capacity of $1317.6 \text{ mAh g}^{-1}$ was attained at 0.1 C .

A similar carbonization reduction process was employed by Wang *et al.* to introduce Ti_4O_7 nanoparticles on the hollow carbon spheres (HCS).^[190] Monodispersed HCS acted as a hard template to coat the TiO_2 shells. Then the obtained HCS@TiO_2 was covered with another polydopamine (PDA) shell. Upon carbonization at high temperatures, TiO_2 was transformed into Ti_4O_7 . The grain growth of Ti_4O_7 was restrained by the PDA shells, resulting in Ti_4O_7 nanoparticles with small size and uniform morphology (**Figure 9d**). The uniformly distributed Ti_4O_7 nanoparticles offered abundant adsorption sites to chemically anchor polysulfides. Compared with the $\text{HCS@TiO}_2/\text{S}$ and HCS/S electrodes, the $\text{HCS@Ti}_4\text{O}_7/\text{S}$ electrodes showed the smallest electrochemical polarization and highest capacity (**Figure 9e**). A very high storage capacity of 1421 mAh g^{-1} at 0.1 C was achieved. Moreover, $\text{HCS@Ti}_4\text{O}_7/\text{S}$ also exhibited significantly enhanced rate capabilities (**Figure 9f**).

TiO also exhibits excellent conductivity because of the high oxygen and titanium vacancies. The Lou group developed TiO@C hollow spheres to improve sulfur cathodes.^[191] These host materials combine a high conductivity with strong polysulfide adsorption. High sulfur content could be loaded into the cavity of the hollow spheres. The polar TiO shell maximized the polysulfide diffusion and enhanced the redox reaction kinetics of sulfur. Further development in their subsequent research demonstrated that the tight packing of the carbon-coated TiO hollow nanospheres resulted in interconnected micro-sized clusters, which achieved significantly higher sulfur loadings.^[192] The as-obtained hierarchically structured sulfur cathodes revealed high capacities at various current densities.

Chen *et al.* integrated conductive polypyrrole (PPy) with heterostructured TiO_x (H-TiO_x , $x = 1, 2$) material to assemble multifunctional sulfur hosts.^[193] H-TiO_x was synthesized from the TiO_2 nanoparticle precursors via thermal reduction followed by acid etching. After sulfur loading, the obtained $\text{H-TiO}_x@\text{S}$ was further covered with PPy shells. The prepared $\text{H-TiO}_x@\text{S}/\text{PPy}$ composite revealed a sandwich-type of morphology (**Figure 9g**). The internal H-TiO_x with Lewis acid properties was capable of anchoring polysulfides via chemical bonding. The external PPy shell physically blocked polysulfides and also formed polar interactions via N-Li bonds. The multifunctional merits of H-TiO_x and PPy contributed to an adequate suppression of polysulfide diffusion and improved the electrochemical charge transfer kinetics. Consequently, the $\text{H-TiO}_x@\text{S}/\text{PPy}$ composite cathode exhibited a very low capacity fading of only 0.04% per cycle over 1000 cycles at 1 C (**Figure 9h**).

6.1.2. Manganese-based oxides

Incorporating sulfur into manganese-based oxide host materials has recently become a promising approach to anchor sulfur species. Among them MnO_2 has been extensively investigated.^[88, 194-196] For instance, Wang *et al.* proposed an innovative design of MnO_2 nanosheets-decorated hollow sulfur spheres (hollow S-MnO_2), which efficiently anchored polysulfides.^[197] As shown in **Figure 10a**, a bottom-up strategy was initially used to prepare almost monodisperse, PVP-encapsulated, hollow sulfur spheres. KMnO_4 was subsequently introduced to react with PVP, generating dense MnO_2 nanosheets covering the hollow spheres. After removing the extra PVP, hollow S-MnO_2 spheres with crumpled shells were obtained. The resulting hollow S-MnO_2 cathodes showed a 644 mAh g^{-1} storage capacity after 1500 cycles at 0.5 C with only 0.028% capacity decay per cycle, demonstrating good utilization of active sulfur species (**Figure 10b**). XPS analyses revealed the interactions between MnO_2 nanosheets and polysulfides. In contrast to the pure MnO_2 , the Mn^{2+} contribution from the Mn $2p_{3/2}$ spectrum of S-MnO_2 indicated a significant increase, implying the partial reduction of

MnO₂. The accompanied Li₂S₄ oxidation was also identified from the S2p spectra. Such redox interactions between MnO₂ and polysulfides substantially enhanced the chemical anchoring of sulfur species. DFT calculations further confirmed that the binding energies of S₈, Li₂S₈, Li₂S₆, Li₂S₄, Li₂S₂ and Li₂S with a δ -MnO₂ nanosheet (100) surface increased from 1.60 to 5.15 eV. These strong bonding energies mainly resulted from the formation of Li-O and S=O bonds.

Although the strong chemical binding of δ -MnO₂ nanosheets with polysulfides can substantially decrease the loss of sulfur species, the conductivity of S-MnO₂ composite electrodes is rather poor. Employing a carbon-coated metal oxide nanoboxes strategy, Rehman *et al.* covered birnessite-type MnO₂ nanosheets with hollow carbon nanoboxes (HCB) to physically and chemically trap polysulfides.^[198] The MnCO₃ nanocubes acted as a template to coat thick SiO₂ layers. Then a thin polymer coating formed the carbon shells. MnO₂@HCB nanoboxes were prepared via carbonization and SiO₂ elimination. **Figure 10c** illustrates the structural advantages of these nanoboxes to be applied as sulfur cathodes: (1) the MnO₂ nanosheets with strong chemical bonds restrained polysulfides inside the cavities; (2) HCB enabled a high sulfur content, alleviated the volume swelling of cathodes, and physically restricted polysulfides from migrating out of the nanoboxes; (3) the hierarchically porous carbon layer facilitated the charge transfer kinetics. The authors proposed an anchoring mechanism of polysulfides to the sulfur host as shown in **Figure 10d**. MnO₂ nanosheets initially *in-situ* oxidized the polysulfides, generating the thiosulfate groups (see reaction step I). Subsequently, the produced polysulfides (step II) were adsorbed by the thiosulfates and converted into polythionate complexes, which mediated the transformation of polysulfides (step III). Hence, the polythionate complexes had a major effect on the polysulfide mediation and anchoring. The prepared MnO₂@HCB/S composite delivered a significant capacity up to 1042 mAh g⁻¹ at 1 A g⁻¹.

Besides MnO₂, MnO and Mn₃O₄ also have been introduced as sulfur host materials.^[199-201] Liu *et al.* developed MnO nanoparticles to anchor polysulfides.^[202] The authors incorporated

MnO nanoparticles in micro-mesoporous carbon (MPC), preparing MnO/MPC composites. Because of the intrinsic polarity, MnO nanoparticles significantly anchored polysulfides within the cathodes. Moreover, the deposition of insoluble Li_2S_2 and Li_2S during the discharge process attained substantial improvement, which accelerated the electrochemical charge transfer kinetics. The resulting MnO/MPC@S cathode with 74% sulfur content exhibited increased specific capacities and capacity retention within 150 cycles in comparison to sulfur cathodes without using MnO.

Chen *et al.* designed a free-standing paper cathode with a layer-by-layer structure.^[203] Such a cathode was composed of Mn_3O_4 nanoparticles embedded in nitrogen-doped CNFs with 3D interconnected structures. The authors started the fabrication from electrospun nanofibers. Subsequent carbonization and base etching resulted in the formation of Mn_3O_4 @CNF paper composites. By direct stacking the Mn_3O_4 @CNF/S layers, the areal sulfur loading can be readily tunable (**Figure 10e**). On the basis of this approach, the authors investigated the Mn_3O_4 @CNF/S cathodes with sulfur loading of 4, 6, and 11 mg cm^{-2} . As shown in **Figure 10f**, the corresponding cathodes delivered a high initial areal capacity of 5 to 12 mAh cm^{-2} and a favorable capacity retention after 100 cycles. The interconnected CNF network enabled sulfur cathodes to create favorable charge transport pathways. The polysulfide shuttle problem was mostly alleviated by both physical confinement and chemical anchoring to CNF and Mn_3O_4 .

6.1.3. Cobalt-based oxides

Cobalt-based oxides have been proven excellent electrocatalytic properties, which have been widely investigated for the oxygen reduction and oxygen evolution reaction.^[204, 205] Using cobalt-based oxides as sulfur hosts has also been reported.^[206-208] Derived from ZIF-67 crystals, Xu *et al.* fabricated a nitrogen-doped Co_3O_4 embedded in nitrogen-doped carbon polyhedrons via simple pyrolysis. With further graphene coating, a nanododecahedra composite was achieved ($\text{N-Co}_3\text{O}_4$ @N-C/rGO).^[209] The synthesized $\text{N-Co}_3\text{O}_4$ @N-C/rGO possessed well-

defined porous structures (**Figure 11a**), desirable conductivities, and special chemical adsorption. As a sulfur host, N-Co₃O₄@N-C/rGO enabled a high sulfur loading, hence achieving a good rate capability of 652 mAh g⁻¹ even up to 3 C (**Figure 11b**). *Ex-situ* Raman spectra verified the strong adsorption of N-Co₃O₄@N-C/rGO towards polysulfides. When the battery was discharged down to 2.1 V for 300 cycles, S₆²⁻ and S₈²⁻ were detected in the N-Co₃O₄@N-C/rGO-S electrode by means of Raman spectroscopy, while the pristine cathode before cycling did not reveal any S₆²⁻ and S₈²⁻ peaks (**Figure 11c**). Furthermore, first-principle calculations indicated that the favorable chemical bond between polysulfides and Co₃O₄, was causing significantly stronger adsorption energies than rGO. These results demonstrated that Co₃O₄ nanocrystals significantly enhanced the polysulfide anchoring.

Combining carbon with Co₃O₄ leads to better electrochemical charge transfer kinetics. Recently, our group reported carbon-coated Co₃O₄ (Co₃O₄/C) double-shelled nanocages as sulfur host.^[57] As illustrated in **Figure 11d**, the ZIF-67 sacrificial template was transformed into hollow nanocages of layered double hydroxides (LDHs), followed by a polydopamine (PDA) layer to form double-shelled LDH/PDA nanocages. Then annealing resulted in the formation of Co₃O₄/C double-shelled nanocages (**Figure 11e**). The as-prepared S@Co₃O₄/C cathodes exhibited a high capacity at 0.2 C (**Figure 11f**). Furthermore, it achieved only 0.083% capacity decay per cycle at 1 C for 500 cycles. The chemical interaction between Co₃O₄ nanocages and polysulfides was validated by the upper- and lower-plateau capacities, visual polysulfide adsorption, and XPS measurements. Such double-shelled nanocages had a combined effect on boosting sulfur cathodes. The highly conductive carbon shells resulted in fast electron transference and charge transfer kinetics. Meanwhile, they also physically confined the polysulfide diffusion. The strong chemical anchoring resulting from the inner Co₃O₄ shells was able to chemically adsorb the polysulfides.

There are also studies involving polar CoO to anchor polysulfides. Ren *et al.* prepared a free-standing 3D porous carbon fiber cloth (PCF) with CoO/Co particles as sulfur host.^[210] Because

of metallic Co and the PCF network, the obtained CoO/Co@PCF host displayed desirable conductivity and therefore the electron transport was greatly accelerated. Moreover, the CoO/Co particles, uniformly dispersed on PCF, allowed abundant adsorption sites to chemically anchor polysulfides. Such strong chemical anchoring was confirmed by immersing CoO/Co@PCF into a Li_2S_4 solution, for which an almost transparent color was observed after 12 h. The corresponding XPS results also demonstrated the presence of electron transfer between Co atoms from CoO/Co and sulfur atoms of Li_2S_4 . Advantageously, the prepared CoO/Co@PCF-S cathode loading of 3 mg cm^{-2} sulfur revealed a storage capacity of $1214.2 \text{ mAh g}^{-1}$ at 0.1 C. When the sulfur content increased to 5.4 mg cm^{-2} , the composite cathode still attained a favorable capacity up to 508.0 mAh g^{-1} after 100 cycles at 0.5 C.

6.1.4. Iron-based oxides

Iron-based oxides like Fe_3O_4 and Fe_2O_3 have been proven to be efficient hosts to improve the cathode performance.^[211-213] Considering the superior conductivity and polar property, Manthiram and co-workers introduced Fe_3O_4 with high conductivity ($5 \times 10^4 \text{ S m}^{-1}$) to sulfur cathodes. As shown in **Figure 11g**, the authors employed Fe_3O_4 cubes as core in combination with carbon shells to construct carbon-coated Fe_3O_4 yolk-shelled nanoboxes ($\text{YSC@Fe}_3\text{O}_4$).^[214] Such a $\text{YSC@Fe}_3\text{O}_4$ host revealed unique materials properties for sulfur cathodes: (1) the inner Fe_3O_4 cubes chemically anchored polysulfides within the nanoboxes; (2) the large cavity of the yolk-shell structure enabled adequate sulfur loading and mitigated the cathode swelling during lithiation; (3) the carbon shells physically confined the polysulfide migration; (4) the high conductivity from Fe_3O_4 cubes and carbon shells facilitated the charge transfer kinetics of the sulfur cathodes. The prepared S/ $\text{YSC@Fe}_3\text{O}_4$ cathodes achieved an areal loading of up to 5.5 mg cm^{-2} , reaching a good areal capacity of 6.1 mAh cm^{-2} (**Figure 11h**). Moreover, The XPS spectra confirmed the chemical interactions between Fe_3O_4 and polysulfides. After exposure to

Fe_3O_4 , Li_2S_6 revealed a significant binding energy shift for sulfur atoms, implying the presence of electron transfer to Fe_3O_4 .

Fe_3O_4 has been combined with various carbon substrate materials to improve sulfur utilization. More recently, employing spray drying, followed by a thermal treatment, Li *et al.* fabricated 3D porous CNT microspheres with uniformly dispersed Fe_3O_4 nanoparticles ($\text{CNT}/\text{Fe}_3\text{O}_4$).^[215] As sulfur host, the interwoven CNT network accelerated the charge transfer and allowed adequate sulfur loading. Moreover, the distributed Fe_3O_4 nanoparticles were able to improve the chemical anchoring towards polysulfides. Consequently, the $\text{S}/\text{CNT}/\text{Fe}_3\text{O}_4$ electrode contributed to an increased capacity at 0.2 C of 1270 mAh g^{-1} and favorable rate capability (602 mAh g^{-1} up to 3 C). The catalytic effect of Fe_3O_4 on the polysulfide conversion has also been reported.^[216, 217] Ding *et al.* designed a ternary sulfur host, consisting of Fe_3O_4 nanoparticles embedded in porous nanocarbon on graphene nanosheets ($\text{Fe}_3\text{O}_4/\text{NC}/\text{G}$), which revealed the accelerated catalytic conversion of polysulfides.^[216] *In-situ* XRD was employed to investigate the polysulfide evolution. The diffraction peaks of polysulfides almost disappeared when the discharging process was finished, meaning that their detrimental migration from cathodes was greatly mitigated. The authors proposed that the polysulfides were effectively anchored and then catalytically converted by Fe_3O_4 nanoparticles. The prepared $\text{Fe}_3\text{O}_4/\text{NC}/\text{G}$ host loaded with the Li_2S_6 catholyte achieved a superior rate capability at 3 C of 755 mAh g^{-1} .

6.1.5. Mixed metal oxides

Mixed metal oxides or spinels with general formula $\text{M}^{2+}\text{M}^{3+}_2\text{O}^{2-}_4$ are good catalysts for various chemical reactions. Benefiting from the interfacial effects between mixed metal ions, their properties are far more superior to those of their single-metal counterparts. Also, they exhibit a better electronic conductivity. Mixed metal oxides like NiCo_2O_4 ,^[218-221] NiFe_2O_4 ,^[222, 223] and ZnCo_2O_4 have therefore been introduced as sulfur hosts.

Gao and co-workers fabricated carbon-free NiCo_2O_4 nanofibers with a high density to anchor sulfur (**Figure 12a**).^[224] Such hollow NiCo_2O_4 nanofibers were prepared by heating the electrospun nanofibers from a mixture of polyacrylonitrile (PAN), $\text{Co}(\text{OAc})_2$, and $\text{Ni}(\text{OAc})_2$. Different from the traditional light-weight carbon-sulfur hosts, the hollow NiCo_2O_4 nanofibers achieved S/ NiCo_2O_4 composites with high tap density. The volumetric capacity of S/ NiCo_2O_4 reached 1867 mAh cm^{-3} (composite-based). Moreover, an 1171 mAh cm^{-3} capacity in the first cycle was achieved at 1 C. The corresponding electrode stability was excellent. Only 0.039% per cycle was lost during 1500 cycles (**Figure 12b**). Optically transparent cells indicated a strong polysulfide adsorption at the polar NiCo_2O_4 nanofibers. Visual observation at various depth-of-discharge evidently revealed that the electrolyte with S/ NiCo_2O_4 cathodes was almost transparent and colorless except for the pale yellow collar in the low voltage plateau range. The redox reaction kinetics of the polysulfides was also enhanced by the strong chemical interactions between NiCo_2O_4 and the polysulfides. Using a similar electrospinning strategy, Gao *et al.* fabricated nickel ferrite (NiFe_2O_4) nanofibers as a novel sulfur host material.^[225] The resulting NiFe_2O_4 nanofibers with strong polarity showed favorable adsorption of polysulfides, significantly inhibiting the shuttle effect of the sulfur cathodes. Because of the high tap density, the obtained S/ NiFe_2O_4 electrode revealed an initial volumetric capacity up to $1281.7 \text{ mAh cm}^{-3}$ at 0.1 C on the basis of the composite content.

Combining mixed metal oxides with highly conductive carbon structures is also beneficial to the redox kinetics of sulfur species. Sun *et al.* employed highly conductive N-doped RGO with stable network structures to support ZnCo_2O_4 nanocubes ($\text{ZnCo}_2\text{O}_4@\text{N-RGO}$).^[226] As shown in **Figure 12c**, numerous ZnCo_2O_4 nanocubes were uniformly dispersed on both sides of the graphene sheets (indicated by white arrows), forming a sandwich-like microstructure. Such architecture can significantly enhance the adsorption of polysulfides due to the chemical anchoring of ZnCo_2O_4 and N-RGO. The interaction between ZnCo_2O_4 and polysulfides has been investigated by calculating the binding energies of Li_2S_4 with ZnCo_2O_4 based on DFT.

The optimized model (**Figure 12d**) revealed the presence of a strong binding energy of 3.1 eV between the (111) planes of ZnCo_2O_4 and Li_2S_4 . The doped nitrogen atoms from N-RGO and the metal ions from ZnCo_2O_4 gave rise to dual chemical anchoring towards polysulfides. As a result, the ZnCo_2O_4 @N-RGO host loading 71% sulfur revealed a capacity of 905 mAh g^{-1} in the first cycle at a current of 1600 mA g^{-1} and maintained 71% of its capacity after 200 cycles (**Figure 12e**).

6.1.6. Other oxides

There also have been other metal oxides applied as sulfur host material to improve the electrode performance, some of which exhibit considerably increased effects on the storage capacity and cycle life performance of sulfur cathodes, such as SiO_2 ,^[227-229] VO_2 ,^[230] V_2O_3 ,^[231, 232] V_2O_5 ,^[89, 233] Al_2O_3 ,^[234, 235] ZnO ^[236-238] and MgO .^[239, 240] For instance, Rehman *et al.* fabricated a cross-linked Si/SiO₂ hierarchically porous carbon-sphere hybrid material (Si/SiO₂/C).^[241] As sulfur host, such Si/SiO₂/C spheres disclosed several structural advantages: (1) the cross-linked architecture restrained polysulfide leakage by physical confinement inside the porous carbon structures and by electrostatic interactions with Si/SiO₂; (2) the favorable porosities with high surface area enabled high sulfur loading and facilitated the charge transfer reaction, leading to desirable rate capabilities; (3) the cross-linked Si/SiO₂ species also boosted the electrochemical charge transfer kinetics of sulfur cathodes. Benefiting from these characteristics, an optimal Si/SiO₂@C-S cathode was loaded with 69.6 wt.% sulfur, exhibiting a capacity up to 825 mAh g^{-1} during the first cycle at 2 C and a high storage capacity was maintained even after 500 cycles.

Li *et al.* designed a binary sulfur host, comprising *in situ* grown VO₂ nanoflakes at rGO (VO₂@rGO).^[242] As shown in **Figure 12f**, The VO₂@rGO composite was obtained via a facile solvothermal reaction. The prepared VO₂ nanoflakes exhibited intense chemical anchoring towards polysulfides and also accelerated the conversion between polysulfides and $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, thus reducing the shuttle problem. Additionally, rGO nanosheets spatially confined polysulfides

and enhanced the conductivity of sulfur cathodes, significantly promoting the electrode redox kinetics. The CV curves at various scan rates indicated that the VO₂@rGO hosts accelerated the redox kinetics and Li⁺ diffusion of the cathodes. With the combined effects from VO₂ and rGO, the VO₂@rGO/S cathode demonstrated a superior prolonged cycle life at 0.2 C (**Figure 12g**). An initial capacity 1358 mAh g⁻¹ was reached and retained 77% of its capacity after 370 cycles, which resulted in a capacity fading of 0.06% per cycle. Ma *et al.* synthesized Al₂O₃-doped ZnO coated with CNT (AZO/CNT) as sulfur hosts through a hydrothermal process, followed by a solid-state reaction.^[243] The AZO component provided a strong chemical bonding to polysulfides, which significantly inhibited the polysulfide shuttling. Moreover, the Al atoms doping into the ZnO lattice increased the electron density of ZnO, thus increasing the electronic conductivity and facilitating the redox kinetics. The AZO@S/CNT cathode, containing 60 wt.% sulfur content, delivered a capacity of 1100 mAh g⁻¹ in the first cycle at 0.2 C and remained 700 mAh g⁻¹ over 200 cycles.

By tailoring the structure and configuration, metal oxides can improve the chemical bonding and accelerate the polysulfide conversion. The present results allow us to have a better understanding of the interactions between metal oxides and polysulfides. Future research on metal oxides has to focus on more efficient adsorption and conversion of polysulfides, high conductivity, and higher cost-effectiveness for practical applications.

6.2. Metal sulfides

Metal sulfides have been explored as sulfur host materials, since their strong polar character induces significant chemical interaction with active sulfur.^[244] Most metal sulfides typically lithiate at voltages below 1.5 V vs. Li⁺/Li, avoiding parasitic reactions of host materials within the operating voltage window of sulfur cathodes. Another important property that has been described in recent literature is that some metal sulfides reveal high catalytic effects, promoting the conversion of polysulfides and, consequently, improving the charge transfer kinetics.^[245]

Moreover, in contrast to metal oxides, metal sulfides typically show better conductivities, which is beneficial for the electrochemistry of sulfur cathodes.

6.2.1. Cobalt-based sulfides

Cobalt-based sulfides, such as Co_9S_8 ,^[81, 246, 247] CoS_2 ,^[30, 248] and Co_3S_4 ,^[249, 250] have been studied in detail to be applied as sulfur host to boost the electrode performance. All of them own superior room temperature conductivity (1.36 S m^{-1} for Co_9S_8 , $6.7 \times 10^5 \text{ S m}^{-1}$ for CoS_2 , and $3.3 \times 10^5 \text{ S m}^{-1}$ for Co_3S_4).^[249] Pang *et al.* proposed a graphene-like Co_9S_8 nanosheet material as sulfur host because of the high conductivity of Co_9S_8 and the strong chemical interaction with polysulfides.^[246] This graphene-like Co_9S_8 , synthesized by a facile microwave solvothermal method, exhibited a 3D network comprising of interconnected nanosheets (**Figure 13a**). The authors studied three different lattice planes of Co_9S_8 to determine the binding effects of Co and S atoms on polysulfides (**Figure 13b**). The (002) surface with a Co/S ratio of 1:4 showed a binding energy of 2.22 eV to Li_2S_2 , while the (202) surface with a higher Co/S ratio increased the energy to 3.24 eV to finally reach 6.06 eV for the (008) surface, comprising of pure cobalt atoms. The higher Co/S ratio indicated the stronger binding energy, implying that Co-S interactions were mainly responsible for the chemical bonding to polysulfides. XPS results also demonstrated the presence of electron transfer between Li_2S_4 and Co_9S_8 . As a result, Co_9S_8 hosts loaded with 75 wt.% sulfur exhibited an ultralow 0.045% capacity loss per cycle during 1500 cycles at 0.5 C. In particular, a cathode loaded with 4.5 mg cm^{-2} sulfur exhibited a stable cycling performance of over 150 cycles (**Figure 13c**). Such a result demonstrated the merit of Co_9S_8 nanosheets for sulfur cathodes with high energy density.

Using a self-template method followed by sulfidation, Chen *et al.* synthesized Co_9S_8 nanocrystals embedded in hollow carbon nanopolyhedra ($\text{Co}_9\text{S}_8/\text{C}$).^[81] Such $\text{Co}_9\text{S}_8/\text{C}$ composite structure has many advantages, such as (1) the large internal void was capable of incorporating high sulfur contents and buffered the electrode swelling during cycling; (2) the

embedded Co₉S₈ nanocrystals effectively anchored polysulfides and restrained their migration out of the cathodes; (3) the 3D conductively porous networks offered adequate charge transfer pathways. Quantum density functional theory (QDFT) simulations revealed that the adsorption energies of Co₉S₈ nanoparticles towards various sulfur species were in the range of 2.97 to 6.08 eV, suggesting strong chemisorption. A visual adsorption test revealed that Li₂S₄ exposed to Co₉S₈/C hollow nanopolyhedra became nearly transparent after a short period of time. The chemical interaction between active sulfur and Co₉S₈ mainly resulted from the formation of Co-S and Li-S bonds. The resulting Co₉S₈/C-S composite cathode stabilized at 560 mAh g⁻¹ over 1000 cycles at 2.0 C.

CoS₂ was initially introduced as an additive to sulfur cathodes by Yuan *et al.*^[30] They found that the introduced CoS₂ exhibited the strong interaction with polysulfides and thus accelerated redox reactions of polysulfides. This discovery has promoted the application of CoS₂ in sulfur cathodes. More recently, Seo *et al.* designed mesoporous hollow carbon spheres with brain-coral-like structures, which were assembled by N-doped graphitic carbon nanoshells (NGCNs) embedded with CoS₂ nanoparticles.^[251] As shown in **Figure 13d**, the mesoporous hollow CoS₂@NGCN nanostructure was composed of numerous surface pores. Because of the large internal voids, CoS₂@NGCN host materials offer sufficient space for sulfur infusion and volume changes during (de)lithiation. Polar CoS₂ nanoparticles in combination with NGCNs not only chemically adsorbs polysulfides but also facilitates the charge transfer reaction. **Figure 13e** illustrated the strong adsorption of CoS₂@NGCN towards polysulfides. After exposing CoS₂@NGCN, the Li₂S₆ solution became transparent in 2 h. The voltage curves in **Figure 13f** show that the CoS₂@NGCN/S cathode delivered a higher specific capacity with mitigated polarization than the other two counterparts. It was concluded that CoS₂@NGCN was beneficial for the utilization of sulfur cathodes and increased polysulfide reaction kinetics. The CoS₂@NGCN/S composite cathode maintained a steady capacity of more than 900 mAh g⁻¹ at 0.1 C after 100 cycles.

Inspired by the high electrocatalytic activity of Co_3S_4 for oxygen reduction, Pu *et al.* proposed that Co_3S_4 could also catalyze the conversion of sulfur species, since both sulfur and oxygen belong to the chalcogen group.^[249] The authors proposed a facile strategy to fabricate $\text{Co}_3\text{S}_4@\text{S}$ nanotubes for high-performance Li-S batteries. The SEM image in **Figure 13g** clearly indicates the hollow structure of the Co_3S_4 nanotubes. A 15 nm thick wall was revealed from the TEM image (**Figure 13h**). Nanoscale Co_3S_4 nanotubes with abundant sites ensured the chemical absorption of sulfur species. Symmetric cells were constructed to investigate the catalytic properties of Co_3S_4 for the polysulfide conversion reactions. The CV curve of the symmetrical Co_3S_4 cell revealed that Co_3S_4 accelerated the conversion of polysulfides (**Figure 13i**). As for the cells without the Li_2S_6 electrolyte, both the Co_3S_4 and acetylene black (AB) cells barely displayed a current response. However, Co_3S_4 indicated significantly enhanced currents than AB after adding Li_2S_6 . Furthermore, $\text{Co}_3\text{S}_4@\text{S}$ nanotube-based cathodes showed a prolonged cycle life of more than 1000 cycles at 5 C.

6.2.2. Molybdenum disulfide

Molybdenum disulfide (MoS_2), consisting of 2D layered structures, has been proven to have a high electrochemical activity for water splitting. The application of MoS_2 has also been explored to be applied in sulfur cathodes.^[252-254] By controlling the sulfur deficiency of few-layer MoS_2 nanoflakes, Lin *et al.* designed rGO decorated with sulfur-deficient MoS_2 nanoflakes ($\text{MoS}_{2-x}/\text{rGO}$) that showed electrocatalytic activities for the polysulfide conversion.^[67] Because of the sulfur deficiencies, the conversion of sulfur species at $\text{MoS}_{2-x}/\text{rGO}$ experienced an energetically favorable pathway, resulting in accelerated redox kinetics and consequently in high sulfur utilization. Similarly, the integration of layered MoS_2 nanosheets with a rGO foam was reported by You *et al.* to construct sulfur cathodes.^[82] As illustrated in **Figure 14a**, a facile hydrothermal process was conducted to synthesize MoS_2/rGO foams, producing 3D interconnected porous networks. The highly conductive rGO nanosheets

with large surface areas exhibited desirable elasticity, which was suitable to load sulfur into the networks. The MoS₂ nanosheets possessed strong bonding and therefore a high electrocatalytic activity towards polysulfides. These features have been validated by the visualized adsorption of Li₂S₆ and CV curves of symmetrical electrochemical cells. As a result, the obtained MoS₂/rGO/S cathodes exhibited enhanced rate capability at various current densities than rGO/S cathodes (**Figure 14b**). Porous MoS₂/rGO foams are therefore promising to be applied for sulfur cathodes.

Due to the ultrathin property, MoS₂ nanosheets were also coated on other matrixes to confine polysulfides. Hu *et al.* designed MoS₂ nanosheet-coated hierarchical carbon spheres (MoS₂@HCS) to improve sulfur cathodes.^[255] A Ni-MOF precursor was used to fabricate HCS consisting of hollow carbon nanobubbles. The HCS was subsequently covered with a layer of MoS₂ nanosheets by making use of a solvothermal process. The as-prepared MoS₂@HCS host materials revealed some interesting characteristics: (1) the hollow carbon bubbles provided many voids for sulfur loading and alleviated the electrode swelling upon lithiation; (2) highly conductive HCS ensured the charge transport, hence improving the sulfur utilization; (3) the polar MoS₂ dispersed at HCS inhibited the polysulfide shuttling process and prolonged the electrodes cycle life by effective polysulfide adsorption; (4) the introduced MoS₂ accelerated the electrochemical redox kinetics. Taking advantage of these structural properties, the capacity of S/MoS₂@HCS cathodes reached 1048 mAh g⁻¹ at 0.2 C. CV revealed the accelerated polysulfide redox kinetics by MoS₂. Compared with the pure sulfur cathode, MoS₂/S cathodes showed significantly reduced overpotentials for the reduction and oxidation reactions.

6.2.3. Nickel-based sulfides

Nickel-based sulfides like NiS₂,^[256, 257] NiS,^[258] and Ni₃S₂^[259, 260] have been employed as sulfur host material because of the desirable sulfiphilicity and accelerated redox kinetics of polysulfides. For example, Luo *et al.* synthesized a novel 3D polysulfide reservoir by

integrating NiS₂ nanoparticles with RGO frameworks.^[261] Such a NiS₂-RGO sponge hybrid was constructed by biomolecule-assisted self-assembly. Uniform NiS₂ nanoparticles with porous morphology were *in situ* grown on a RGO substrate by a hydrothermal reaction. The hybrid NiS₂-RGO sponge delivered multiple benefits: (1) the porous RGO matrix provided sulfur species with the sufficient space, facilitated 3D electron pathways, and physical blocking; (2) uniformly dispersed NiS₂ nanoparticles offered abundant sites for the chemical anchoring of polysulfides; (3) the strong chemically coupled NiS₂-RGO enabled continuous electron channels from RGO to the adsorption interface of NiS₂-polysulfides, considerably boosting the conversion of polysulfides and rate capabilities. DFT calculations visualized in **Figure 14c** revealed a high binding energy of 3.60 eV between Li₂S₄ and NiS₂, which was much stronger than that of graphene. In addition, the electron density distribution provided a more straightforward comparison. Compared to the C-Li bonding, the electron density between Ni atoms of NiS₂ and Li atoms of Li₂S₄ was evidently enhanced (highlighted with a black circle). These features enabled the NiS₂-RGO sponge host loaded with a 75 wt.% sulfur content. The obtained sulfur cathodes with a 21 mg cm⁻² areal loading achieved a 16 mAh cm⁻² areal capacity (**Figure 14d**).

Combining nanosized NiS with 3D carbon hollow spheres is another effective approach to confine polysulfides. Combining an *in situ* thermal reduction with the sulfidation process, Ye *et al.* fabricated a hybrid sulfur host consisting of NiS nanoparticles homogeneously dispersed on 3D carbon hollow spheres (NiS@C-HS).^[258] Such a 3D network enlarged the chemical anchoring of NiS nanoparticles towards polysulfides by exposing many more active sites (**Figure 14e**). Moreover, C-HS provided the 3D electron transport pathways and sufficient physical blocking for polysulfides. The strong coupling interaction between the NiS nanoparticles and C-HS networks accelerated the electrode redox kinetics. The hybrid NiS@C-HS loaded with 2.3 mg cm⁻² sulfur attained a very stable cycle life of over 300 cycles at 0.5 C (**Figure 14f**). The authors compared the adsorption capability of the hosts by visual adsorption

tests, finding that NiS@C-HS exhibited stronger adsorption than other compared host materials. After treatment with polysulfides, the Raman spectra revealed that the four main peaks of NiS showed a slight redshift, indicating chemical bonding of NiS towards polysulfides.

6.2.4. Titanium disulfide

Titanium disulfide (TiS_2) is a cathode material which was firstly investigated in rechargeable lithium batteries. Because of its high conductivity and effective adsorption for polysulfides, TiS_2 has been demonstrated a promising sulfur host material.^[262, 263] Chung *et al.* employed conductive TiS_2 to adsorb polysulfides.^[83] The authors encapsulated the fabricated TiS_2 -polysulfide in carbon electrode shells, assembling a so-called core-shell composite cathode. A catholyte composed of a high concentration of Li_2S_6 was employed to be the active species. Sulfur loading reached as high as 12 mg cm^{-2} . Even with a low electrolyte content of $5 \text{ }\mu\text{L}$ electrolyte per mg sulfur, this hybrid cathode achieved a 10 mAh cm^{-2} areal capacity after 200 cycles at 0.2 C ,

Recently, Huang *et al.* initially reported sandwich-like ultrathin TiS_2 nanosheets encapsulated in the N and S co-doped porous carbon ($\text{TiS}_2@\text{NSC}$).^[264] $\text{TiS}_2@\text{NSC}$ was prepared from the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene precursor via PDA coating and sulfuration process. From TEM observations (**Figure 15a, b**) it has been concluded that $\text{TiS}_2@\text{NSC}$ consisted of few-layer TiS_2 nanosheets sandwiched by a thin layer of porous carbon. Such an architecture was beneficial for trapping polysulfides and therefore greatly promoted the use of sulfur. Integrated with cotton-derived carbon fibers (CFs), $\text{TiS}_2@\text{NSC}$ gave a freestanding cathode ($\text{TiS}_2@\text{NSC}@\text{CFs}$) with high areal sulfur loading up to 7.7 mg cm^{-2} . The freestanding sulfur cathode achieved a high initial areal capacity of 7.9 mAh cm^{-2} and maintained 5.9 mAh cm^{-2} after 100 cycles (**Figure 15c**). These results position $\text{TiS}_2@\text{NSC}$ as one of the best sulfur hosts reported at that time.

6.2.5. Others metal sulfides

Some other metal sulfides involving VS_2 ,^[265, 266] ZnS ,^[267] FeS_2 ,^[20, 268] WS_2 ,^[269, 270] and NiCo_2S_4 ^[271, 272] have also been explored as sulfur host electrode material. For instance, integrating VS_2 grown on rGO sheets with sulfur layers into an alternating structure, Wang and co-workers developed a variety of flexible sandwich-like cathodes ($\text{rGO-VS}_2/\text{S}$).^[273] As illustrated in **Figure 15d**, a facile hydrothermal process produced rGO-VS_2 nanosheets. $\text{rGO-VS}_2/\text{S}$ composites with various sulfur loadings were obtained by tuning the content of sulfur infusion, revealing the following materials properties: (1) the sandwich-like structure mitigated the cathode swelling during lithiation; (2) a low content of VS_2 enhanced the conductivity and tap density of the sulfur cathodes; (3) the spatial confinement and chemical anchoring from rGO-VS_2 gave rise to reduced polysulfide shuttling; (4) the catalytic activity of VS_2 promoted the cathode reaction kinetics. Benefiting from these features, the $\text{rGO-VS}_2/\text{S}$ cathode displayed longer discharge plateaus and higher capacity than rGO/S (**Figure 15e**). The cell polarization was also mitigated, *i.e.* ΔE shows a smaller potential gap. The authors further evaluated $\text{rGO-VS}_2/\text{S}$ electrodes with various sulfur loading, reporting that cathodes with 89 wt.% sulfur exhibited an optimal volumetric capacity of up to 1182 mAh cm^{-3} (**Figure 15f**). This performance is highly competitive with state-of-the-art capacities in Li-S batteries.

Polar WS_2 nanosheets deposited on carbon nanofibers (CNFs) were first developed by Lei *et al.* via a facile hydrothermal process.^[274] Such a C@WS_2 composite revealed a freestanding architecture, in which dense WS_2 nanosheets were vertically arranged along CNFs. DFT calculations revealed that WS_2 exhibited binding strengths to polysulfides throughout lithiation process. Active sulfur species were adequately anchored by the physical forces of CNFs and the chemical adsorption of WS_2 . The initial capacity of the freestanding $\text{C@WS}_2/\text{S}$ cathode reached about 1500 mAh g^{-1} at 0.1 C. Even at 2 C, a prolonged cycling stability of 1500 cycles was obtained with an extremely low capacity loss of only 0.00072% per cycle. More recently, Lu *et al.* synthesized NiCo_2S_4 nanosheets, *in situ* grown on carboxylated CNTs by a simple

hydrothermal reaction.^[275] The NiCo_2S_4 flake morphology revealed abundant micropores, firmly anchored at the surface of CNTs. As a sulfur host, such a composite structure showed a better electrode conductivity and anchoring of polysulfides. The corresponding $\text{NiCo}_2\text{S}_4@\text{CNT}/\text{S}$ electrode sustained a 1000 cycle life at 0.6 C with a capacity loss as low as 0.049% per cycle. The authors proposed a mechanism to unveil the role of the $\text{NiCo}_2\text{S}_4@\text{CNT}$ host. CNTs provided highly electron conductive pathways, effectively improving the charge transport inside the cathodes. Furthermore, the bimetallic NiCo_2S_4 nanosheets facilitated strong adsorption towards polysulfides, effectively suppressing the diffusion of polysulfides.

The excellent conductivity, strong chemical adsorption of polysulfides, and good electrocatalytic activity of metal sulfides significantly increased the utilization of sulfur cathodes. The current exploration of metal sulfides for Li-S batteries gradually focuses on the catalytic effect on active sulfur species. However, the catalytic mechanism has not been well unveiled, which should be further investigated in future studies.

6.3. Metal hydroxides

Compared with metal oxides and sulfides, hydroxides employed as a sulfur host material is rather limited, which may result from their relatively low conductivity and weak adsorption with polysulfides. The research mainly focuses on the performance of nickel hydroxides and layered double hydroxides.

6.3.1. Nickel hydroxides

Nickel hydroxides ($\text{Ni}(\text{OH})_2$) with layered structures are typically employed as coating layers to inhibit the active sulfur dissolution into electrolytes by both their physical confinement and chemical adsorption.^[276-278] For example, Xia *et al.* modified a thin $\text{Ni}(\text{OH})_2$ layer on porous yeast carbon/sulfur (PYC/S) microspheres.^[279] As illustrated in **Figure 16a**, the obtained $\text{Ni}(\text{OH})_2@\text{PYC}/\text{S}$ was coated with fluffy $\text{Ni}(\text{OH})_2$ layers, resulting in a unique core-shell

structure. The conductive porous PYC matrices are favorable for electrolyte penetration and effective electron transport, as well as to provide sufficient internal voids for sulfur loading. In addition, the polar $\text{Ni}(\text{OH})_2$ shells ensured the strong chemical adsorption of polysulfides, effectively suppressing the polysulfide shuttling. Visual cycling tests confirmed the electrochemical stability of $\text{Ni}(\text{OH})_2@\text{PYC}/\text{S}$ cathodes (**Figure 16b**). The electrolyte in $\text{Ni}(\text{OH})_2@\text{PYC}/\text{S}$ nearly kept transparent for more than 100 cycles, implying good adsorption of polysulfides. By contrast, the electrolyte in PYC/S clearly changed into yellow, indicating that polysulfides diffused out of the cathode. Due to these structural characteristics, the $\text{Ni}(\text{OH})_2@\text{PYC}/\text{S}$ composite cathodes exhibited a good cycling stability for more than 200 cycles at 0.2 C and the separator color remained unchanged during the cycling process (**Figure 16c**).

Another research, involving nickel-based hydroxides in sulfur cathodes, was developed by Meng *et al.*^[280] They designed a thin-layered nickel-based hydroxide (NNH) to wrap the activated carbon cloth/sulfur composite (ACC/S). Firstly, sulfur was infused into ACC by a facile “ethanol-transfer-adsorption” process. Then a hydrothermal reaction resulted in the formation of NNH coated on ACC/S (NNH/ACC/S). The microporous ACC was an effective sulfur scaffold which provided many electronic pathways. The outer NNH layers acted as a shield to spatially inhibit the polysulfide migration. Furthermore, the oxygen-containing groups at NNH chemically adsorbed polysulfides. Interestingly, an irreversible reaction of NNH with lithium generated a mixed hydroxide protection layer with good ionic conductivity for lithium. The XPS spectra proved the chemical interaction between NNH and polysulfides as electronic charge was transferred from oxygen of NNH to the lithium in the polysulfides, forming Li-O bonds. Consequently, a freestanding NNH/ACC/S cathode loaded with 4.3 mg cm^{-2} sulfur has a high and stable areal storage capacity of 4.3 mAh cm^{-2} at 0.15 C.

6.3.2. Layered double hydroxides

Layered double hydroxides (LDHs) are a class of inorganic lamellar compounds composed of metal ions with different valences octahedrally coordinating the hydroxyl groups. The general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively, while A^{n-} are interlayer anions. Due to the high chemical activity of LDHs, they are widely used as nanocomposites, catalysts, and anion exchangers. LDHs have also been introduced to sulfur cathodes because of ample sulfiphilic and hydroxyl groups, as well as its electrocatalytic properties, accelerating the redox kinetics of polysulfides.^[281-283]

Lou and co-workers developed different LDHs to improve sulfur cathodes.^[281] Recently, they fabricated MOF-derived hollow Ni/Fe LDH polyhedrons to host sulfur.^[284] As illustrated in **Figure 16d**, polyhedral MIL-88A particles were employed as sacrificial template. With a facile solvothermal reaction, MIL-88A converted into hollow Ni/Fe LDH polyhedrons. The final S@Ni/Fe LDH composite was obtained by sulfur melting infusion. As sulfur host, The Ni/Fe LDH polyhedrons displayed several characteristics: (1) the polar shells lead to abundant sulfiphilic sites, chemically anchoring polysulfides; (2) the hollow cavities enabled numerous sulfur storage and also buffered the cathode swelling; (3) the redox reactions kinetics of polysulfides was accelerated, achieving a uniform deposition of solid discharge products. Consequently, S@Ni/Fe LDH cathodes exhibited a 1091 mAh g⁻¹ storage capacity in the first cycle at 0.2 C (**Figure 16e**). The initial capacity at 1 C reached 844 mAh g⁻¹ and could be cycled for more than 1000 cycles with only 40% capacity loss.

Another strategy, proposed by Chen *et al.*, was to cover P-doped activated biomass-derived carbons (PAB) with NiAl-LDH fences by a simple hydrothermal process.^[285] The prepared NiAl@PAB hybrid host combined the merits of PAB and NiAl-LDH, the cooperative interface of which effectively encapsulated polysulfides through physical confinement and chemical adsorption. Moreover, the decorated NiAl-LDH fences with sufficient adsorption sites had a catalytic effect on the polysulfide conversion, hence substantially boosting the electrode

reaction kinetics. The NiAl-LDH modification increased the Li_2S_4 adsorption as was demonstrated by DFT calculations with an enhanced binding energy of 3.03 eV. Therefore, the prepared NiAl@PAB/S composite loaded with 66 wt.% sulfur delivered a 1216.3 mAh g^{-1} initial storage capacity at 0.2 C.

6.3.3. Other hydroxides

Cobalt-based hydroxides have also been investigated as sulfur host. Niu *et al.* coated $\text{Co}(\text{OH})_2$ nanosheets on a sulfur/conductive carbon black (CCB) electrode by thermal and hydrothermal reactions, in which CCB provided the conductive network and $\text{Co}(\text{OH})_2$ nanosheets stabilized the electrode surface to prevent the polysulfide diffusion from CCB.^[286] The obtained composite cathode ($\text{Co}(\text{OH})_2@\text{S}/\text{CCB}$) delivered an optimal capacity of 1026 mAh g^{-1} at 0.1 C and 71.2% capacity retention over 200 cycles at 1 C, better than those of S/CCB electrodes. It was shown that $\text{Co}(\text{OH})_2$ nanosheets considerably inhibited the diffusion of polysulfides.

More recently, Wang *et al.* proposed CoOOH sheets with high conductivity to anchor sulfur.^[287] The synthesized CoOOH sheets displayed uniformly hexagonal morphology with tiny cubes at the surface (**Figure 16f**). As a carbon-free sulfur host, the highly conductive CoOOH sheets revealed specific electrode properties. The large surface area exposed adequate active sites to anchor and then catalyze polysulfides. On the basis of these structural features, the authors proposed a two-step reaction process between polysulfides and CoOOH . Co-O bonds were partially split and polysulfides were oxidized to thiosulfate/polythionate species. The exposed Co atoms received electrons from the polysulfides, forming Co-S bonds by Lewis acid-base interactions. This process effectively promoted the polysulfide conversion and mitigated the shuttling process. Taking advantage of these favorable anchoring effects, the prepared sulfur/ CoOOH composite cathode was successfully loaded with 91.8 wt.% sulfur, attaining 1.26 g cm^{-3} in tap density. At 1 C, a good cycle life was obtained for more than 500 cycles with only 0.09% capacity loss per cycle (**Figure 16g**).

6.4. Metal carbides

Metal carbides have been investigated as electrocatalyst due to their excellent conductivity, unique structure, and low material cost. These intrinsic natures make them interesting to improve sulfur cathodes. Some transition metal carbides such as TiC, Fe₃C, and Mo₂C have been introduced as sulfur host, which exhibit a considerably enhanced electrochemical performance for Li-S batteries.

6.4.1. Titanium carbides

Polar titanium carbides (TiC) with high conductivity were initially applied for sulfur cathodes by Peng *et al.*^[288] Analyzing the charge transfer kinetics of sulfur species at various substrates, the authors concluded that conductive polar TiC had strong interactions with polysulfides and played a crucial role in the redox kinetics. First-principle calculations in **Figure 17a** revealed that the binding energies of the TiC (100) surface with Li₂S₄ and Li₂S were 1.89 and 2.75 eV, respectively. Such affinity was substantially stronger than those with graphene. Polysulfide conversion studies were conducted with carbon-fiber paper (CP), CP-supported TiO₂ (CP-TiO₂), and CP-supported TiC (CP-TiC) electrodes. The electrochemical impedance spectroscopy (EIS) of symmetric cells in **Figure 17b** revealed that CP-TiC delivered a significantly decreased impedance, indicating the improved interfacial bonding of TiC with polysulfides. Moreover, a higher redox current of CP-TiC in CV curves (**Figure 17c**) indicated that conductivity was another favorable impact on the polysulfide conversion. TiC also effectively induced and accelerated the Li₂S precipitation. This can be validated by the potentiostatic discharge tests in a Li₂S₈/tetraglyme solution. As shown in **Figure 17d**, CP-TiC exhibited a higher capacity of the Li₂S precipitation than CP and CP-TiO₂. The authors designed a hybrid sulfur host, incorporating TiC nanoparticles in a mesoporous graphene framework (TiC@G), to validate

the superiority of TiC. As a result, a TiC@G/S composite cathode loaded with 3.5 mg cm⁻² sulfur displayed an enhanced capacity and a more durable lower voltage plateau.

Further research on TiC hosts was based on combining various matrix configurations to improve sulfur cathodes. For instance, Zhou *et al.* designed a hybrid host covering TiC nanoparticles at carbon nanofibers to develop sulfur cathodes.^[289] Taking advantage of the desired conductivity and intense adhesion, the prepared hybrid host material provided fast electron transport pathways and abundant active sites, hence significantly enhancing the cathode utilization.

Cao *et al.* employed a facile reduction process to incorporate TiC nanoparticles on hollow carbon nanospheres (TiC@C).^[290] The uniformly dispersed TiC nanoparticles showed effective adsorption of polysulfides. The novel TiC@C structure helped the composite cathodes to achieve outstanding long-term cycling stability at high rates. By using a supercritical CO₂ liquid process, Huang *et al.* embedded TiC particles in CMK-3 mesoporous carbon (TiC/C).^[291] The prepared TiC/C composite with high mesoporous structures displayed a large surface area. Moreover, the uniform distribution of the embedded TiC particles offered adequate sites to anchor polysulfides. The resulting TiC/C-S cathode delivered good capacities at various current densities. Integrating TiC with other metal compounds as sulfur host materials may enhance the performance of sulfur cathodes further.

Lang *et al.* combined the conductivity of TiC and strong adsorption of the TiO₂ with respect to polysulfides to synthesize a stable TiO₂/TiC composite material as sulfur immobilizers.^[292] Such dual effects were reported to be beneficial for the utilization of sulfur cathodes. The TiO₂/TiC composites material loaded with various contents of sulfur were investigated. An optimal cathode performance was achieved with 55 wt.% sulfur loading. Another similar TiO₂/TiC composite host has also been reported, showing enhanced performance.^[293]

6.4.2. Iron carbides

Due to the high conductivity and effective polysulfide adsorption, iron carbides (Fe_3C) have also been employed as sulfur hosts. Wang *et al.* incorporated uniformly dispersed Fe_3C nanoparticles in nitrogen-doped porous carbon sheets (NPCS) via a simple carbonization reaction, producing a porous Fe_3C @NPCS nanocomposite with high conductivity.^[294] As shown in **Figure 17e**, the carbon sheets allowed the uniform distribution of the Fe_3C nanoparticles and accommodated sulfur with mitigated the volume expansion during cycling. The redox kinetics was also accelerated due to the highly conductive NPCS and Fe_3C nanoparticles. Moreover, the Fe_3C nanoparticles offered strong chemical adsorption to polysulfides, which was confirmed by DFT calculations. The calculated binding energies of the Fe_3C (100) surface to Li_2S and Li_2S_2 were 4.87 and 6.37 eV, respectively. The Fe_3C @NPCS composite significantly boosted the utilization of active sulfur species and accelerated the electrochemical performance. Based on these features, the prepared Fe_3C @NPCS-S composite delivered electrochemical stability for 1500 cycles at 2 C with only 0.036% capacity loss per cycle (**Figure 17f**).

Li and co-workers proposed a novel mechanism of polysulfide anchoring by built-in magnetic field enhancement. The authors employed a facile thermal treatment to produce activated cotton textile (ACT), in which ferromagnetic iron/iron carbide ($\text{Fe}/\text{Fe}_3\text{C}$) nanoparticles were *in situ* grown.^[295] The resulting ACT@ $\text{Fe}/\text{Fe}_3\text{C}/\text{S}$ composite revealed a uniform distribution of sulfur. Owing to the ferromagnetic $\text{Fe}/\text{Fe}_3\text{C}$ nanoparticles, an intrinsic magnetic field was introduced, which formed a Lorentz force for the cathode. Such effects changed the diffusion pathway of the polysulfide anions and effectively restrained the ions into the cathode. The composite cathode exhibited a distinct electrochemistry. Only a single discharge plateau was observed in the voltage profiles.

Similarly, Liu *et al.* encapsulated nitrogen-doped CNTs with $\text{Fe}/\text{Fe}_3\text{C}$ nanoparticles ($\text{Fe}/\text{Fe}_3\text{C}$ @N-CNT) in a carbonized melamine sponge, forming freestanding conductive frameworks to anchor sulfur.^[296] As a sulfur host, the hierarchical porosities have large internal

voids, allowing a 14.44 mg cm^{-2} sulfur loading. The wrapped Fe/Fe₃C nanoparticles in N-CNT effectively suppressed the polysulfide shuttling. The prepared freestanding Fe/Fe₃C@N-CNT/S cathodes exhibited remarkably good electrochemical performance. On the basis of DFT calculations, Li *et al.* synthesized Fe₃C nanosheets with an ultra-thin thickness of about 1 nm, grown on mesoporous carbon (Fe₃C-MC).^[297] The Fe₃C nanosheets provided sufficient active sites to chemically anchor and convert polysulfides. The Fe₃C-MC sulfur composite cathode delivered a 1530 mAh g^{-1} capacity during the initial cycles at 0.1 C.

Using an evaporation-induced self-assembly approach, Wei *et al.* prepared ordered mesoporous graphitic carbon/Fe₃C nanocomposites (GC/Fe₃C) as sulfur host.^[298] The obtained mesoporous GC/Fe₃C composite revealed an ultra-high surface area of more than $3000 \text{ m}^2 \text{ g}^{-1}$. Together with the high porosities, 85 wt.% sulfur was loaded. Due to the desirable charge transport pathways, the prepared sulfur cathode revealed high capacities of up to 1350 mAh g^{-1} at 0.1 C.

6.4.3. Other carbides

Other carbides, such as B₄C,^[299, 300] Mo₂C,^[301-303] MoC,^[304, 305] NbC,^[84, 306] and WC,^[307] have also been investigated as sulfur host. For example, Luo *et al.* designed a simple catalyst-assisted approach to grow B₄C nanowires at CNFs.^[299] The obtained B₄C@CNF composite owned several merits for sulfur cathodes: Experimental analyses in combination with DFT calculations confirmed that the chemical anchoring of the B₄C nanowires resulted in the strong polysulfide adsorption. Moreover, B₄C also exhibited a high catalytic activity for sulfur conversion, accelerating the cathode redox kinetics. Such favorable electrode properties contributed to outstanding storage capacities and rate capabilities. As a result, sulfur cathodes, employing B₄C@CNF as host materials, maintained 80% of its original storage capacity after 500 cycles at 1 C.

Wang *et al.* reported porous molybdenum carbide nanorods (Mo_2C NRs) as a bifunctional sulfur host.^[302] XPS spectra proved that Mo_2C NRs strongly anchored polysulfides due to the strong chemical interactions between Mo_2C and polysulfides, resulting in the formation of Mo-S bonds. Due to the introduction of Mo_2C , the activation overpotential of Li_2S was significantly mitigated, implying that Mo_2C facilitated the decomposition of Li_2S during charging. Benefiting from these positive effects, the Mo_2C NRs-S cathodes sustained a long-lasting cycle life of over 500 cycles at 2 C.

Shen *et al.* incorporated conductive NbC nanoparticles in bowl-like trichoderma spore carbon (TSC) with nitrogen and phosphorus codoping, forming a highly porous TSC/NbC network.^[84] As sulfur host, the codoped TSC and conductive NbC enhanced the electron transport and the chemical anchoring of polysulfides. Moreover, the porosities of TSC/NbC networks allowed the uniform distribution of sulfur. The TSC/NbC-S cathode exhibited a discharge capacity of 810 mAh g^{-1} at even 5 C-rate.

6.5. Metal nitrides

Similar to metal carbides, metal nitrides with polarity also show desirable conductivity and good structural stability, some of which, such as TiN and VN, have been developed to confine active sulfur species.^[308]

6.5.1. Titanium nitrides

Goodenough and co-workers initially introduced mesoporous titanium nitride (TiN) to sulfur cathodes. The prepared TiN-S composite electrodes revealed a good reversibility of more than 500 cycles.^[309] Further studies showed that TiN is beneficial to improve the electrochemistry of sulfur cathodes. Li *et al.* introduced TiN nanowires to *in situ* grow these on 3D nitrogen-doped graphene (3DNG), forming a freestanding architecture.^[310] As shown in **Figure 18a**, uniform TiN nanowires were tightly attached to the wrinkled graphene nanosheets. The TiN

surface was coarse and porous (**Figure 18b**). This structure was able to provide abundant sites to adsorb polysulfides. DFT calculations showed that the TiN nanowires revealed strong chemical bonding with polysulfides. The binding energies of various sulfur species on TiN (200) surfaces were in a range from 3.28 to 4.60 eV. This result was consistent with the XPS analyses, in which the S-N-Ti bonding was observed. When employed as sulfur host, the interconnected 3DNG/TiN networks enabled efficient pathways for charge transfer and enough space for sulfur loading. The composite cathode loaded with 4.8 mg cm⁻² sulfur delivered a capacity of 1510 mAh g⁻¹ at 0.5 C. Moreover, with a higher sulfur loading up to 9.6 mg cm⁻², 3DNG/TiN achieved an ultrahigh areal capacity of 12.0 mAh cm⁻² (**Figure 18c**). This work provided a high potential for high energy density Li-S batteries.

Considering the inherent surface properties, Lim *et al.* designed a hierarchically porous TiN (h-TiN) to boost high-rate sulfur cathodes.^[311] The hierarchical porosities were generated via a tunable evaporation-induced self-assembly approach. Owing to the multiscale porous structure, the prepared h-TiN effectively anchored sulfur species. This has been confirmed by XPS studies. In contrast to bare h-TiN, Li₂S₈-treated h-TiN showed new peaks of Ti-S and Ti-N-S bonds, implying the chemical bonding between Li₂S₈ and h-TiN. h-TiN also showed good electrocatalytic properties. Compared with the mesoporous carbon, h-TiN exhibited the enhanced current intensities and beneficial peak shifts in CV, implying mitigated polarization and facilitated redox reactions of sulfur species. Because of these advantages, the h-TiN hosts, loaded with 72 wt.% sulfur, sustained over 1000 cycles at 5 C with a storage capacity of up to 557 mAh g⁻¹. Besides, various structures of TiN, such as hollow spheres^[32, 312, 313] and tubes,^[314] have been studied to make sulfur cathodes more efficient.

6.5.2. Vanadium nitrides

Vanadium nitrides (VN) have desirable conductivities and strong bonding capabilities with respect to polysulfides. Combining porous VN nanoribbons with graphene, Sun *et al.* confirmed

that VN was able to anchor polysulfides and accelerated their electrochemical conversion. By facile chemical etching, associated with a solvothermal-supercritical fluid process, Zhong *et al.* fabricated VN arrays onto porous carbon fibers (PCF).^[48] An acid-etched PCF was used as substrate to grow V_2O_5 via a solvothermal reaction. Subsequent annealing under NH_3 produced PCF/VN scaffolds. From the SEM observation (**Figure 18d, e**), vertically aligned VN nanobelts with an average of 150-200 nm in diameter were uniformly covering PCF. The interconnected porous PCF exhibited a large surface area, allowing high sulfur loadings and physically retarding the polysulfide shuttling. In addition, the conductive VN arrays showed strong chemical adsorption, tightly locking polysulfides inside the pores. Consequently, the designed PCF/VN/S electrode achieved a highly steady capacity of more than 1300 mAh g⁻¹ (**Figure 18f**). The structural merits made PCF/VN/S lower cell polarization with the smallest voltage gap than other counterparts.

Ren *et al.* also noticed the positive effects of VN on the polysulfide immobilization. They synthesized homogenous yolk-shell VN nanospheres with cobalt doping (Co-VN) by a template-free solvothermal reaction followed by a calcination process.^[315] A thin nitrogen-doped carbon was further coated on Co-VN to prepare a Co-VN@C composite as sulfur host. This yolk-shell structure confined polysulfides in the enclosed cavities and alleviated the volumetric swelling upon cycling. The conductive polar VN gave rise to good electronic conductivity and strong affinity with respect to polysulfides. Co-doped VN also showed good electrocatalytic properties. The electrode capacity of Co-VN@C/S reached nearly 1400 mAh g⁻¹ at 0.1 C. The results of other investigations, including VN nanowires^[316] and nanobubbles^[317], have also been reported, showing the efficient suppression of polysulfide shuttling.

6.5.3. Other nitrides

The exploration of various other nitrides to confine sulfur species has also been carried out. Such sulfur hosts include Co_4N ,^[85, 318, 319] WN ,^[320, 321] NbN ,^[322] BN ,^[323] and MoN .^[324] For instance, Xiao *et al.* fabricated Co_4N nanoparticles homogeneously embedded in 2D nitrogen-doped carbon grown onto carbon cloth.^[85] As a freestanding electrode, it significantly boosted the rate capabilities and cycling performance. Theoretical simulations and experimental results showed that Co_4N nanoparticles were able to generate strong chemical anchoring towards polysulfides. Moreover, the catalytic activities of Co_4N benefited the conversion of polysulfides and the precipitation of Li_2S , resulting in accelerated redox kinetics and mitigated cell polarization. These freestanding sulfur cathodes achieved a high capacity up to 1425 mAh g^{-1} at 0.1 C. A storage capacity still reached 745 mAh g^{-1} after 400 cycles.

Huang and coworkers explored the interaction between WN and polysulfides.^[320] They designed 3D porous WN foam blocks as reservoirs to spatially confine sulfur species inside the pores. Theoretical calculations demonstrated that the chemisorption strength of WN towards active sulfur species varied during the lithiation process. For soluble polysulfides, the binding energies gradually decreased from Li_2S_8 to Li_2S_4 , while a significant binding energy recovery occurred for the insoluble Li_2S_2 and Li_2S . The prepared composite cathode delivered high rate capabilities. The capacities at 0.5 and 5 C reached 1090 and 510 mAh g^{-1} , respectively. Ye *et al.* fabricated a 2D MoN-VN heterostructure as a model sulfur host material.^[324] The integration of V allowed tailoring the electronic structure of MoN . The strong coupling between MoN and VN considerably promoted the polysulfide adsorption. MoN-VN -based cathodes loaded with 3.0 mg cm^{-2} sulfur combined a storage capacity of up to 708 mAh g^{-1} at 2 C with a relatively low capacity loss of 0.068% per cycle during the first 500 cycles.

6.6. MXenes

MXenes are a class of 2D transition metal carbides, nitrides or carbonitrides with only a few atom-thick layers.^[325] Their typical formula is $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1-3$), in which M represents

transition metals, X refers to carbon and/or nitrogen, and T_x stands for surface functional groups, such as hydroxyl, oxygen or fluorine. In an MXene structure, $n+1$ M layers and n X layers alternately stack, forming an $[MX]_nM$ arrangement. Various MXene compositions have successively been synthesized since they were firstly reported in 2011.^[326] Due to the structural characteristics, MXenes have high conductivity and are rich in the number of active surface sites, which make them promising candidates for sulfur host materials.^[327-329] The number of MXene chemistries are meanwhile expanding, for example, to $Ti_3C_2T_x$,^[330, 331] Ti_2CT_x ,^[87] and Mo_2CT_x .^[332]

Nazar and co-workers initially investigated the application of MXenes for sulfur cathodes. They proposed Ti_2C to be an excellent sulfur host.^[87] Benefiting from the high metallic conductivity and desirable anchoring effect, Ti_2C with 70 wt.% sulfur content displayed a long-term cycling stability. XPS analyses determined that the exposed terminal Ti atoms acted as Lewis acid sites to form strong Ti-S bonds with active sulfur species.

In their follow-up study, the authors further investigate the surface interaction between polysulfide species and two new MXene materials (Ti_3C_2 and Ti_3CN).^[90] XPS studies (**Figure 19a, b**) revealed that both of the Li_2S_4 -treated Ti_3C_2 and Ti_3CN composites indicated significant Ti-S interaction by a peak from a Ti-S bond (455.6 eV). This can be ascribed to the strong Lewis acid-base interaction between Ti atoms and polysulfide ions. The corresponding S 2p spectra of the Li_2S_4 -treated MXene confirmed the formation of thiosulfate and polythionate complexes, implying the reduction of the hydroxyl terminal groups on MXene. On the basis of the XPS analyses, a two-step process was proposed to describe the interaction between MXene and polysulfides, as illustrated in **Figure 19c**. The hydroxyl groups of Ti_3C_2 and Ti_3CN initially underwent a redox process with polysulfides to produce thiosulfate/polythionate species, resulting in the cleavage of Ti-OH bonds and exposure of acid-active sites. Subsequently, the exposed Ti atoms with empty orbitals accepted electrons from the electronegative polysulfides, forming S-Ti bonds through Lewis acid-base interactions. Such dual adsorption of polysulfides

enabled the uniform Li_2S deposition and substantially suppressed the diffusion of polysulfides. The authors incorporated CNTs into these TMXene layers, building sulfur hosts with a porous conductive network. The storage capacities of about 450 mAh g^{-1} after 1200 cycles were achieved with a fading rate of 0.043% per cycle.

6.6.1. Functionalized MXenes

Considering the abundant surface functional groups of MXenes, investigating their interactions with polysulfide species is beneficial to the design of better sulfur anchoring host materials. Relevant theoretical studies have been conducted on O/F-functionalized Ti-based MXenes.^[333-335] These simulation results demonstrated that O/F-functionalized groups can effectively anchor active sulfur species. Experimental results further revealed their immobilization mechanism.

For instance, Tang *et al.* encapsulated nanoscale sulfur particles into 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets to form a viscous aqueous ink. By vacuum-filtration, such ink could directly form a freestanding and flexible $\text{S@Ti}_3\text{C}_2\text{T}_x$ electrode.^[336] A facile two-step process resulted in the formation of an $\text{S@Ti}_3\text{C}_2\text{T}_x$ ink (**Figure 19d**). With sodium polysulfides and formic acid in a $\text{Ti}_3\text{C}_2\text{T}_x$ suspension, sulfur was *in situ* formed. The uniform and viscous $\text{S@Ti}_3\text{C}_2\text{T}_x$ ink was obtained after washing and centrifugation (**Figure 19e**). According to the experimental analyses, the authors discovered that a thick sulfate complex layer was *in situ* formed as protective barrier, mitigating the migration of polysulfides from the sulfur cathodes. Consequently, the $\text{S@Ti}_3\text{C}_2\text{T}_x$ electrodes with 70 wt.% sulfur loading revealed favorable rate capabilities. A good capacity of 1244 mAh mg^{-1} at 0.1 C was achieved (**Figure 19f**).

On the basis of a similar strategy, Tang *et al.* further developed another robust and freestanding $\text{Ti}_3\text{C}_2\text{T}_x/\text{S}$ paper by a filtration-evaporation approach. As a sulfur cathode, this $\text{Ti}_3\text{C}_2\text{T}_x/\text{S}$ paper exhibited a durable cycling performance and ultralow capacity fading.^[337] Besides, S-functionalized groups have also been introduced to MXenes for anchoring

polysulfides.^[338] The moderate adsorption of polysulfides from S-functionalized V_2C not only effectively restricted the shuttling but also prevented polysulfide decomposition.

6.6.2. MXene composites

Due to the hydrogen bond formation, surface functional groups in MXenes may cause the restacking of MXene nanosheets. Such aggregation considerably decreases the active area and the number of anchoring sites. Therefore, various conductive carbons and inorganic compounds have been integrated with MXenes in order to achieve enhanced capacity and increased cycle life.^[339-343] The Wang group developed a series of 3D MXene/carbon hybrid structures to further improve Li-S batteries.^[344-346] For example, they reported a hybrid 3D $Ti_3C_2T_x$ @mesoporous carbon architecture ($Ti_3C_2T_x$ @Meso-C) as sulfur host material.^[344] The introduced Meso-C have a homogeneously porous structure, which offered sufficient voids for sulfur incorporation and effectively reduced the swelling of sulfur cathodes. Moreover, due to the strong hydrophilic surface, the $Ti_3C_2T_x$ nanosheets were successfully stabilized by Meso-C. XPS analyses demonstrated the chemisorptive nature of $Ti_3C_2T_x$ nanosheets. With sulfur loading, S-Ti-C bonds were formed during the heat treatment. The resulting $Ti_3C_2T_x$ @Meso-C/S cathodes attained an initial storage capacity of 1225.8 mAh g^{-1} at 0.5 C and 704.6 mAh g^{-1} after 300 cycles.

Wang and co-workers further designed a freestanding 3D porous $Ti_3C_2T_x$ /rGO hybrid aerogel (MX/G) as polysulfide reservoir.^[346] An MX/G composite cathode was directly obtained with the Li_2S_6 catholyte. The 3D interconnected network (**Figure 19g**) offered high conductivity and enabled fast Li^+ diffusion. The planar polar interface of $Ti_3C_2T_x$ chemically anchored polysulfides via Ti-S bonds. This 3D porous MX/G substantially boosted the cathode utilization and improved the sulfur reaction kinetics. The optimal MX/G aerogel cathode with 30% $Ti_3C_2T_x$ (MX/G-30) revealed a high capacity of 1270 mAh g^{-1} at 0.1 C and a prolonged cycle life with very low capacity fading of only 0.07% per cycle (**Figure 19h**). In addition,

cathodes loaded with high sulfur content up to 6 mg cm^{-2} attained a 5.27 mAh cm^{-2} areal capacity. The Wang group also explored the heteroatom doping strategy to MXenes.^[31] Nitrogen doping applied to MXene nanosheets revealed a strong physical and chemical adsorption towards polysulfides.

6.7. Metal-organic frameworks

Metal-organic frameworks (MOFs) are compounds composed of metal ions coordinated with organic linkers. Due to the diversity of the coordination between metal ions and organic linkers, MOFs possess tunable chemical composition, structures, and porosity, making these materials highly interesting for applications in energy, catalysis, and gas storage. With regard to Li-S batteries, the intrinsic porosity of MOFs enables high sulfur loading and deep electrolyte penetration. In addition, MOFs have abundant metal sites, which can serve as Lewis acid to anchor sulfur species. Based on these advantages, MOFs are promising candidates to be applied as sulfur host materials. Another merit is that the tunable properties allow MOFs as good precursor materials to construct various nanoscale materials with favorable porosity. By either direct annealing or template-engaged reactions, MOF precursors can readily convert into porous/hollow nanocarbon or metal-based architectures, including oxides, hydroxides, and sulfides. Such MOF-derived materials are also promising sulfur hosts, which have been discussed in detail above. In this section, we mainly focus on pristine MOFs and MOF composites as sulfur host materials.

6.7.1. Pristine MOFs

Pristine MOFs were initially introduced to Li-S batteries by Tarascon and co-workers. They employed MIL-100 (Cr) as sulfur host.^[347] Combining TEM and XPS analyses, the pores of MIL-100 (Cr) were confirmed to reversibly capture and release polysulfides upon cycling, and the S-MOF interaction was demonstrated. Such effects contributed to the increased capacity

retention of sulfur cathodes. The adsorption of MOFs towards polysulfides has been investigated by theoretical calculations. Park *et al.* revealed that the coordinately unsaturated metal sites (CUS) of MOFs were responsible for the dominant adsorption of all sulfur species.^[348] The anchoring of polysulfides was tunable by substituting CUS. 16 metal-substituted variants of MOF-74 were computationally screened as optimal compositions, exhibiting outstanding anchoring to polysulfides. Li *et al.* investigated the adsorption of a Cu-benzenehexathial (Cu-BHT) monolayer towards sulfur species via first-principles calculations.^[349] The results showed that the Cu-BHT monolayer had a moderate interaction with polysulfides to suppress their dissolution. In addition, Cu-BHT enabled the uniform deposition of Li_2S , improving the sulfur utilization and enhancing the conversion between polysulfides and Li_2S .

Due to the nature of MOFs as Lewis acid, tailoring the coordination of metal ions is a major strategy to anchor polysulfides.^[350] Baumann *et al.* systematically analyzed favorable sulfur adsorption sites of CuBTC via theoretical calculations and experiments.^[351] They found that the decrease in particle size of CuBTC caused the increased density of Cu sites, which substantially improved the polysulfide retention and discharge capacity. Hong *et al.* developed a bi-functional nano-sized MOF (Cu-TDPAT) as a sulfur host material.^[352] Cu-TDPAT combined the Cu(II) Lewis acidic sites with the nitrogen Lewis basic sites from the ligands to anchor sulfur species and lithium ions. By further optimizing the particle size, Cu-TDPAT with an average size of 100 nm effectively anchored polysulfides. The prepared S@Cu-TDPAT cathode exhibited a prolonged 500 cycle cell lifespan at 1 C with a stable capacity of about 745 mAh g⁻¹.

Liu *et al.* synthesized a unique manganese cluster-based porous MOF ($\text{Mn-CC-}x\text{H}_2\text{O}$).^[353] As illustrated in **Figure 20a**, the coordinated water molecules in $\text{Mn-CC-}x\text{H}_2\text{O}$ were readily removed by thermal activation, resulting in the conversion from the central Mn ions to unsaturated metal sites. With the elimination of coordinated water molecules, the activated Mn-

CC provided abundant open metal Lewis acid sites to anchor polysulfides. Integrating the porosity of Mn-CC as sulfur host effectively inhibited the polysulfide shuttling through spatial confinement and chemical anchoring. The resulting composite cathode delivered a 1420 mAh g⁻¹ capacity during the initial cycles at 0.2 C and stabilized at 990 mAh g⁻¹ after 200 cycles (**Figure 20b**). Other research involving highly conductive Ni-based MOF of Ni₃(HITP)₂ has been synthesized by Cai *et al.*, which revealed favorable adsorption of polysulfides and enhanced electrochemical performance.^[354]

6.7.2. MOF composites

Despite the superiority of MOFs, their poor conductivity incurs severe cell polarization and sluggish redox kinetics of sulfur cathodes. Moreover, the structural fragility of MOFs also causes performance instability of batteries upon prolonged cycling. Constructing flexible and highly conductive MOF composites is capable of overcoming these hurdles. There have been many studies that introduce CNTs,^[355-357] rGO,^[358] polymers,^[359] and other carbon materials^[360] to MOFs to produce composite materials. For instance, Mao *et al.* designed a foldable interpenetrated MOF/CNT thin film as binder-free and flexible host.^[355] Such films possess a hierarchically porous structure of 3D conductive networks, in which sulfur species were anchored by the hierarchical pores and open metal sites of MOFs. The interwoven CNTs contributed to the enhanced conductivity and structural integrity of electrodes. The authors compared three MOFs (HKUST-1, MOF-5, and ZIF-8) with different pore sizes to determine the porosity effects on the electrochemistry of sulfur cathodes (**Figure 20c**). The results revealed that the loaded S₈ ring with a diameter of 0.68 nm was barely encapsulated in the cavity of ZIF-8 with an entrance of 0.34 nm, which was mainly dispersed at the surface of ZIF-8. The narrow pore effect gave rise to poor utilization of sulfur and fast capacity decay. With regard to MOF-5, the 0.8 nm entrance size was sufficient for S₈ to access the cavity, but such size was still smaller than HKUST-1. These relatively small pores resulted in fast capacity

fading in the initial cycles. Furthermore, the open copper sites of HKUST-1 were able to anchor polysulfides via Lewis acid-base interactions, while the lack of open metal sites in MOF-5 and ZIF-8 was not. Benefiting from these advantages, the selfstanding S@HKUST-1/CNT cathode exhibited an initial capacity of 1263 mAh g⁻¹ at 0.2 C and sustained 500 cycles, in which the capacity decayed only 0.08% per cycle (**Figure 20d**).

The enhancement in conductivity of MOFs will contribute to high rate sulfur cathodes. Jiang *et al.* combined polypyrrole (ppy) with MOFs, resulting in increased conductivity by 5 to 7 orders of magnitude.^[361] The constructed ppy-MOF composites with proper ion channels promoted ion diffusion and achieved high rate performance. PCN-224 with cross-linked pores and tunnels enabled shortest ions diffusion pathways and provided the largest pore apertures, leading to the fastest ion transfer. As a result, even at 10 C, the ppy-S-in-PCN-224 composite cathode exhibited a 680 mAh g⁻¹ capacity from the first cycle and sustained 440 mAh g⁻¹ after 1000 cycles.

Liu *et al.* presented a 3D free-standing monolithic electrode comprising ZIF-67 and HKUST-1 well dispersed in highly conductive N, P codoped carbon.^[362] The 3D monolithic carbon network enabled the encapsulation and electrical correlation of MOF nanodomains, which were responsible for prolonged capacity retention of sulfur species and increased sulfur loading. An optimized 3D carbon-HKUST-1 cathode achieved high areal and volume capacities of 16 mAh cm⁻² and 1231 mAh cm⁻³ at 0.2 C, respectively. Besides, the combination of polypyrrole and ZIF-67 has also been proven improved electrochemical performance for Li-S batteries.^[363] These results demonstrated that MOFs with proper entrance pore sizes and open metal sites are favorable for high volumetric energy density cathodes.

Overall, various metal compound host materials employed in Li-S batteries significantly improve the sulfur utilization and battery cycling stability. Their strong polysulfide anchoring, resulting from chemical bonding, effectively inhibits the shuttle problem of polysulfides. Furthermore, in combination with other nanostructured carbon, metal compound hosts are able

to improve the electrochemical performance enabling long-life Li-S batteries. **Table 3** summarizes the latest research advances on metal compound host materials applied in Li-S batteries.

7. Conclusions and outlook

In this review, recent advances in various sulfur host materials anchoring polysulfides have been comprehensively discussed. Two anchoring strategies were shown to be important: physical confinement and chemical bonding. With regard to physical confinement, sulfur hosts with porous and layered or shelled electrode structures can serve as physical barriers to successfully confine polysulfides upon cycling. As for chemical bonding, four chemical interactions between sulfur hosts and active sulfur species have been identified: (1) polar-polar interactions; (2) Lewis acid-base interactions; (3) redox interactions; (4) covalent binding interactions. These four interactions can effectively confine polysulfides by chemical anchoring.

Combining the characteristics of the physical confinement and chemical bonding, various sulfur hosts have been proposed and synthesized. Subsequently, three classes of sulfur host materials have been discussed: (1) nanostructured carbon; (2) polymers; (3) metal compounds. A number of studies have demonstrated that all three materials are able to inhibit active sulfur species from diffusing into the electrolyte. Nanostructured carbon hosts generally suppress the polysulfide diffusion from cathodes by physical confinement due to their diverse structures and large surface area. Soluble polysulfides can be tightly stowed away in the pores, cavities, or layers of the carbon architecture, leading to significant increases in sulfur utilization and electrochemical performance. Furthermore, nonpolar carbon-based materials can also be converted into polar host materials by adopting certain approaches, such as doping. Consequently, these polar carbon hosts simultaneously own the physical confinement and chemical bonding towards sulfur species.

The multifunctional advantages of polymers also play an essential role in enhancing the utilization of sulfur cathodes. Their readily tunable structure and abundant surface groups integrate the physical confinement and chemical bonding ability to anchor sulfur species. Another important characteristic is that polymers can immobilize sulfur by covalent bonding. In sulfurized polymers, sulfur is covalently bonded to the backbones of polymers via the C-S bonds. As a result, no soluble polysulfides exist during the whole charging and discharging process. The shuttle problem can, therefore, be completely eliminated.

Metal compounds are another major type of sulfur host. The anchoring of polysulfides by metal compound hosts has been developed making use of the various mechanisms. Several metal compound hosts have been analyzed with respect to their fundamental polysulfide-anchoring properties. The intrinsic polarity allows metal compounds to strongly bind with polar polysulfides. The active sites of metal compounds can chemically anchor polysulfides via polar and Lewis acid-base interactions. Some of the metal compounds have been shown to catalyze the conversion of active sulfur species by redox interactions. The chemical interactions concluded in this review are able to explain most anchoring mechanisms of metal compound hosts towards polysulfides. On the other hand, the poor conductivity of many metal compounds also incurs a sluggish charge transfer and high electrochemical polarization. These drawbacks impede the charge transfer reaction kinetics. The prevalent solution is, therefore, to integrate highly conductive carbon with metal compounds to fabricate composite host materials.

The discussion above has identified that the three classes of host materials are promising for high-performance Li-S batteries. However, the different types of host materials exhibit distinct improvement in terms of battery capacity, cycle life and rate capability. Due to the high conductivity and large surface area, nanostructured carbon hosts favor a high rate capability. They can facilitate electron/ion pathways and accelerate charge transfer. Therefore, battery polarization is significantly mitigated. Some of conductive polymer hosts also reveal such characteristics. In addition, sulfurized polymers can achieve more durable cycle life owing to

the elimination of polysulfide shuttling. As regards metal compounds, their favorable chemical bonding to polysulfides suppresses the polysulfide loss and improves the utilization of active species. Thus better battery capacity and cycle life are expected. If we take all characteristics into account, conductive polar metal compounds would be the most promising host materials at this moment, which can achieve high sulfur utilization and fast redox kinetics. This class of host materials intrinsically possess two major advantages: (1) high conductivity for charge transfer; (2) strong anchoring effects on polysulfides. Integrating rational structural design and tailoring, they are expected to solve the current problems of sulfur cathodes. Significant outcomes have confirmed that some conductive polar metal compounds, such as manganese oxides,^[88, 197] titanium oxides,^[78, 191] cobalt sulfides,^[81, 246, 249] and VN,^[53] can successfully achieve balanced performance in terms of capacities and rate capabilities.

By reviewing various sulfur host materials, it can be concluded that there are still several problems that should be further investigated. The first one is the amount of host material in the electrodes. Since the major merit of Li-S batteries compared with traditional Li-ion counterparts is the high energy density, the electroactive species in sulfur cathodes should be kept as high as possible to achieve this highly relevant energy density. The reported sulfur/host composites normally contain 20-30 wt.% host materials. Together with the conductive agent and binder, the actual active sulfur mass in the electrodes is mostly below 75 wt.%. This value is notably inferior to that of commercial Li-ion batteries, in which the electroactive species can account for as high as 95 wt.% of the whole electrode. Moreover, because of the low density of sulfur and the large porosity of cathodes, Li-S batteries typically exhibit only limited volumetric energy densities. The excessive use of host materials will further decrease this volumetric energy density.

In order to achieve commercial applications, decreasing the content of host materials should therefore be explored in more detail. The present approach mainly focuses on *ex-situ* integrating host materials with sulfur to fabricate host/sulfur composites. The exploration of the *in situ*

formation of robust protection layers at the surface of sulfur cathodes might be effective to protect sulfur species from dissolving into the electrolyte. Electrolyte tuning or physical/chemical pre-treatment may play a vital role in constructing such layers. Relevant studies are barely reported.

Another problem that has been extensively addressed is the interaction between sulfur hosts and polysulfides. Both theoretical calculations and experimental results have demonstrated that these interactions contribute to the polysulfide confinement. However, there have not been sufficient studies to clarify the underlying interaction mechanisms. The chemical bonding between the surface sites of the host materials and sulfur species typically combined different interactions, *e.g.* polar-polar and Lewis acid-base interactions, which are difficult to be distinguished using a single characterization approach. In addition, the interaction strength is another major factor that affects the utilization of sulfur cathodes. The stronger the interaction, the stronger the bonding. However, a too strong bonding will negatively influence the conversion of sulfur species and cause their decomposition and consequently capacity loss. A more detailed understanding of the mechanisms will help to design even more efficient host materials and reduce the host material content in sulfur electrodes.

The third problem is related to the catalytic properties of host materials. Many metal compounds exhibit high electrocatalytic activities that facilitate the electrochemical conversion of active sulfur species during cycling. This promotes sulfur utilization and the redox kinetics, significantly improving the battery performance. However, the catalytic mechanism of host materials is still inadequate, which is expected to be further elucidated from theoretical and experimental analyses. In addition, host materials with favorable catalytic properties only are unable to prevent the polysulfide diffusion from the cathodes. For instance, when a sulfur cathode partly discharges above 2 V and then stops, in which sulfur species mainly exist in the form of soluble polysulfides, the catalytic effects will also stop. In this case, polysulfides will dissolve and diffuse into the electrolyte if the host material does not have any confinement.

Therefore, the principal concern is still to confine polysulfides into the cathode. Combined confinement and electrocatalytic conversion is therefore of critical importance for the design of efficient sulfur host materials. As long as a host can effectively confine polysulfides during the whole discharge stage, the catalytic effect will contribute to the performance increase.

Li-S batteries have fulfilled a major breakthrough over the last few years. However, recent research on sulfur host materials seems to level off. Designing an ideal host material still faces some challenges. As a conversion reaction electrode, sulfur converts into various soluble polysulfide intermediates during (de)lithiation. A sulfur host is essential for polysulfide anchoring in the cathode. At present, there is not been a single host material that can address all the problems. Integrating the advantages of different types of host materials will further boost the performance of Li-S batteries.

Despite many problems and difficulties faced by sulfur cathodes, it is believed that Li-S batteries, which exhibit high energy density and long-term cycling stability, will eventually be commercialized through further theoretical studies and experimental analyses.

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List of Abbreviations

2D	two-dimensional
3D	three-dimensional
3DNG	3D nitrogen-doped graphene
3DOMC	3D ordered macro/mesoporous carbon
AAO	anodic aluminum oxide
AB	acetylene black
ACC	activated carbon cloth
ACT	activated cotton textile
ALD	atomic layer deposition
APS	almost pure sulfur
AZO	Al_2O_3 -doped ZnO
BPCS	boron-doped porous carbon sphere
CCB	conductive carbon black
CEID	capillary evaporation-induced drying
CFs	carbon fibers
C-HS	carbon hollow spheres
CMC	carboxymethyl cellulose
CNFs	carbon nanofibers
CNTs	carbon nanotubes
CP	carbon-fiber paper
CUS	coordinately unsaturated metal sites
CV	cyclic voltammetry
CVD	chemical vapor deposition
d	pore diameter
DCNTs	disordered CNTs

DFT	density functional theory
EDA	Ethylenediamine
EFG	EDA-functionalized rGO
EIS	electrochemical impedance spectroscopy
E-CNT	ethylenediamine modified CNT
G	graphene
GF	graphene foam
GM	graphene monolith
GN	graphene nanosheets
GO	graphene oxide
GS	graphene sheets
HCB	hollow carbon nanoboxes
HCD	hollow cathode discharge plasma
HCFs	hollow carbon nanofibers
HCS	hollow carbon spheres/hierarchical carbon spheres
HMCN	hollow mesoporous carbon nanosheets
HPCNF	hierarchically porous carbon nanofiber
IB	ink-bottle-like
IBGM	ink-bottle-like graphene monolith
ImIP	imidazolium-based ionic polymer
LBL	layer-by-layer
LDHs	layered double hydroxides
Li-S	lithium-sulfur
MCNF	multichannel carbon nanofibers
Meso-C	mesoporous carbon architecture
MOFs	metal-organic frameworks

MPC	Microporous carbon/micro-mesoporous carbon
MSPAN	mesoporous sulfurized polyacrylonitrile
MTDNTs	mesoporous TiO ₂ nanotubes
MWCNTs	multi-walled CNTs
MX/G	Ti ₃ C ₂ T _x /rGO hybrid aerogel
NCC	nitrogen-doped carbon comb
NCNTs	nitrogen-doped CNTs
NG/rNGO	nitrogen-doped graphene
NGCN	nitrogen-doped graphitic carbon nanoshells
NNH	nickel-based hydroxide
NONPCM	nonporous carbonaceous material
NPC	nitrogen-doped porous carbon
NPCS	nitrogen-doped porous carbon sheets
NPDSCS	nitrogen and phosphorous doped carbon spheres
NRGO	nitrogen-doped reduced graphene oxide
NSC	nitrogen and sulfur co-doped porous carbon
OMC	ordered mesoporous carbons
OMCNS	ordered mesoporous carbon nanosheets
P3HT	poly(3-hexylthiophene)
PAB	phosphorous-doped activated biomass-derived carbons
PAN	polyacrylonitrile
PANi/Pani	polyaniline
PAQS	poly(anthraquinonyl sulfide)
PCF	carbon fiber cloth/porous carbon fibers
PCN	porous C ₃ N ₄ nanosheets
PCNF	porous carbon nanofibers

PDA	polydopamine
PEG	polyethylene glycol
PEI	polyethylenimine
PEMs	polyelectrolyte multilayers
PGC	porous graphitic carbon
PMMA	polymethyl methacrylate
POF-HS	porphyrin organic framework hollow spheres
PPy	polypyrrole
PRC	puffed rice derived carbon
PS	polystyrene
PVDF	polyvinylidene fluoride
PVP	polyvinylpyrrolidone
PYC	porous yeast carbon
QDFT	quantum density functional theory
rGO/RGO	reduced graphene oxide
SACNT	super-aligned CNT
SDCNTs	sulfur-impregnated disordered CNTs
SEI	solid electrolyte interphase
SEM	scanning electron microscope
SPAN	sulfurized polyacrylonitrile
SWCNT	single-wall CNT
TABQ	tetra(allyloxy)-1,4-benzoquinone
TEM	transmission electron microscope
TSC	trichoderma spore carbon
TTCA	trithiocyanuric acid
UMC	ultra-microporous carbon

UV-vis	ultraviolet-visible spectroscopy
VACNTs	vertically aligned CNTs
XANES	X-ray absorption near-edge structure
XPS	X-ray photoelectron spectroscopy
YSC	yolk-shelled carbon nanoboxes

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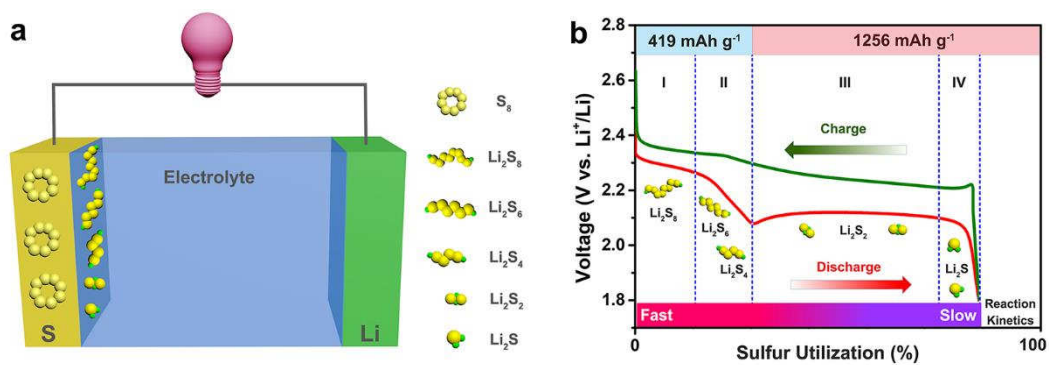


Figure 1. a) Schematic representation and b) typical charging and discharging voltage profile of Li-S batteries, also indicating the various intermediate sulfur species.

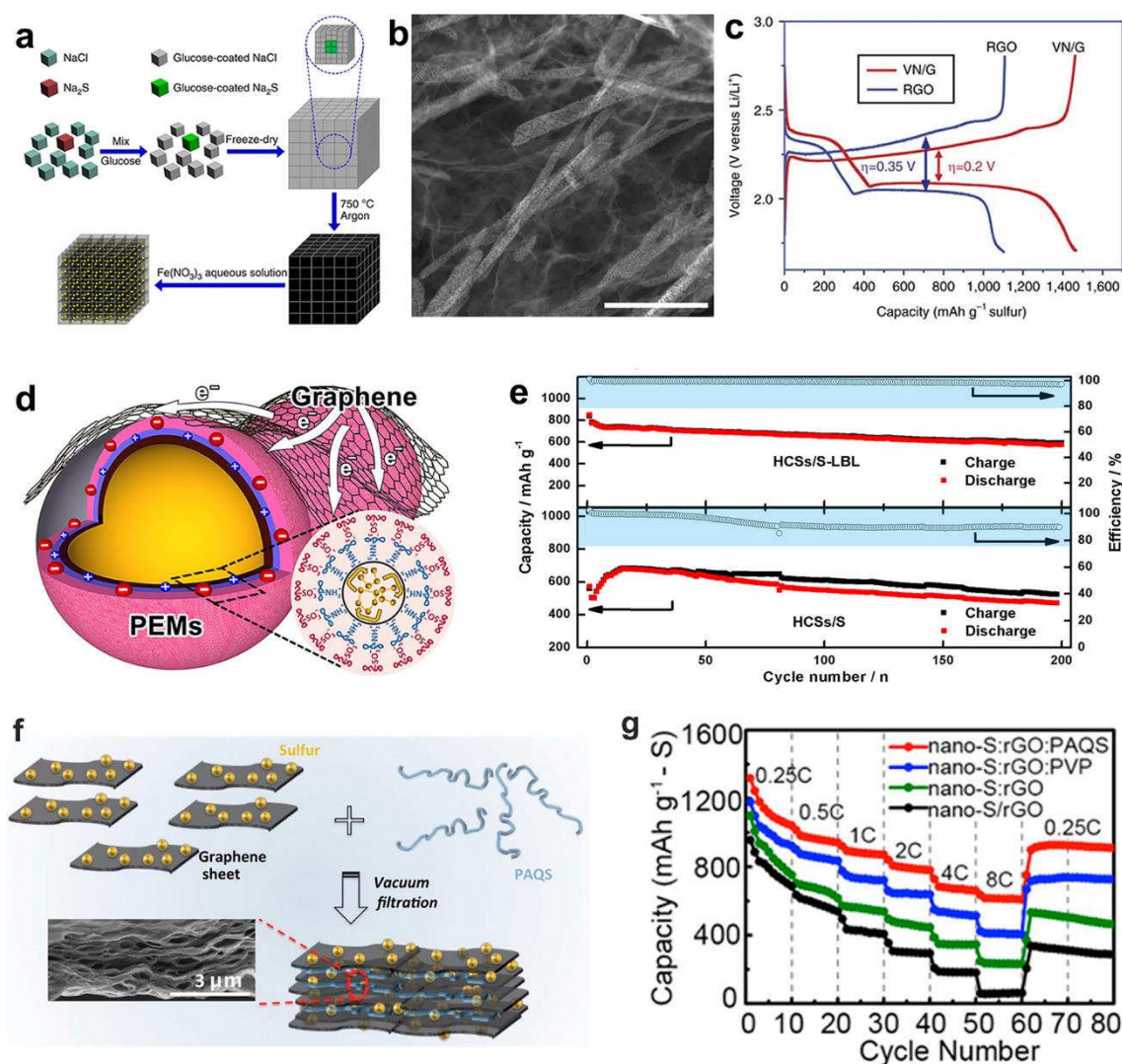


Figure 2. a) Schematic representation of *in situ* preparation of 3D S@PGC. b) STEM image of VN/G (scale bar: 500 nm). c) Voltage profile of an VN/G electrode at 0.2 C. d) LBL film coated HCS/S composites. e) Cycle life performance and Coulombic efficiency of HCS/S-LBL at 1 A g⁻¹. f) Schematic illustration and g) rate performance of a nano-S:rGO:PAQS thin film cathode.

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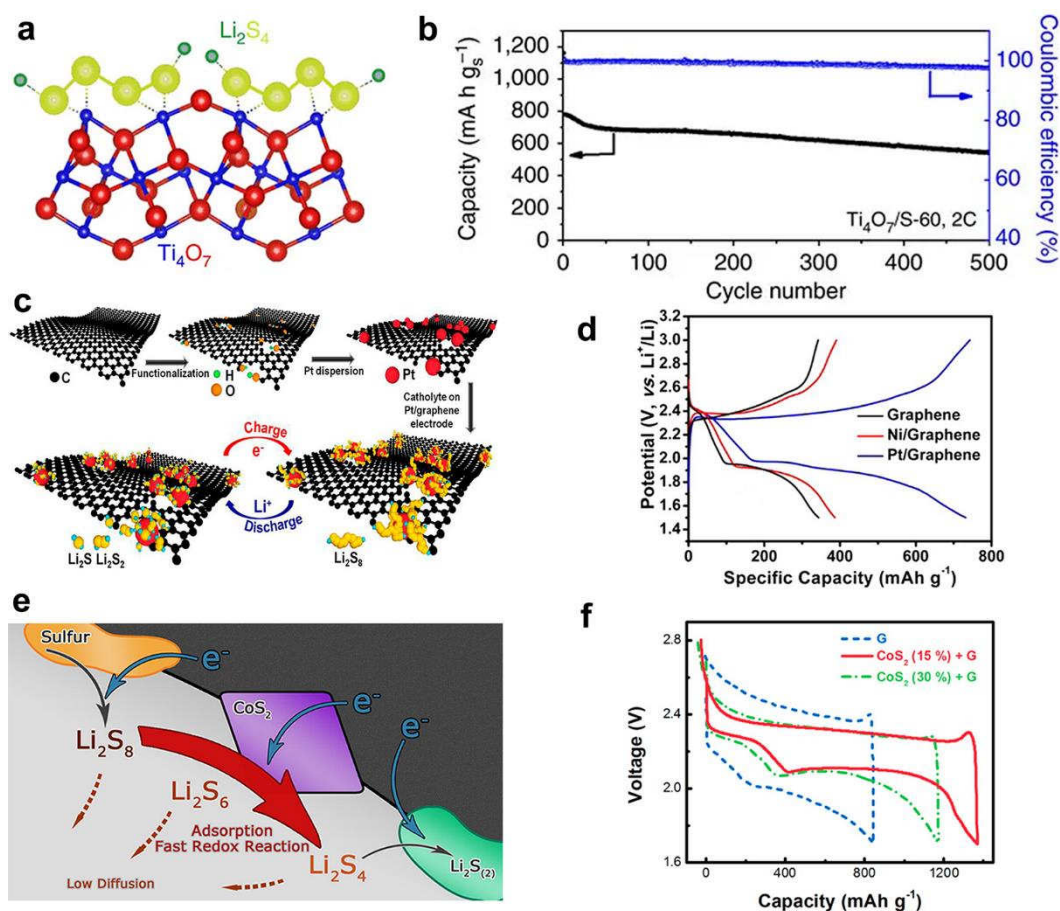


Figure 3. a) Schematic illustration of electron density transfer between Li_2S_4 and Ti_4O_7 . b) Cycle life performance of a $\text{Ti}_4\text{O}_7/\text{S-60}$ electrode at 2 C. c) Synthesis of electrocatalyst anchored graphene nanocomposite and its interaction with polysulfides. d) Voltage profiles of pristine and electrocatalyst anchored graphene electrodes. e) Schematic illustration of the adsorption and accelerated redox reaction of polysulfides by CoS_2 . f) Voltage profiles of S/G cathodes with and without CoS_2 . a, b) Reproduced with permission.^[78] Copyright 2014, Springer Nature. c d) Reproduced with permission.^[91] Copyright 2015, American Chemical Society. e, f) Reproduced with permission.^[30] Copyright 2016, American Chemical Society.

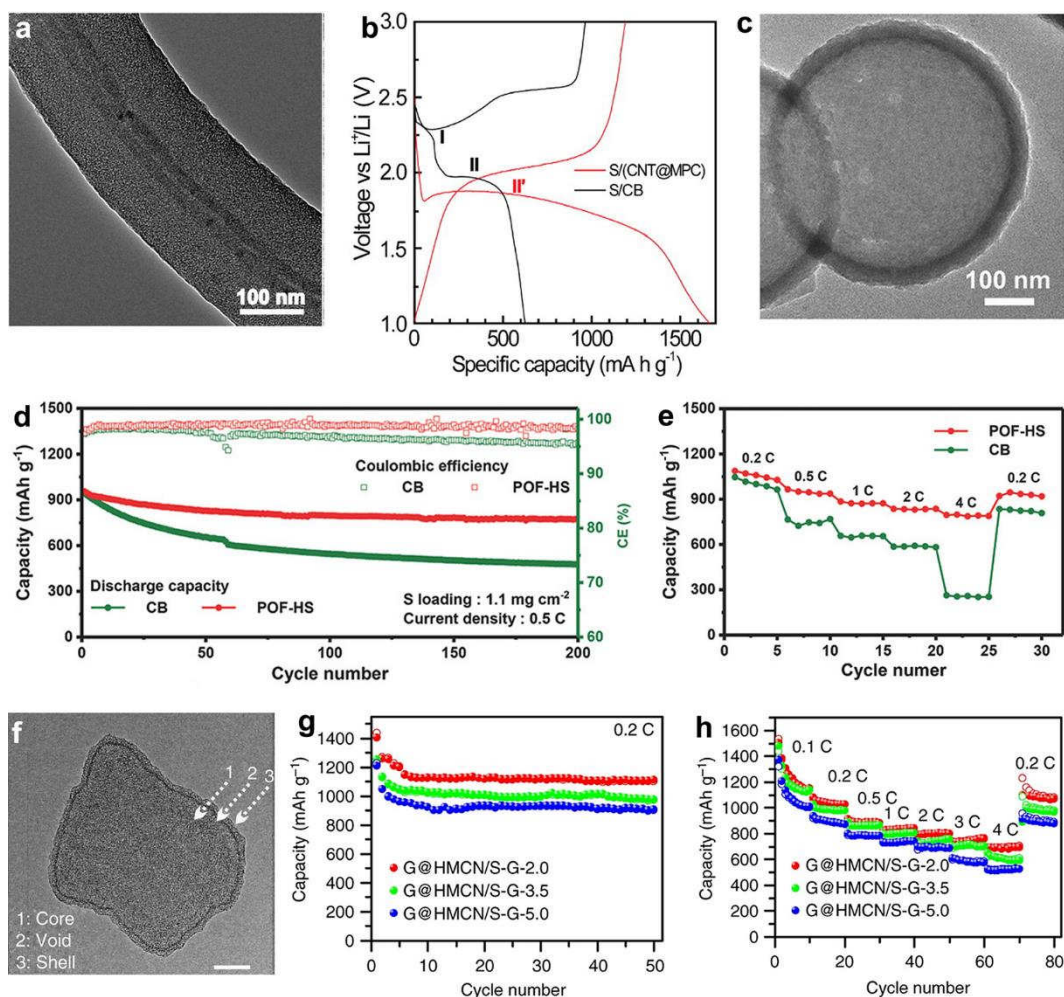


Figure 4. a) TEM image of a CNT@MPC nanocable. b) Voltage profile of S/(CNT@MPC) at 0.1 C. c) TEM image of POF-HS with the typical hollow spherical morphology. d) Cycling performance and e) rate performance of POF-HS/S. f) TEM image of G@HMCN (scale bar: 50 nm). g) Voltage profiles and h) rate performance of G@HMCN/S-G cathodes with various sulfur loading. a, b) Reproduced with permission.^[103] Copyright 2012, American Chemical Society. c-e) Reproduced with permission.^[108] Copyright 2018, Wiley-VCH. f-h) Reproduced with permission.^[111] Copyright 2017, Springer Nature.

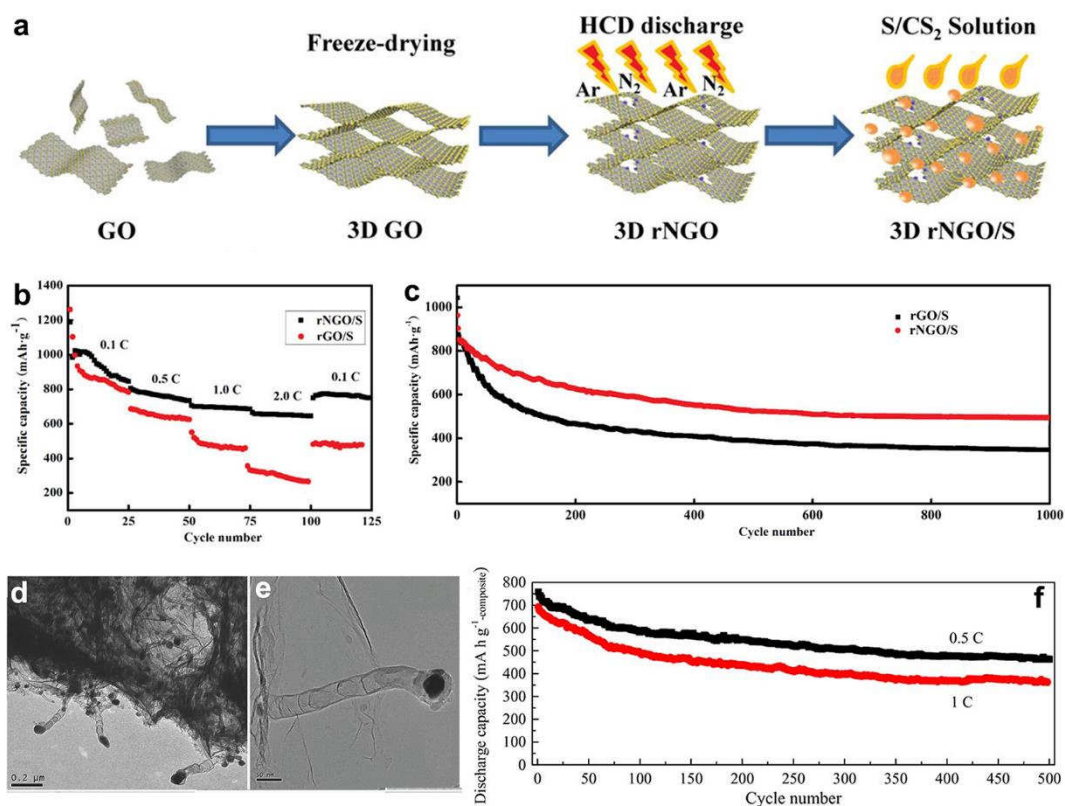


Figure 5. a) Schematic illustration of the fabrication of rNGO/S. b) Rate capability and c) cycling performance of rNGO/S composite cathodes. d, e) TEM images of the GN-CNT matrix. f) Prolonged cycling performance of S/GN-CNT composites. a-c) Reproduced with permission.^[116] Copyright 2019, Wiley-VCH. d-f) Reproduced with permission.^[124] Copyright 2017, Wiley-VCH.

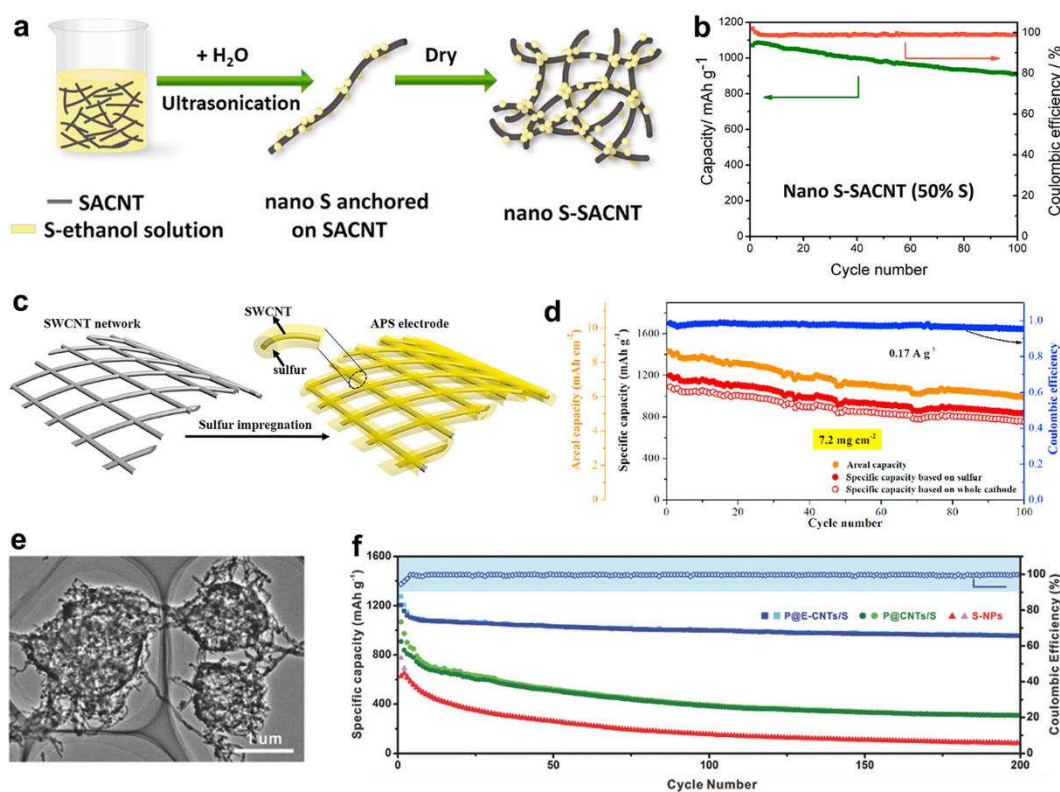


Figure 6. a) Schematic representation of the synthesis of nano S-SACNT composites. b) Cycling performance of S-SACNT at 1 C. c) SWCNT network of an APS electrode. d) Cycling performance of 3-stacked SWCNT electrode. e) TEM image of P@E-CNT/S. f) Cycling performance of P@E-CNT/S at 0.2 C. a, b) Reproduced with permission.^[130] Copyright 2014, American Chemical Society. c, d) Reproduced with permission.^[133] Copyright 2017, Elsevier. e, f) Reproduced with permission.^[135] Copyright 2018, Wiley-VCH.

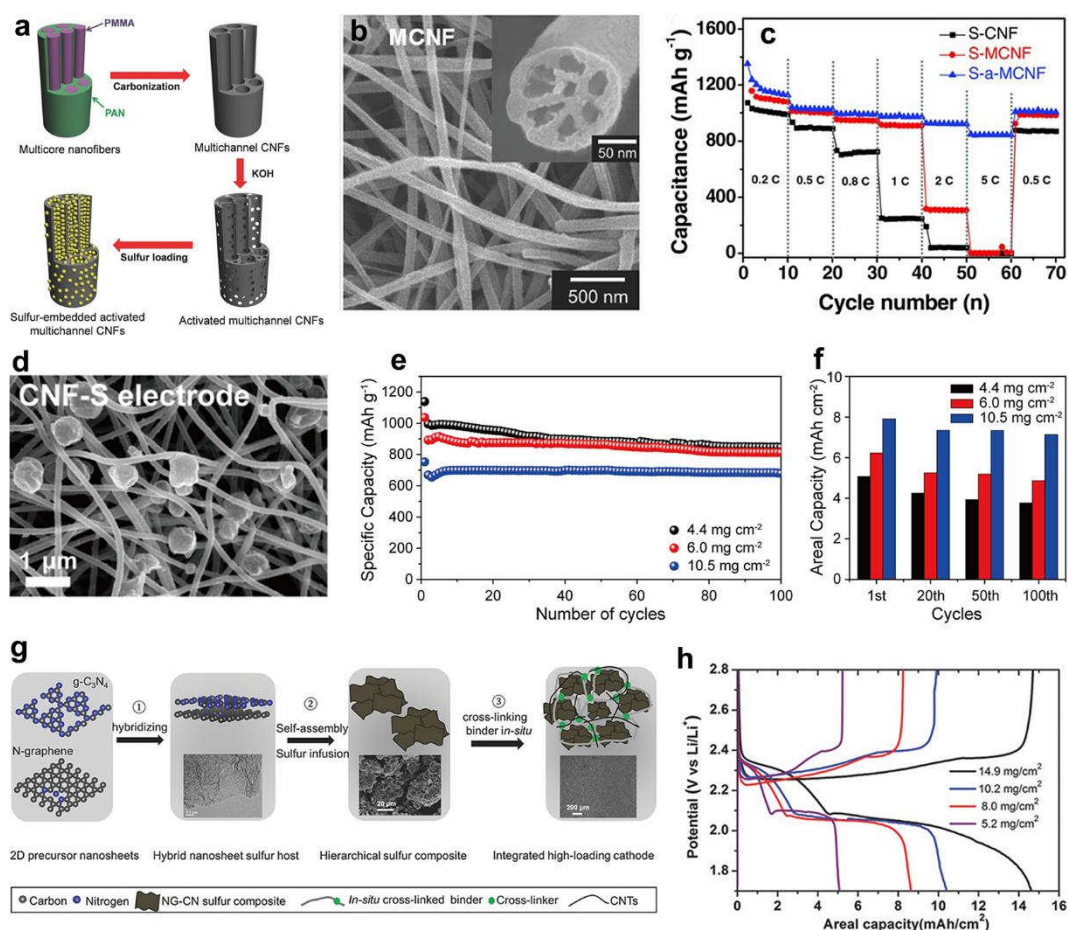


Figure 7. a) Illustration of the fabrication of S-a-MCNF. b) Low and enlarged cross-sectional (inset) SEM images of MCNF; the inset shows the microporous shell. c) Rate capabilities of S-a-MCNF. d) SEM image of CNF-S electrodes. e) Cycling performance and f) areal capacities of CNF-S electrodes with various sulfur loading. g) Concept of coupling hierarchical sulfur composite with *in-situ* cross-linked binder to fabricate stable high-loading cathodes. h) Voltage profiles of a NG-CN/CMC-CA sulfur cathode with various sulfur loadings at 0.5 mA cm⁻². a-c) Reproduced with permission.^[141] Copyright 2017, Wiley-VCH. d-f) Reproduced with permission.^[142] Copyright 2018, American Chemical Society. g, h) Reproduced with permission.^[162] Copyright 2016, Wiley-VCH.

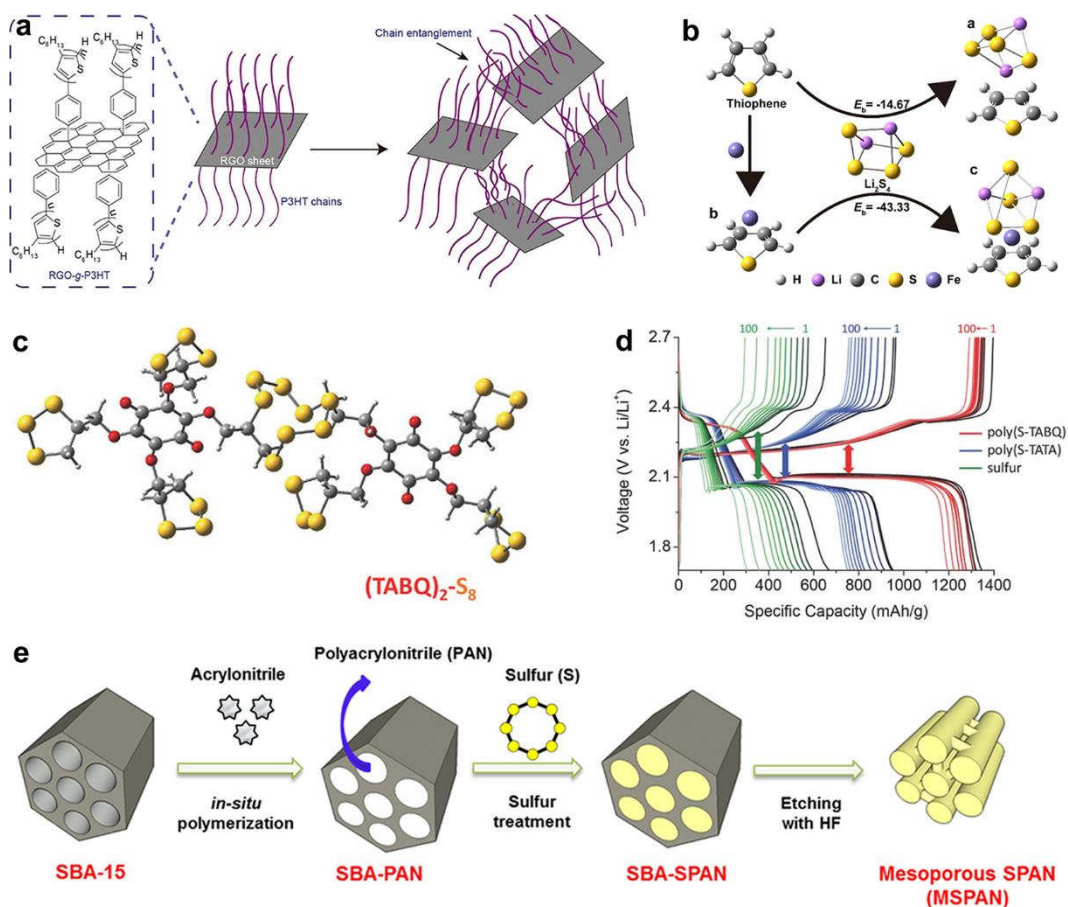


Figure 8. a) Chemical structure of an RGO-g-P3HT sheet and schematic representation of the gelation via physical cross-linking between P3HT chains. b) Enhanced binding by Fe atoms between polysulfides and P3HT frameworks. c) Conformations of TABQ dimers with optimized geometries. d) Voltage profiles of the cells based on poly(S-TABQ). e) Illustration of the fabrication for MSPAN composites. a, b) Reproduced with permission.^[172] Copyright 2019, American Chemical Society. c, d) Reproduced with permission.^[175] Copyright 2018, Wiley-VCH. e) Reproduced with permission.^[178] Copyright 2017, American Chemical Society.

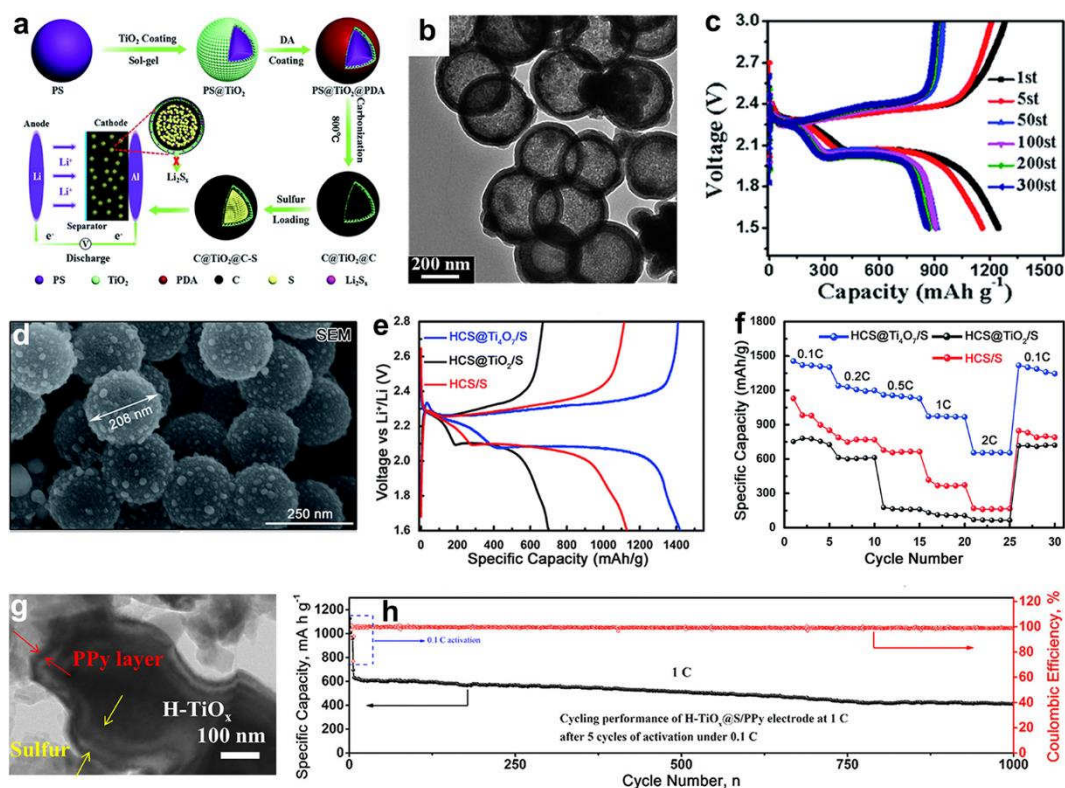


Figure 9. a) Schematic illustration of the preparation of sandwich-type $C@TiO_2@C-S$ microspheres. b) TEM image of sandwich-type $C@TiO_2@C$ hollow microspheres. c) Voltage profiles of a $C@TiO_2@C-S$ cathode at various cycles at 0.2 C. d) SEM image of $HCS@Ti_4O_7$. e) Voltage profiles and f) rate performance of $HCS@Ti_4O_7/S$. g) TEM image of sandwich-type $H-TiO_x@S/PPy$ composites. h) Cycling performance of $H-TiO_x@S/PPy$ cathodes. a-c) Reproduced with permission.^[185] Copyright 2018, Royal Society of Chemistry. d-f) Reproduced with permission.^[190] Copyright 2019, Royal Society of Chemistry. g, h) Reproduced with permission.^[193] Copyright 2019, American Chemical Society.

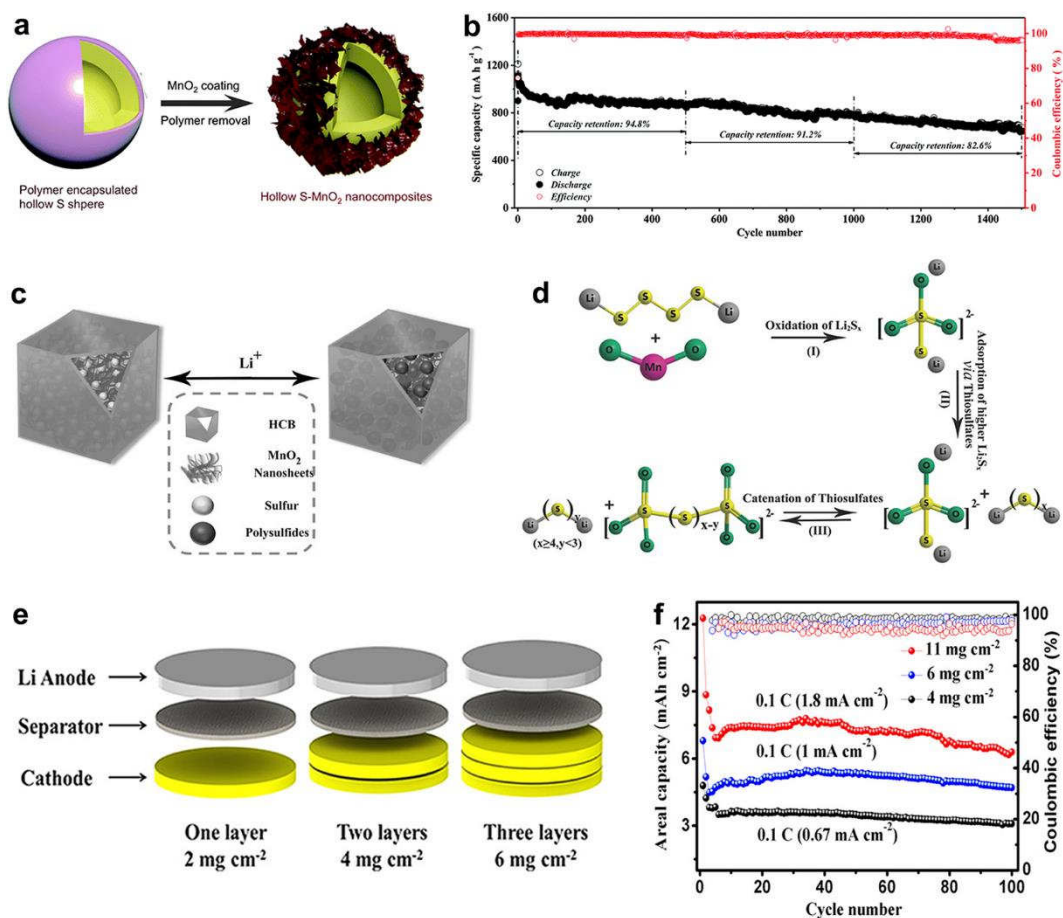


Figure 10. a) Schematic representation of the synthetic process and b) Prolonged cycling stability of S-MnO₂ at 0.5 C. c) A reversible electrochemical reaction mechanism of polysulfides retention via MnO₂@HCB/S hybrid nanoboxes. d) Schematic illustration of polysulfides adsorption via MnO₂. e) Enhanced cathode thickness by stacking individual layers. f) Areal capacities of electrodes with different sulfur areal loadings at 0.1 C. a, b) Reproduced with permission.^[197] Copyright 2016, Royal Society of Chemistry. c, d) Reproduced with permission.^[198] Copyright 2017, Wiley-VCH. e, f) Reproduced with permission.^[203] Copyright 2018, American Chemical Society.

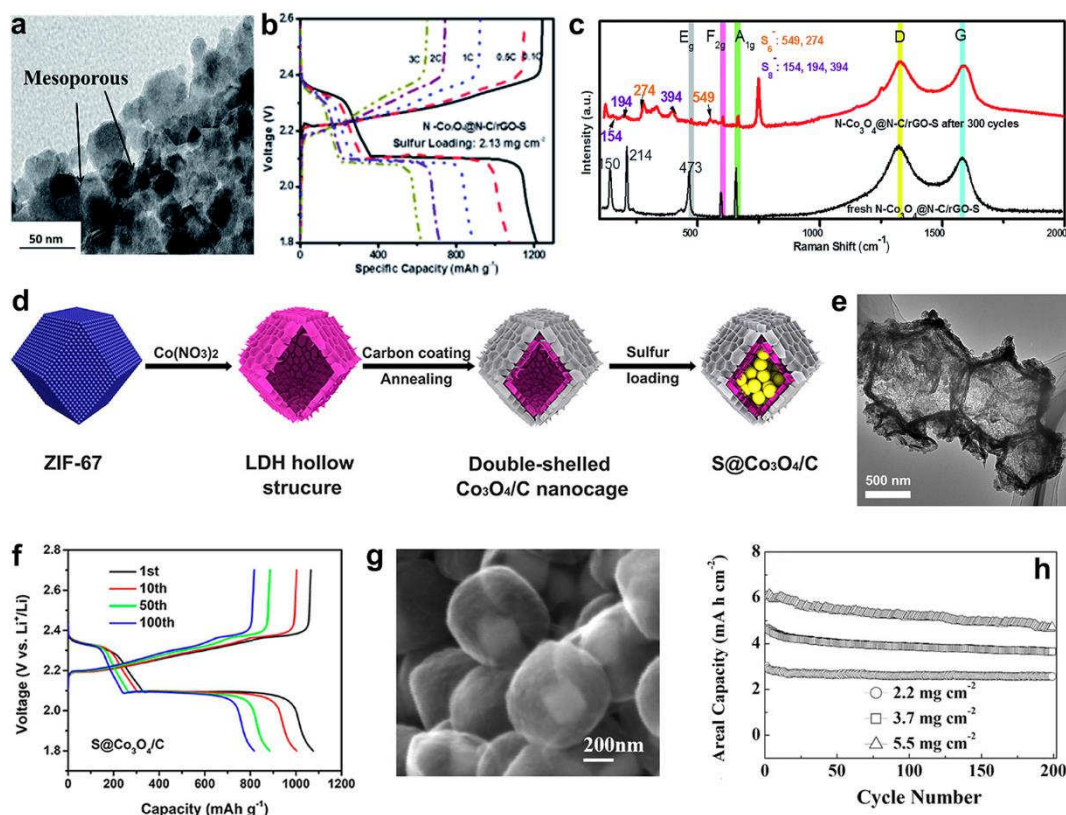


Figure 11. a) HRTEM image of N-Co₃O₄@N-C. b) Voltage profiles of a N-Co₃O₄@N-C electrode at various rates. c) *Ex-situ* Raman spectra of N-Co₃O₄@N-C-S before and after 300 cycles (discharged down to 2.1 V). d) Schematic representation of the fabrication and e) TEM image of Co₃O₄/C nanocages. f) Voltage profiles of a S@Co₃O₄/C cathode at 0.2 C at various indicated cycle numbers. g) SEM image of yolk-shelled YSC@Fe₃O₄ nanoboxes. h) Areal capacities of S/YSC@Fe₃O₄ electrodes with various sulfur loadings. a-c) Reproduced with permission.^[209] Copyright 2018, Royal Society of Chemistry. d-f) Reproduced with permission.^[57] Copyright 2019, American Chemical Society. g, h) Reproduced with permission.^[214] Copyright 2017, Wiley-VCH.

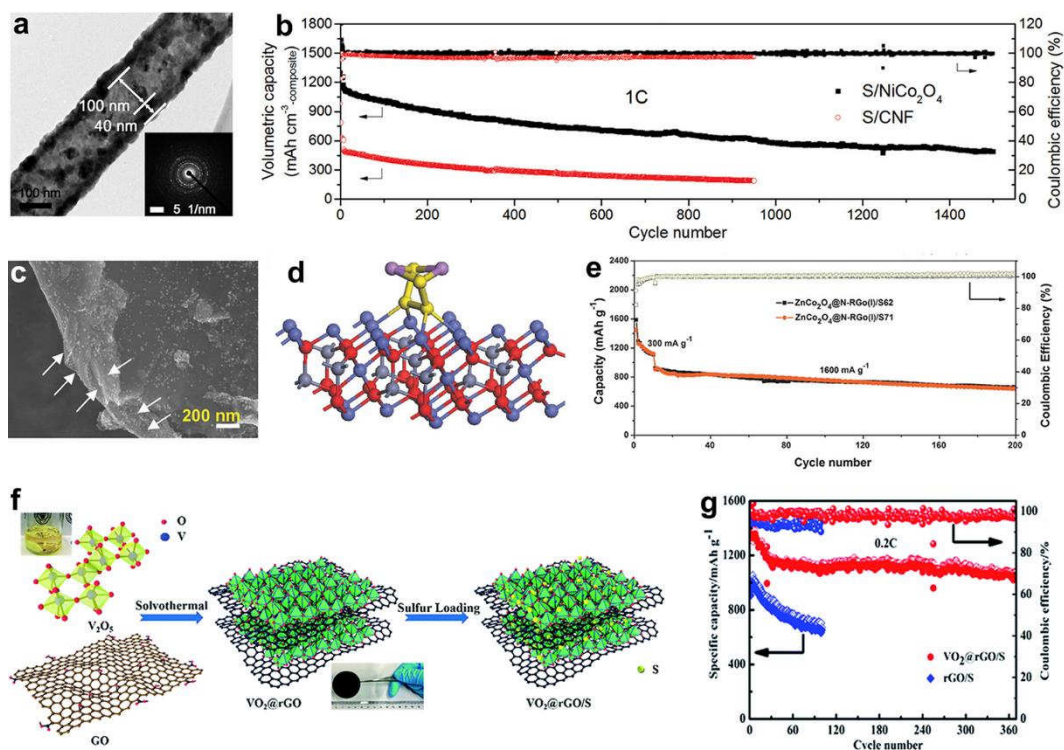


Figure 12. a) TEM image of NiCo_2O_4 nanofibers and the corresponding SAED pattern (inset). b) Prolonged cycle life of an $\text{S/NiCo}_2\text{O}_4$ electrode at 1 C. c) SEM image of $\text{ZnCo}_2\text{O}_4\text{@N-RGO}$. d) Optimized atomic geometries of Li_2S_4 adsorbed at ZnCo_2O_4 (111) crystal plane. e) Cycle life of $\text{ZnCo}_2\text{O}_4\text{@N-RGO/S}$ with 71 wt.% sulfur content. f) Fabrication scheme of the fabrication and g) cycle life performance of $\text{VO}_2\text{@rGO/S}$ composites. a, b) Reproduced with permission.^[224] Copyright 2019, Wiley-VCH. c-e) Reproduced with permission.^[226] Copyright 2018, Wiley-VCH. f, g) Reproduced with permission.^[242] Copyright 2019, Royal Society of Chemistry.

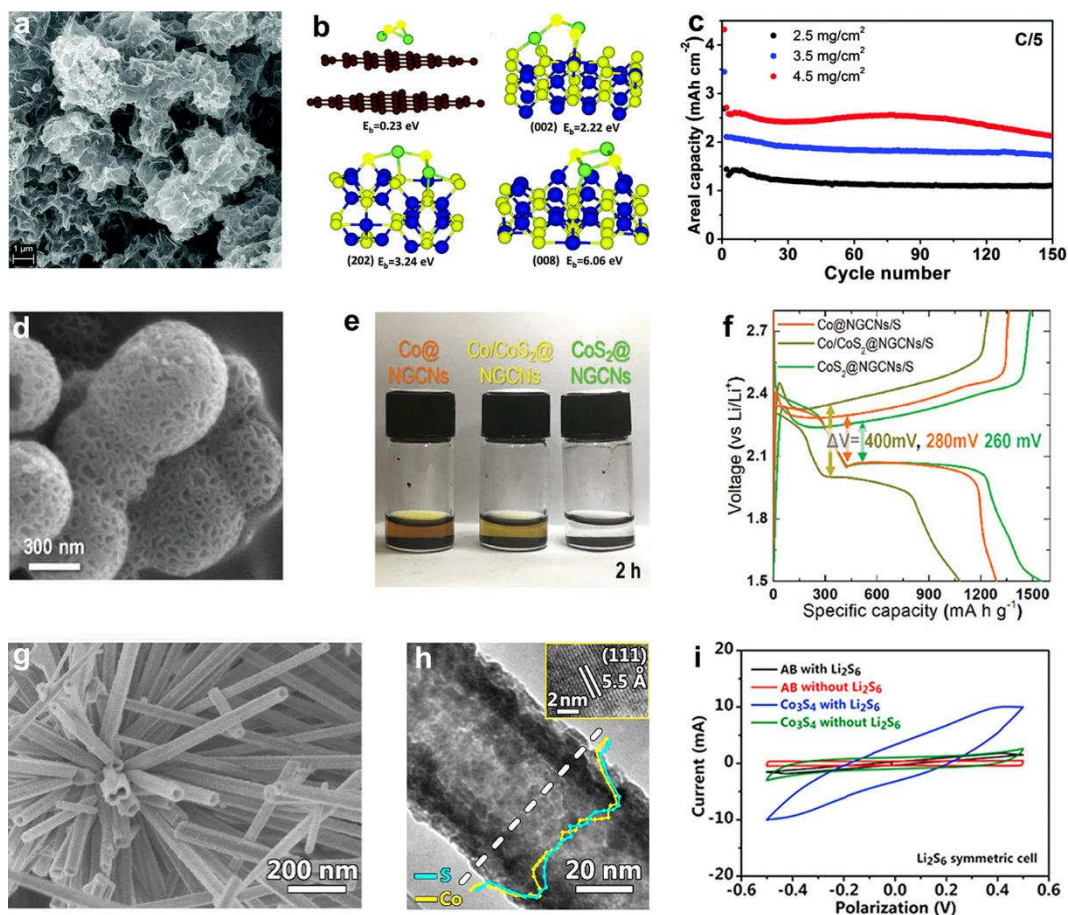


Figure 13. a) SEM image of graphene-like Co_9S_8 . b) Schematic representation of the most stable Li_2S_2 binding geometric configuration for double-layered graphitic carbon and four-layered Co_9S_8 surface slabs. c) Cycling performance of the $\text{Co}_9\text{S}_8/\text{S75}$ electrodes at 0.2 C. d) SEM image of mesoporous hollow $\text{CoS}_2@\text{NGCNs}$. e) Li_2S_6 adsorption with the addition of $\text{CoS}_2@\text{NGCNs}$. f) Voltage profile of a hollow $\text{CoS}_2@\text{NGCN}$ electrode. g) SEM and h) TEM images of Co_3S_4 nanotubes. The inset in d) is the HRTEM image of Co_3S_4 nanotube walls. The plots are EDX of Co and S. i) CV curves of Li_2S_6 symmetrical cells. a-c) Reproduced with permission.^[246] Copyright 2016, Royal Society of Chemistry. d-f) Reproduced with permission.^[251] Copyright 2019, Wiley-VCH. g-i) Reproduced with permission.^[249] Copyright 2017, Elsevier.

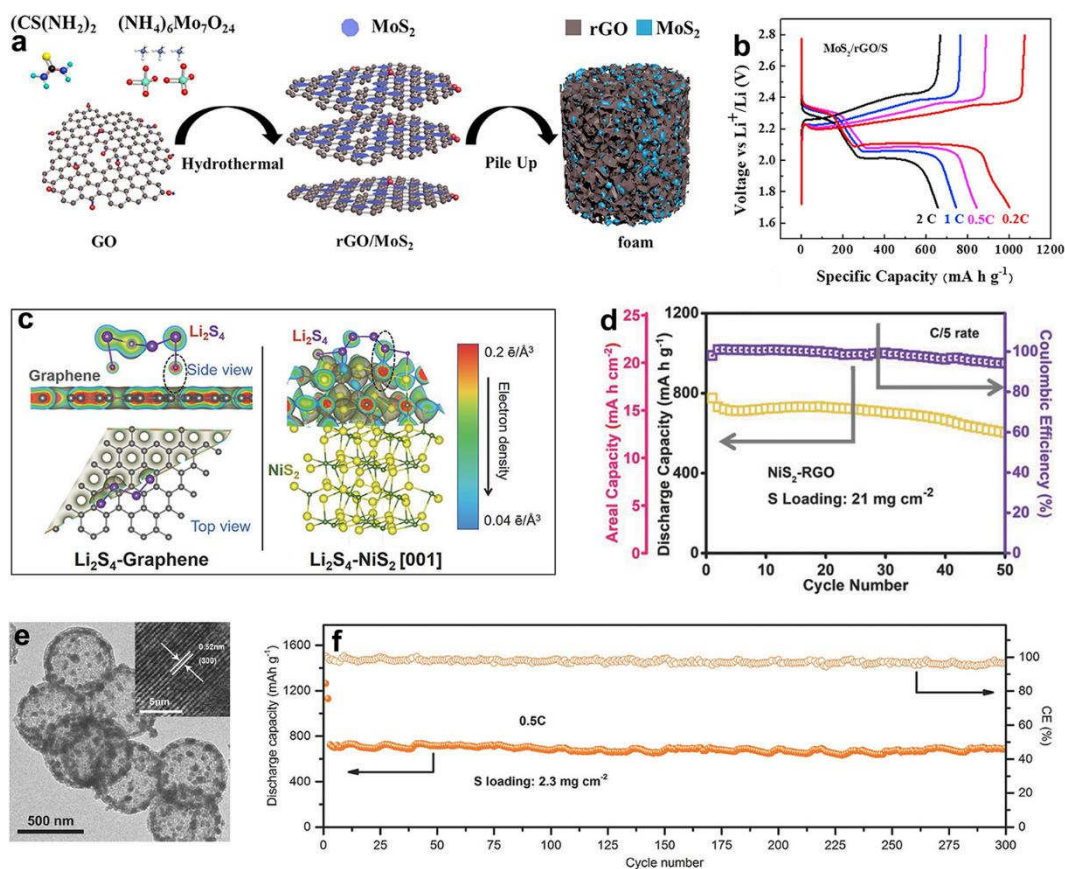


Figure 14. a) Synthesis scheme of MoS_2/rGO foam. b) Voltage profiles of $\text{MoS}_2/\text{rGO}/\text{S}$ at various current rates. c) Binding geometries and electron densities of Li_2S_4 at graphene and NiS_2 . d) Cycle life performance of NiS_2 -RGO cathodes with higher sulfur loading. e) TEM image of $\text{NiS}@C$ -HS and HRTEM of NiS in the inset. f) Cycle life of an $\text{S}/\text{NiS}@C$ -HS electrode. a, b) Reproduced with permission.^[82] Copyright 2019, Elsevier. c, d) Reproduced with permission.^[261] Copyright 2018, Wiley-VCH. e, f) Reproduced with permission.^[258] Copyright 2017, Wiley-VCH.

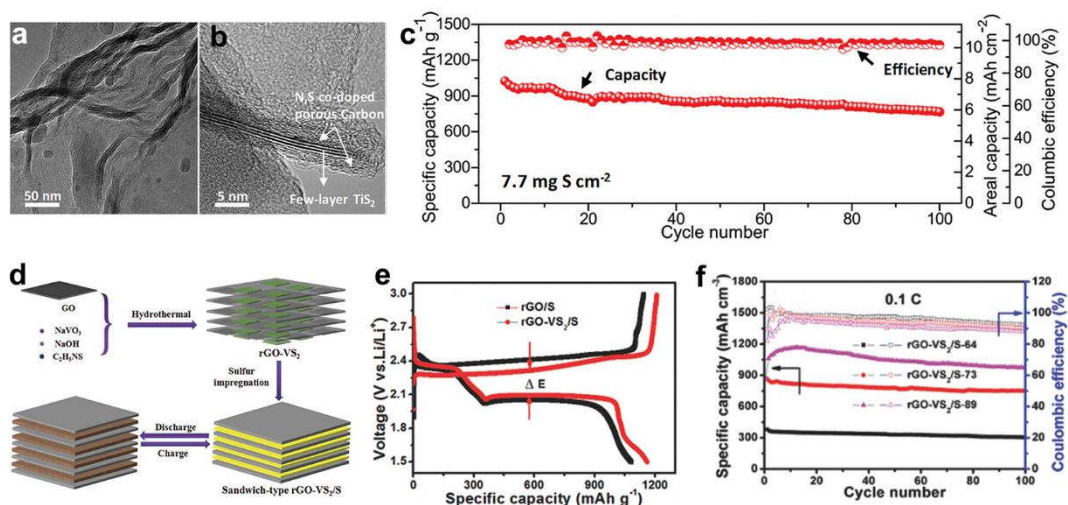


Figure 15. a) TEM and b) HRTEM of TiS_2 @NSC. c) Cycle life performance of freestanding S/ TiS_2 @NSC@CFs cathodes. d) Schematic illustration for the synthesis of a sandwich-structured rGO-VS₂/S composite. e) Voltage profile of rGO-VS₂/S at 0.2 C. f) Volumetric capacities of VS₂-rGO/S with various sulfur contents. a-c) Reproduced with permission.^[264] Copyright 2019, Wiley-VCH. d-f) Reproduced with permission.^[273] Copyright 2018, Wiley-VCH.

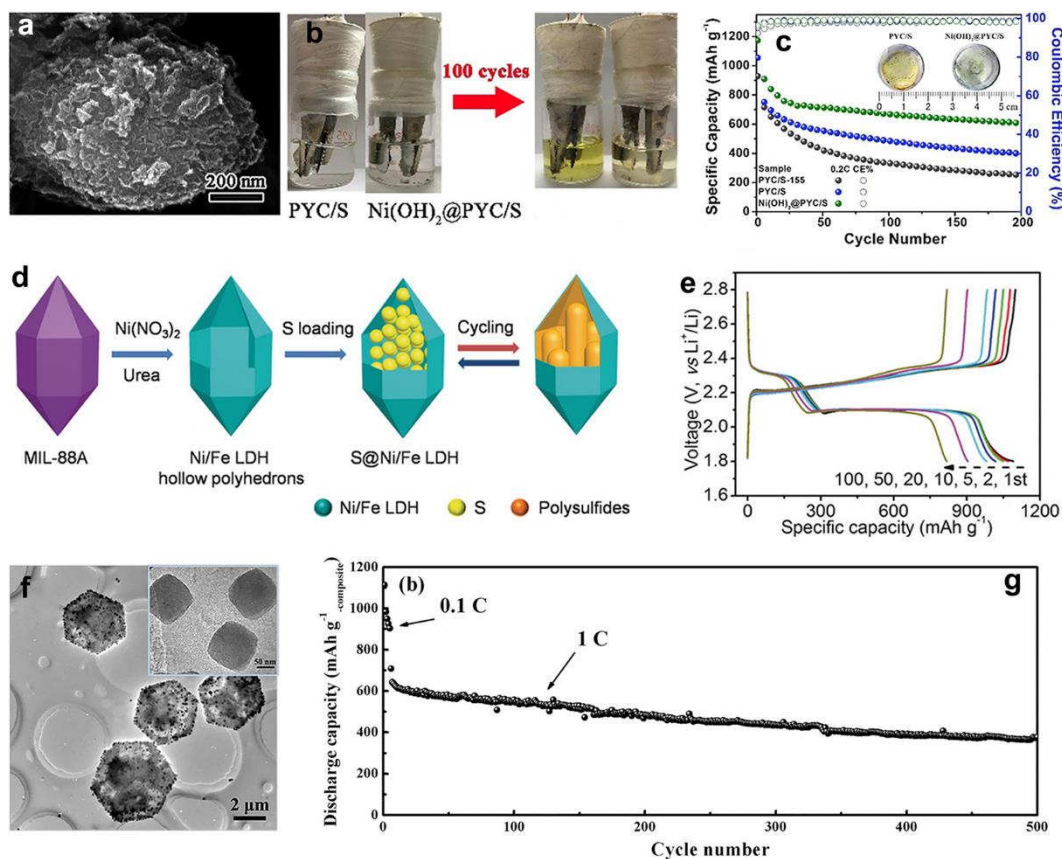


Figure 16. a) SEM image of Ni(OH)₂@PYC/S composites. b) Photos of PYC and Ni(OH)₂@PYC/S before and after 100 cycles. c) Cycling stability of Ni(OH)₂@PYC/S at 0.2 C. d) Synthesis scheme of S@Ni/Fe LDH. e) Voltage profiles of a S@Ni/Fe LDH cathode at 0.2 C. f) TEM image of CoOOH sheets. g) Long-term cycle life test of an S/CoOOH electrode. a-c) Reproduced with permission.^[279] Copyright 2018, Elsevier. d, e) Reproduced with permission.^[284] Copyright 2018, Wiley-VCH. f, g) Reproduced with permission.^[287] Copyright 2019, Wiley-VCH.

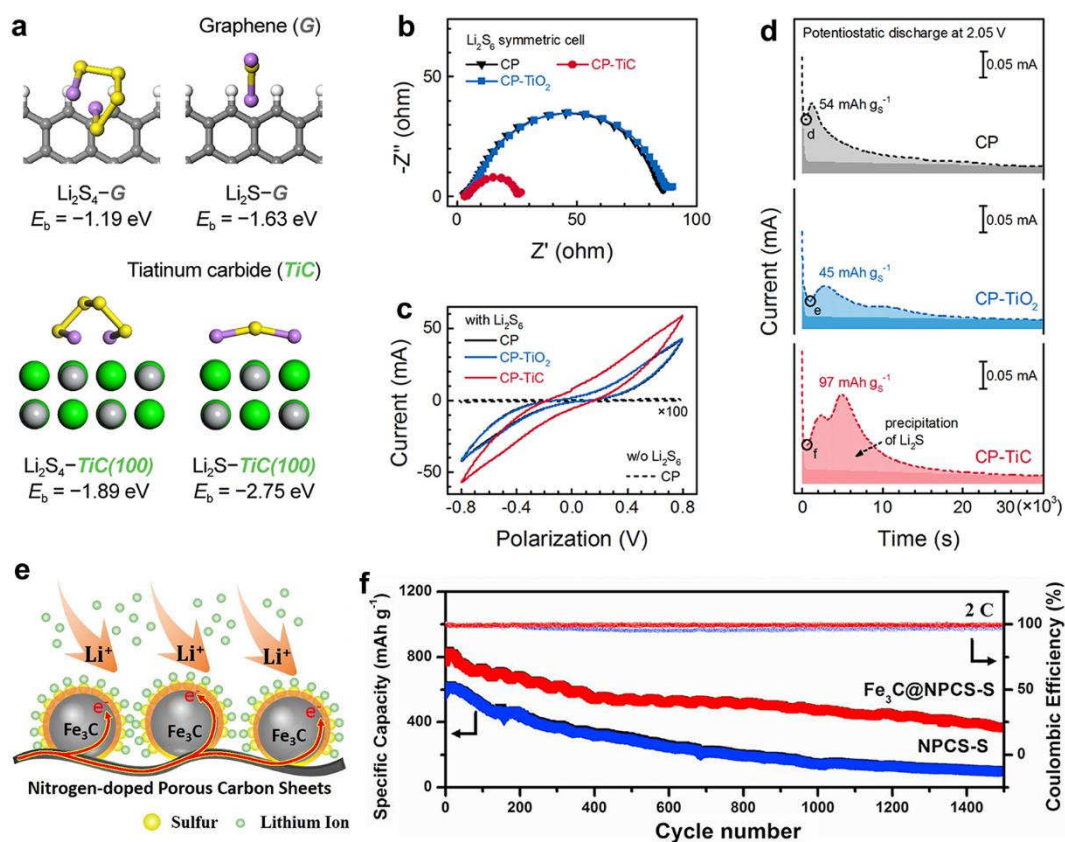


Figure 17. a) Binding energies of TiC at Li_2S_4 and Li_2S compared to pristine graphene. b) EIS and c) CV of symmetric cells. d) Potentiostatic current discharge curves of a Li_2S_8 tetraglyme solution at different substrates. e) Schematic illustration of the role of Fe_3C @NPCS upon cycling. f) Cycling performance of the Fe_3C @NPCS-S electrodes at 2 C. a-d) Reproduced with permission.^[288] Copyright 2016, Wiley-VCH. e, f) Reproduced with permission.^[294] Copyright 2019, Elsevier.

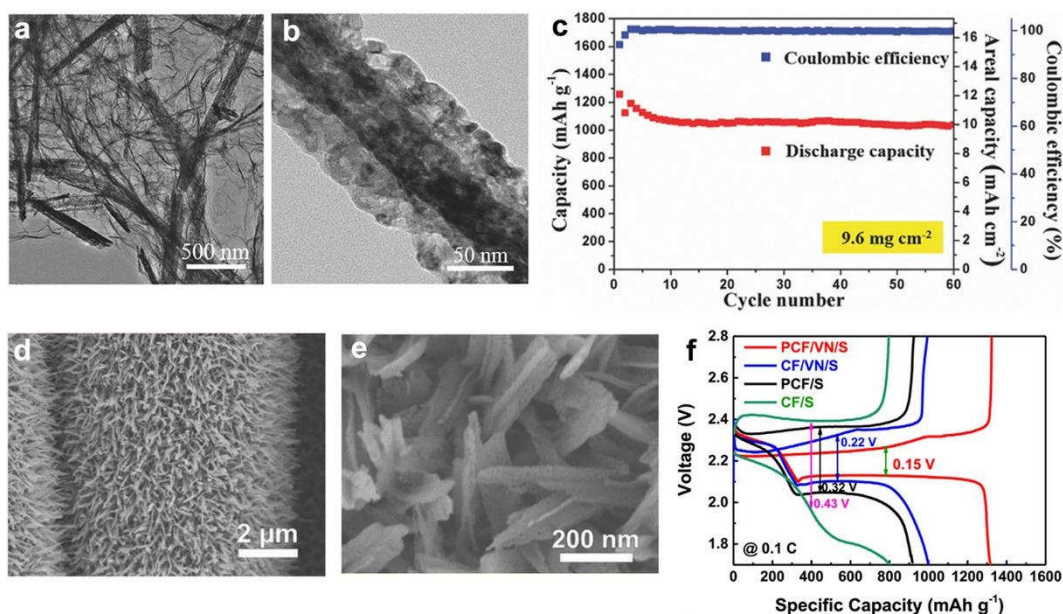


Figure 18. a, b) TEM images of 3DNG/TiN. c) Cycling performance of 3DNG/TiN cathodes with 9.6 mg cm⁻² sulfur loading. d, e) SEM images of PCF/VN composites. f) Cycling performance of PCF/VN/S cathodes. a-c) Reproduced with permission.^[310] Copyright 2018, Wiley-VCH. d-f) Reproduced with permission.^[48] Copyright 2018, Wiley-VCH.

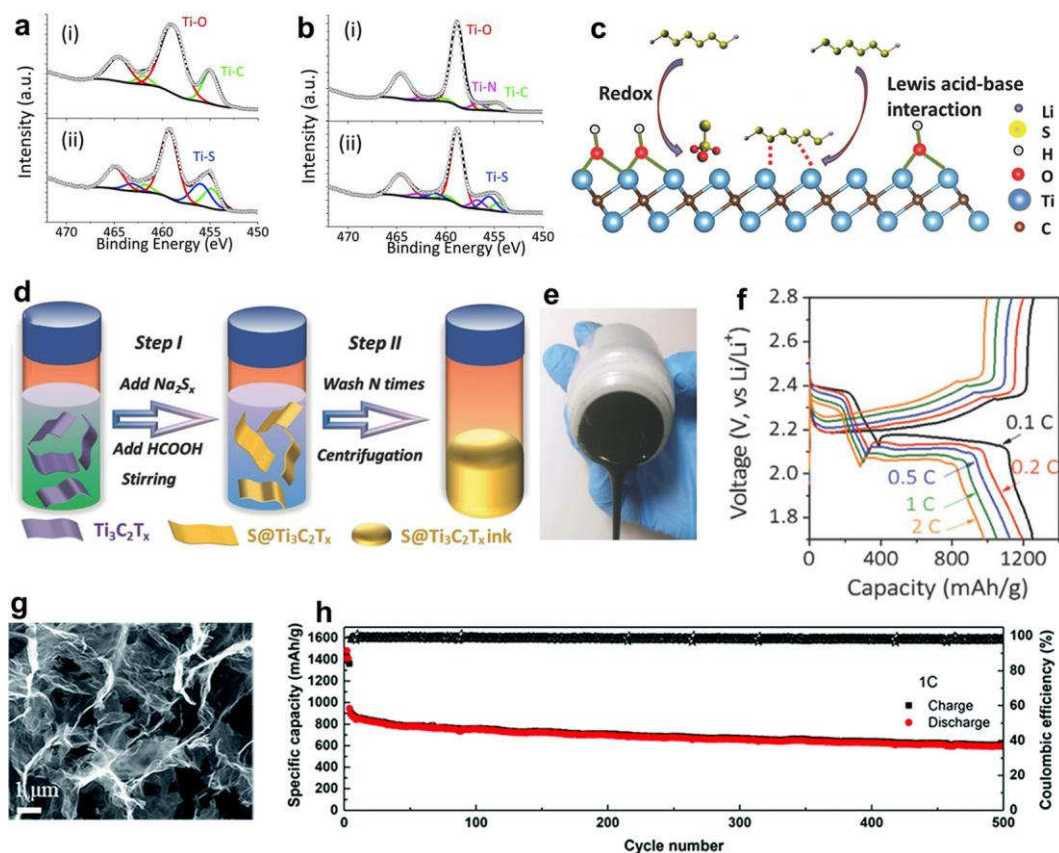


Figure 19. a) Ti 2p spectra of Ti₃C₂ (i) and Ti₃C₂-Li₂S₄ (ii). b) Ti 2p spectra of Ti₃CN (i) and Ti₃CN-Li₂S₄ (ii). c) Schematic representation of the interaction between a representative hydroxyl-decorated MXene phase and polysulfides. d) Preparation scheme and e) optical image of S@Ti₃C₂T_x ink. f) Voltage profiles of 70% S@Ti₃C₂T_x at various current rates. g) SEM image of a MX/G-30 aerogel. h) Long-term cycle life performance of a Li-S cell with a MX/G-30 cathode for 500 cycles at 1 C. a-c) Reproduced with permission.^[90] Copyright 2017, Wiley-VCH. d-f) Reproduced with permission.^[336] Copyright 2018, Wiley-VCH. g, h) Reproduced with permission.^[346] Copyright 2019, Royal Society of Chemistry.

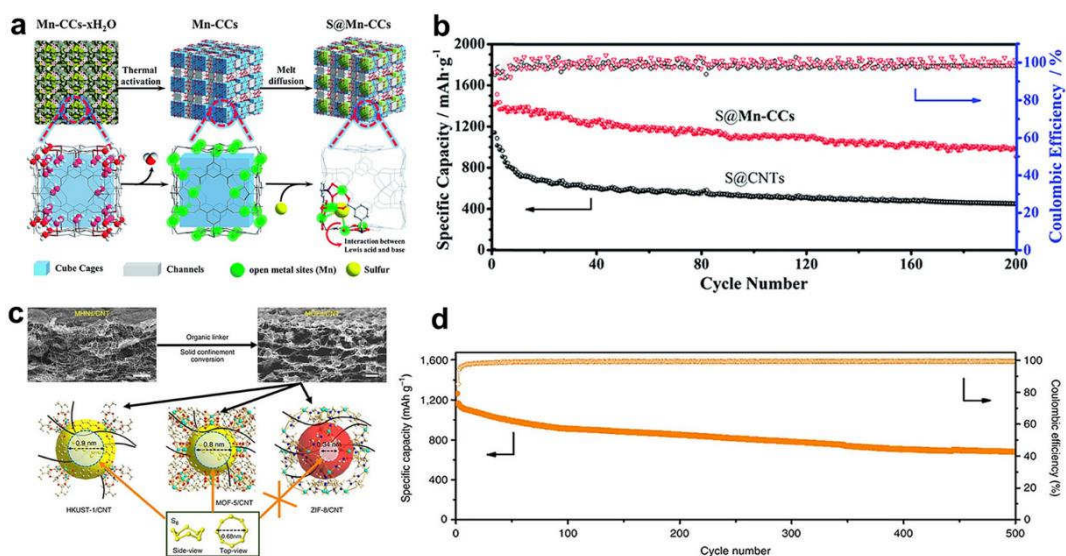


Figure 20. a) Schematic diagram of the various synthesis steps to produce S@Mn-CC. b) Voltage profiles of an S@Mn-CC and S@CNT electrodes at 0.2 C. c) Synthesis of S₈ loaded MOF/CNT composite thin films. d) Cycle life of an S@HKUST-1/CNT electrode. a, b) Reproduced with permission.^[353] Copyright 2019, Royal Society of Chemistry. c, d) Reproduced with permission.^[355] Copyright 2017, Springer Nature.

Table 1. Summary of performance parameters for nanostructured carbon host materials used in Li-S batteries.

Host material	Sulfur content [wt.%] ^{a)}	Sulfur loading [mg cm ⁻²]	Voltage range [V]	Rate [C] ^{b)}	Cycle number	Initial capacity [mAh g ⁻¹]	Retained capacity [mAh g ⁻¹]	Ref.
CNT@MPC	32	1.0	1.0-3.0	0.1	200	1670	1142	[103]
UMC	32	1.0	1.0-3.0	1.0	100	≈1000 ^{c)}	510	[105]
2D OMCNS	49	1.1-1.2	1.7-2.8	0.5	500	N/A	505	[107]
POF-HS	52.2	1.1	1.8-2.8	0.5	200	955	773	[108]
PRC/Ni	60.9	2.0	1.7-2.8	0.2	500	1257	813	[46]
Carbon microspheres	48	0.3-0.5	1.7-2.8	2.0	2000	728	449	[102]
G@HMCN	73	5.0	1.7-2.8	1.0	500	900	719	[111]
IBGM	43.2	5.6	1.5-3.0	0.5	500	714	379	[114]
rNGO	56	1.2	1.5-3.0	1.0	1000	≈970 ^{c)}	578	[116]
GF-rGO	83	9.8	1.5-2.8	0.2	350	1000	645	[118]
rGO-PVP	68	1.3-1.6	1.7-2.6	0.2	100	1021	631	[119]
GO-CNT	70	4.0	1.7-2.6	0.1	500	≈650 ^{c)}	500	[123]
GN-CNT	53.5	1.3-1.6	1.7-2.8	0.5	500	758 ^{e)}	464 ^{e)}	[124]
NCNT-G	49	1.4-1.8	1.5-3.0	1.0	400	835	635	[125]
CNT paper	54	6.3	1.7-2.8	0.05	150	995	700	[132]
SWCNT	95	7.2	1.8-2.8	0.17 (A g ⁻¹)	100	≈1200 ^{c)}	≈850 ^{d)}	[133]
E-CNT	57.6	2.0	1.4-2.8	0.2	200	1215	975	[135]
a-MCNF	64	4.6	1.8-2.8	0.5	200	990	753	[141]
CNF	79	10.5	1.6-2.9	0.1	100	753	680	[142]
HPCNF	56	12.1	1.7-2.8	0.2	100	943	N/A	[143]
PCNF/CNT	62	12	1.7-2.8	0.6 (mA cm ⁻²)	50	1126	≈900 ^{d)}	[149]
N-doped CNTs embedded with Co nanoparticles	64	1.84	1.7-2.8	1.0	400	N/A	700	[73]
NPDS	58	5.8	1.5-3.0	1.0	500	952	814	[75]
Co-embedded N, P-doped porous carbon	56	0.8-1.0	1.7-2.8	5.0	400	480	411	[152]
NONPCM	52.5	1.39	1.5-3.0	1.6 (A g ⁻¹)	300	654	540	[153]
BPCS-G	49	1.0-1.3	1.8-2.8	0.5	500	740	555	[159]
NG/g-C ₃ N ₄ hybrid	65.5	2.0	1.7-2.8	0.5	100	≈1100 ^{c)}	N/A	[162]
PCN@rGO	55	4.0	1.7-2.8	0.1	200	1025	720	[164]
rGO/g-C ₃ N ₄ /CNT	56.6	4.2	1.7-2.8	0.2	300	1017	712	[167]

^{a)} Sulfur content in cathodes^{b)} 1 C ≈ 1675 mA g⁻¹^{c)} initial^{d)} retained capacity estimated from the figure as the specific value was not given in the reference^{e)} capacity with respect to composites.

Table 2. Summary of performance parameters for polymer host materials used in Li-S batteries.

Host material	Sulfur content [wt.%] ^{a)}	Sulfur loading [mg cm ⁻²]	Voltage range [V]	Rate [C] ^{b)}	Cycle number	Initial capacity [mAh g ⁻¹]	Retained capacity [mAh g ⁻¹]	Ref.
PEDOT:PSS-coated CMK-3	43	1.0	1.7-2.6	0.2	150	1140	600	[168]
PVP	49	1.0	1.5-2.6	0.5	1000	≈750 ^{c)}	535	[169]
Chemically anchored polymer	50	N/A	1.8-2.6	2.0	100	N/A	665	[171]
RGO-g-P3HT	49	1.0	1.5-3.0	0.1	100	1103	780	[172]
ImIP	38.4	4.2	1.5-3.0	1.06 (mA cm ⁻²)	120	1131	914	[173]
TTCA	45	0.8	1.7-2.7	0.5	300	1050 ^{c)}	886	[174]
TABQ	45	1.2-2.5	1.7-2.7	0.1	400	1346	911	[175]
TABQ	45	1.2-2.5	1.7-2.7	1.0	500	1077	772	[175]
carbonized PAN	36	3.0	1.5-3.0	0.5	100	1500	735	[177]
MSPAN	37	2.45	1.0-3.0	2.0	900	717	610	[178]
Polyaniline	N/A	N/A	1.0-3.0	1.0 (A g ⁻¹)	300	≈500 ^{c)}	312	[179]

^{a)} Sulfur content in cathodes^{b)} 1 C ≈ 1675 mA g⁻¹^{c)} initial capacity estimated from the figure as the specific value was not given in the reference.

Table 3. Summary of performance parameters for metal compound host materials used in Li-S batteries.

Host material	Sulfur content [wt.%] ^{a)}	Sulfur loading [mg cm ⁻²]	Voltage range [V]	Rate [C] ^{b)}	Cycle number	Initial capacity [mAh g ⁻¹]	Retained capacity [mAh g ⁻¹]	Ref.
TiO ₂ microboxes	49	1.0	1.8-2.6	1.0	500	605	626	[182]
C@TiO ₂ @C	61	2.5	1.5-3.0	2.0	500	774	511	[185]
HCS@Ti ₄ O ₇	56	N/A	1.6-2.8	0.5	800	1168	609	[190]
Heterostructured TiO _x	46.4	0.8-1.0	1.7-2.8	1.0	1000	694	412	[193]
MnO ₂	56.6	1.7-2.1	1.5-3.0	0.5	1500	898	644	[197]
MnO ₂ @HCB	51	0.7-1.0	1.7-2.8	4.0 (A g ⁻¹)	200	496	N/A	[198]
MnO/MPC	52	2.8	1.0-2.8	1.6 (A g ⁻¹)	150	475	290	[202]
Mn ₃ O ₄ @CNF	50	11.0	1.7-2.8	0.1	70	1055	744	[203]
N-doped Co ₃ O ₄	60	2.13	1.7-2.7	2.0	1000	≈900 ^{c)}	611	[209]
Co ₃ O ₄ /C	56	1.4	1.8-2.7	1.0	500	889	520	[57]
CoO/Co	61.2	3.0	1.7-2.8	1.0	300	N/A	514	[210]
YSC@Fe ₃ O ₄	64	5.5	1.8-2.8	0.1	200	1104	854	[214]
Fe ₃ O ₄ nanoparticles	N/A	3.85	1.7-2.8	0.1	100	N/A	1007	[216]
NiCo ₂ O ₄	52.5	1.3-1.5	1.7-2.8	1.0	1500	1171 (mAh cm ⁻³) ^{e)}	487 (mAh cm ⁻³) ^{e)}	[224]
ZnCo ₂ O ₄	50	1.1-1.3	1.7-2.8	0.8 (A g ⁻¹)	200	1322	761	[226]
VO ₂ @rGO	53	1.5	1.7-2.8	0.2	370	1358	1049	[242]
Co ₉ S ₈	60	1.5	1.8-3.0	0.5	1500	≈890 ^{c)}	≈290 ^{d)}	[246]
Co ₃ S ₄	59	2.0	1.6-2.6	5.0	1000	517	305	[249]
MoS _{2-x} /rGO	60	1.5	1.8-2.6	0.5	600	≈1200 ^{c)}	628	[67]
MoS ₂ /rGO	56	0.85	1.7-2.8	1.0	300	≈830 ^{c)}	480	[82]
NiS@C-HS	50	2.3	1.7-2.8	0.5	300	723	695	[258]
NiS ₂ -RGO	75	21	1.7-2.8	0.2	50	776	N/A	[261]
TiS ₂	65	12	1.7-3.0	0.2	200	959	605	[83]
TiS ₂ nanosheets	56	7.7	1.8-2.8	0.1	100	1025	767	[264]
rGO-VS ₂	51.2	1.15	1.5-3.0	1.0	1200	1130	879	[273]
C@WS ₂	11	1.0-1.2	1.7-2.7	2.0	1500	563	502	[274]
Nickel-based hydroxide	32	4.3	1.8-2.8	0.5	350	838	650	[280]
Ni/Fe LDH	49	2.0-3.0	1.7-2.8	1.0	1000	844	501	[284]
CoOOH	64	1.0-1.3	1.6-2.8	1.0	500	N/A	376 ^{c)}	[287]
TiC	55	3.5	1.7-2.8	0.2	100	1032	670	[288]
Fe ₃ C@NPCS	59.6	1.5	1.8-2.8	2.0	1500	≈800 ^{c)}	≈370 ^{d)}	[294]
B ₄ C@CNF	70	2.0	1.6-3.0	1.0	500	1020	815	[299]
Mo ₂ C	53	0.8-1.2	1.6-2.8	1.0	500	968	669	[302]

Host material	Sulfur content [wt.%] ^{a)}	Sulfur loading [mg cm ⁻²]	Voltage range [V]	Rate [C] ^{b)}	Cycle number	Initial capacity [mAh g ⁻¹]	Retained capacity [mAh g ⁻¹]	Ref.
TiN	N/A	9.6	1.6-2.8	0.5	60	≈1250 ^{c)}	≈1000 ^{d)}	[310]
Porous TiN	57.6	1.5-2.0	1.7-2.8	5.0	1000	662	557	[311]
PCF/VN	60.1	8.1	1.7-2.8	0.1	250	1310	1052	[48]
VN nanospheres	49	1.3-1.5	1.6-3.0	1.0	300	800	602	[315]
WN	47	0.92	1.7-2.8	2.0	500	1050	358	[320]
MoN-VN	58.5	3.0	1.7-2.8	2.0	500	N/A	708	[324]
Ti-based MXenes	≈64	1.5	1.7-3.0	0.5	1200	N/A	450	[90]
Ti ₃ C ₂ T _x	70	2.49	1.7-2.8	0.2	800	1184	724	[336]
MX/G	45	6.0	1.7-2.8	1.0	500	946	596	[346]
Cu-TDPAT	40	1.2	1.8-2.8	1.0	500	900 ^{e)}	745	[352]
Mn-CC	49	2.0	1.7-2.8	0.2	200	1420	990	[353]
HKUST-1/CNT	40	1.0	1.7-2.8	0.2	500	1263	758	[355]

^{a)} Sulfur content in cathodes

^{b)} 1 C ≈ 1675 mA g⁻¹

^{c)} initial

^{d)} retained capacity estimated from the figure as the specific value was not given in the reference

^{e)} capacity with respect to composites.



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The design and development of sulfur host materials are promising approaches for high-performance Li-S batteries. This review comprehensively discusses the recent advances of sulfur host materials. The advantages of various sulfur host materials are presented. Perspectives are provided on the critical issues that should be addressed for the practical application of Li-S batteries.

Keywords: lithium-sulfur batteries, sulfur hosts, polysulfides, physical confinement, chemical bonding

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Host Materials Anchoring Polysulfides in Li-S Batteries Reviewed

ToC figure

