

Review

Accelerating Redox Kinetics of Lithium-Sulfur Batteries

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Lithium-sulfur (Li-S) batteries exhibit great promise for next-generation energy storage due to their high theoretical energy density and low cost. However, their practical application is largely hindered by the shuttle effect. Although previous studies on the adsorption of lithium polysulfides (LiPSs) have achieved significant progress, simple adsorption cannot fundamentally eliminate the shuttle effect. Physical and chemical confinement are useful to anchor LiPSs to some extent, but these are not effective for utilizing the blocked intermediates. Accordingly, accelerating polysulfide redox kinetics is crucial to radically mitigate the shuttle effect and increase sulfur utilization. Herein, recent advances in catalysts for boosting redox kinetics of Li-S batteries are reviewed. We also provide prospects on the design of more efficient catalysts for Li-S batteries.

Catalytic Effect in Lithium-Sulfur Batteries

The rapid development of electric vehicles is driving an ever increasing demand for rechargeable batteries with higher energy density and lower cost than that of current lithium-ion batteries [1–3]. Among alternative battery technologies, lithium-sulfur (Li-S) batteries are regarded as one of the most promising systems for next-generation energy storage owing to their high theoretical energy density (2500 Wh kg⁻¹), low cost, and low environmental impact [4–7]. Despite these desirable benefits, the practical application of Li-S batteries has been impeded by several issues, including the low conductivity of sulfur and lithium sulfide, shuttle effect of lithium polysulfides (LiPSs), and large volume change of sulfur upon cycling [8–11]. Among these obstacles, the shuttle effect has been regarded as the major barrier that limits the commercial application of Li-S batteries [12–14]. Accordingly, many efforts have been devoted to solving this complex problem over the past decade. One of the most common strategies is to infiltrate sulfur into various carbon nanostructures due to their high conductivity and large surface area [15–18]. Nevertheless, due to the weak physical entrapment of nonpolar carbon to the polar LiPSs, polysulfide shuttling is difficult to restrain, especially during long cycling times. Therefore, polar transition-metal compounds such as metal oxides [19–23], sulfides [24–28], nitrides [29,30], and carbides [31,32] having strong chemical interactions with LiPSs have been applied as sulfur hosts to suppress the diffusion of LiPSs more efficiently.

However, simple adsorption of LiPSs on polar hosts can only address the problem superficially. Especially with a high sulfur loading, the sluggish conversion of LiPSs to solid lithium sulfides limits the full utilization of intermediates [33,34]. In the reverse reaction, the kinetics of the oxidation process of lithium sulfides is much slower and involves larger activation energy [35–37]. In this regard, to fundamentally inhibit the shuttle effect and increase sulfur utilization, accelerating the kinetics of the transformation between LiPSs and lithium sulfide on a substrate via a catalytic effect would be more beneficial than simple adsorption of LiPSs on a host (Figure 1). On the catalytic surface, LiPSs undergo a smooth ‘immobilization-diffusion-conversion’ process due to the moderate interaction, facilitated electron transfer to the sulfur species, and abundant electroactive sites for boosting the reduction rate. Recent studies show that some hosts, such as metal-free polar

Highlights

It is critical to suppress the shuttle effect and increase sulfur utilization through designing host materials that can not only adsorb lithium polysulfides (LiPSs) but also catalyze their conversion.

Catalytic materials for accelerating the sulfur redox reaction include metal-free polar materials, transition-metal compounds, and metals.

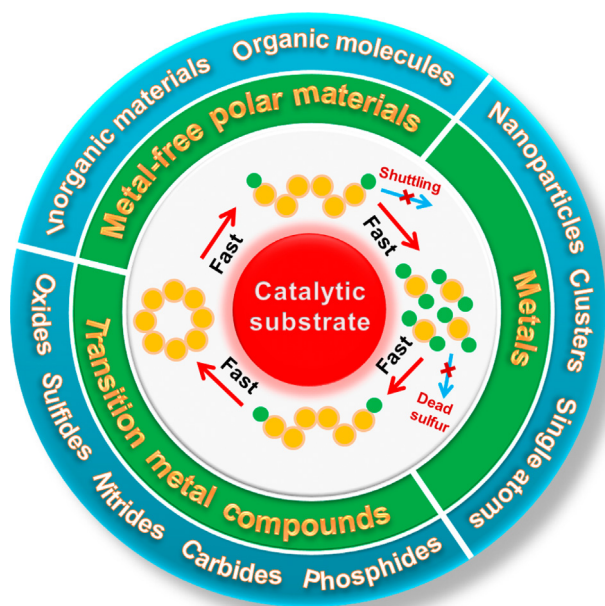
The design of catalytic materials should consider the balance of LiPS trapping ability, surface reactivity, diffusivity of lithium ions and LiPSs, and electrical conductivity.

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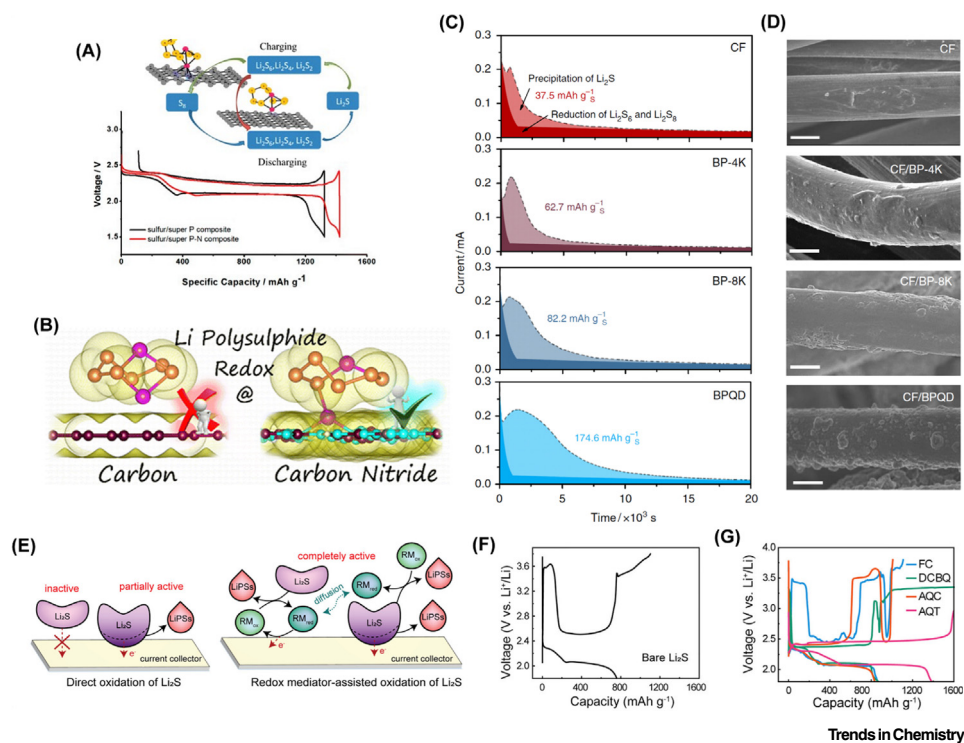
Figure 1. Schematic of the Catalysis Effect in Li-S Batteries.

materials, transition-metal compounds, and metals, can not only capture LiPSs but also accelerate the transformation process between LiPSs and lithium sulfide [38–43]. This provides new opportunities for developing practically useable Li-S batteries. This short review summarizes the recent progress on catalytic materials for Li-S batteries and presents prospects for the future design of high-performance materials.

Metal-Free Polar Materials

Over the past decade, metal-free catalysts have attracted extensive research interests in both fuel cells and water splitting owing to their low cost and relatively high catalytic activity [44–46]. Due to similar requirements of high catalytic activity for polysulfide conversion, metal-free catalysts have also been applied in Li-S batteries in recent years. Among the metal-free polar materials, heteroatom-doped carbon nanostructures are the most common catalysts. Using density functional theory (DFT) calculations, Dong and coworkers found that nitrogen doping can enhance the affinity of carbon surfaces for LiPSs and N-doped carbon can act as a conductive Lewis base catalyst to enhance polysulfide conversion in Li-S batteries [47]. Consequently, a sulfur/super P composite with N doping showed an enhanced specific capacity compared with the non-doped variants (Figure 2A). Li's group reported that carbon nitride can also facilitate the redox kinetics of polysulfide conversion in Li-S batteries [48]. DFT calculations revealed that the enhancement of kinetics originated from the distortion of molecule configurations of LiPSs anchored on carbon nitride (Figure 2B).

Recently, Lau and coworkers reported that black phosphorus (BP) can not only effectively capture LiPSs but also catalyze their conversion [49]. To study the influence of BP size on the catalytic effect in Li-S batteries, potentiostatic discharge measurements were performed on different substrates (Figure 2C). The capacities for Li_2S deposition on carbon fibers (CF), CF/BP-4K, CF/BP-8K, and CF/BP quantum dots (CF/BPQD) were measured to be 37.5, 62.7, 82.2, and 174.6 mA h g^{-1} , respectively. These results indicate that the capacity of Li_2S



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Figure 2. Metal-Free Polar Materials as Catalysts for Li-S Batteries. (A) Comparison of the first cycle voltage profiles of sulfur/super P composite with and without N doping. Reproduced, with permission, from [47]. (B) Illustration of molecular configurations of lithium polysulfide (LiPS) on carbon and carbon nitride. Reproduced, with permission, from [48]. (C) Potentiostatic discharge curves of Li_2S_8 solution on different substrates at 2.05 V. (D) Scanning electron microscopy images of Li_2S precipitated on different substrates, as indicated in (C). The scale bar is 5 μm . Reproduced, with permission, from [49]. (E) Schematic illustration of direct oxidation of Li_2S and redox mediator-assisted oxidation of Li_2S . (F) First-cycle voltage profiles of a bare Li_2S electrode at 0.3 C. (G) First-cycle charge-discharge voltage profiles of Li_2S electrodes with different redox mediators at 0.3 C rate. Reproduced, with permission, from [50]. Abbreviations BP-4K, black phosphorus that was centrifuged at 4000 rpm; BP-8K, black phosphorus that was centrifuged at 8000 rpm; BPQD, black phosphorus quantum dots; CF, carbon fibers.

precipitation increases when decreasing the BP particle size. The morphology of precipitated Li_2S on the different substrates was further observed by scanning electron microscopy (Figure 2D). Compared with the routine 2D precipitation of Li_2S , the BPQDs facilitated 3D deposition of Li_2S by the strong adsorption and conversion of LiPSs on abundant catalytic sites. By adding a small amount of BPQDs into the CF/S composite, the cathode showed enhanced reaction kinetics and no shuttling of LiPSs. As a result, it demonstrated stable cycling performance over 1000 cycles with a low capacity decay rate of only 0.027% per cycle.

Besides inorganic materials, organic molecules have also been studied as redox mediators for Li-S batteries. Cui and coworkers found that the addition of a small amount of quinone derivative into the electrolyte can promote the oxidation of Li_2S (Figure 2E) [50]. As indicated in Figure 2F, the initial charging of bare Li_2S electrode exhibits a high activation voltage over 3.6 V and the discharge capacity is less than 800 mA h g^{-1} , suggesting insufficient utilization of active materials. However, upon addition of appropriate redox mediator, 1,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) anthra-9,10-quinone (AQT), into the electrolyte, the initial charging of Li_2S occurred below 2.5 V and the subsequent discharge capacity was as high as 1300 mA h g^{-1} (Figure 2G). Chen and coworkers also reported that anthraquinone can promote redox reactions in Li-S batteries [51].

Overall, metal-free catalysts have the benefit of being light weight, which is advantageous for achieving a high gravimetric energy density. The high electrical conductivity of heteroatom-doped carbon materials can afford fast electron transfer. However, they do not render abundant polar active sites for trapping and boosting LiPS reduction. For organic molecules, although they have relatively abundant polar sites, the electrical conductivity and thermal stability are unsatisfactory. From this perspective, future research may focus on designing conductive organic materials or coupling organic molecules with carbon materials.

Transition-Metal Oxides

Transition-metal compounds have also been applied as catalysts for Li-S batteries. In 2015, Nazar and coworkers proposed that MnO_2 can oxidize polysulfides to form thiosulfate on the surface and thiosulfate can function as a redox mediator to anchor long-chain LiPSs and trigger conversion to lithium sulfides via disproportionation reactions (Figure 3A) [52]. This catalytic mechanism was different from previous studies and the resultant MnO_2/S composite demonstrated stable cycling performance over 2000 cycles with a capacity fading rate of only 0.036% per cycle, which was among the best at that time. Nazar's group also reported that the metallic and polar Ti_4O_7 can capture LiPSs and propel their conversion (Figure 3D) [53]. As shown by the *operando* X-ray absorption near-edge structure (XANES) measurements in Figure 3B, compared with carbonaceous hosts, the fraction of LiPS was much lower during discharge and Li_2S precipitated earlier for Ti_4O_7 , indicating the catalytic effect of Ti_4O_7 for polysulfide conversion.

Lee and coworkers reported that oxygen deficiency in WO_{3-x} can increase the catalytic effect for polysulfide conversion (Figure 3E) [54]. Consequently, the sulfur cathode with WO_{3-x} as host can improve both cycle life and rate performance. Recently, Mai's group reported that engineering oxygen vacancies in TiO_2 can improve the ability for both capturing LiPSs and enhancing their conversion (Figure 3F) [55]. The cells with oxygen-vacancies $\text{TiO}_2@PP$ separators (OVs- $\text{TiO}_2@PP$) show more positive shifts of peak current upon discharge and more negative shifts of peak current during the subsequent charge process (Figure 3G), indicating a more kinetically enhanced redox process. Moreover, symmetric cells with OVs- $\text{TiO}_2@PP$ showed much higher current than comparison materials, suggesting a heightened catalytic effect for TiO_2 with oxygen vacancies (Figure 3H).

Although metal oxides have the superior advantage of abundant polar active sites for bonding LiPSs, most suffer from poor conductivity. This lowers the electron transport rate during the redox reactions. Creating oxygen deficiency such as Magnéli phase Ti_4O_7 is considered as an effective strategy to increase the conductivity. However, the synthesis procedure is normally complex and requires extremely high temperatures. Therefore, a promising strategy is to couple metal oxides with carbon materials to optimize the overall conductivity and catalytic kinetics.

Transition-Metal Sulfides

Metal sulfides have been widely used as electrocatalysts for water splitting [56–58]. In Li-S batteries, apart from their strong chemical anchoring ability for LiPSs, recent studies have found that metal sulfides have superior catalytic activity for polysulfide conversion. Zhang and coworkers reported that sulfiphilic CoS_2 can provide strong adsorption and catalytic sites for LiPS conversion (Figure 4A) [59]. Symmetric cells with $\text{CoS}_2/\text{graphene}$ electrodes showed much higher current density than plain graphene electrodes (Figure 4B), indicating the facilitated redox kinetics by CoS_2 . Recently, Wang and colleagues reported that ZnS nanospheres can also effectively catalyze the polysulfide conversion (Figure 4C) [60]. Compared with carbon black (CB) electrodes (Figure 4D), the ZnS-CB electrodes facilitated much more Li_2S precipitation (Figure 4E), which was a vital step during the discharge process of Li-S batteries.

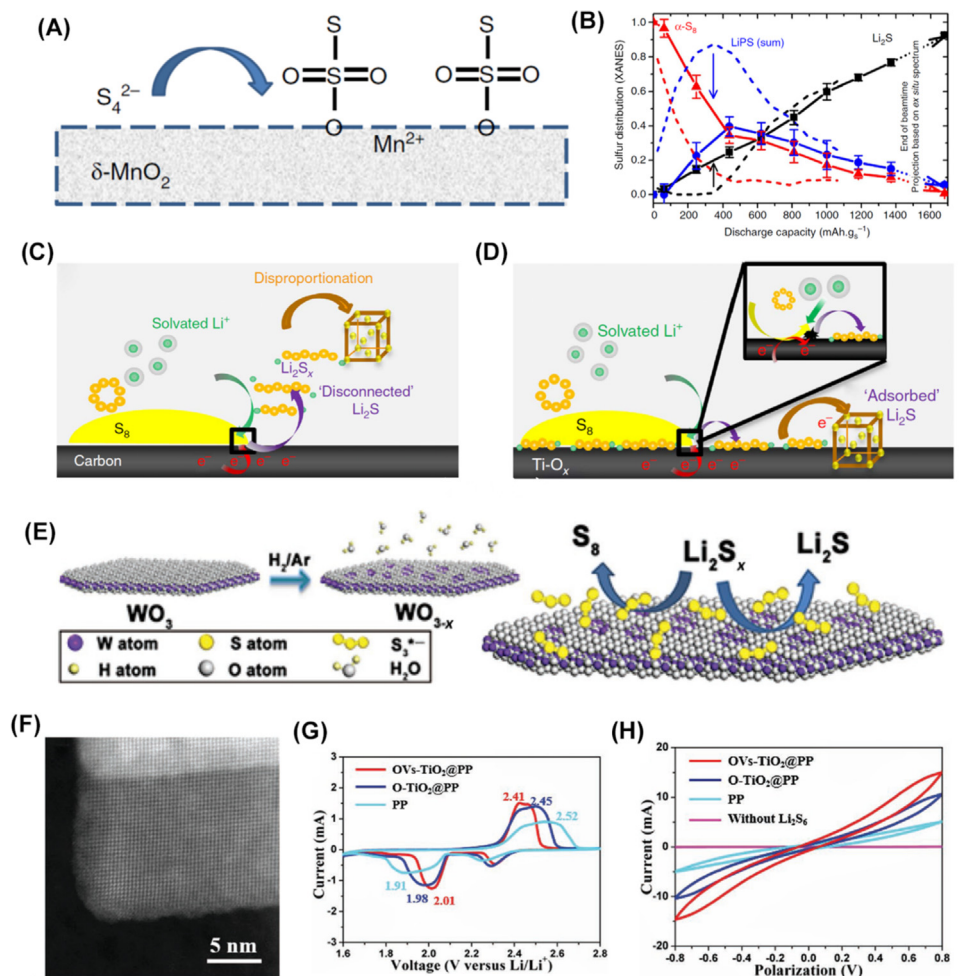
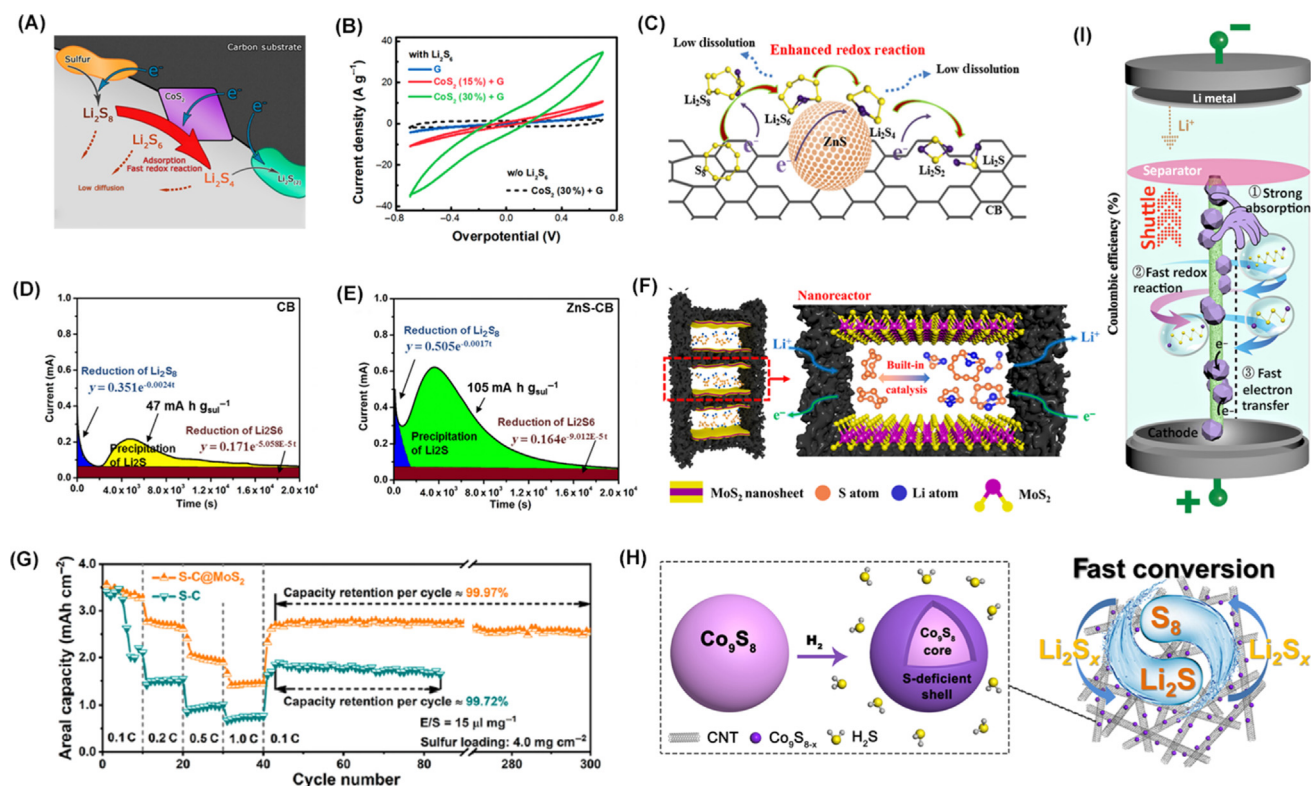


Figure 3. Transition-Metal Oxides as Catalysts for Li-S Batteries. (A) Schematic showing the oxidation of polysulfides by MnO_2 to form thiosulfate, along with the reduction of Mn^{4+} to Mn^{2+} . Reproduced, with permission, from [52]. (B) Distribution of sulfur species during discharge determined by *operando* X-ray absorption near-edge structure (XANES). Schematic illustration of sulfur reduction on (C) carbon and (D) Ti_4O_7 . Reproduced, with permission, from [53]. (E) Schematic of the synthesis of oxygen-deficient WO_{3-x} and sulfur reduction on WO_{3-x} surface. Reproduced, with permission, from [54]. (F) Scanning transmission electron microscopy image of TiO_2 nanosheets with oxygen vacancies. (G) Cyclic voltammetry (CV) curves with different separators. (H) CV curves of symmetric cells. Reproduced, with permission, from [55].

To overcome the limitation of surface catalysis under high sulfur loading, Li and coworkers recently proposed a concept of ‘built-in catalysis’ to propel polysulfide conversion in confined nanoreactors (Figure 4F) [61]. The nanoreactors are composed of 2D carbon shells with internal surface decorated with MoS_2 nanosheets. With this unique nanostructure, the sulfur-loaded C@MoS_2 exhibited significantly improved electrochemical performance (Figure 4G). The use of metal sulfides as catalysts has been widely studied in Li-S batteries. For example, Lee and coworkers reported that Co_9S_8 with a sulfur-deficient shell supported on carbon nanotubes (CNTs) can be used as an interlayer to suppress polysulfide shuttling and accelerate polysulfide conversion (Figure 4H) [62]. Sun and coworkers reported that VS_4 facilitated adsorption and catalytic conversion of LiPSs (Figure 4I) [63].



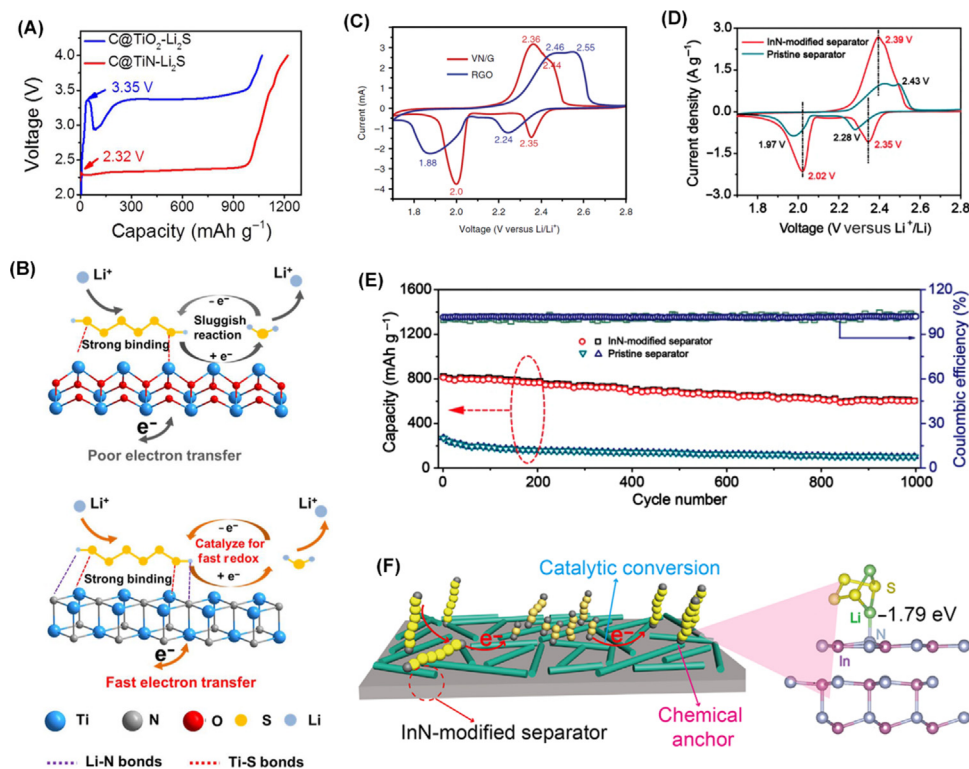
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Figure 4. Transition-Metal Sulfides as Catalysts for Li-S Batteries. (A) Schematic of polysulfide conversion on CoS₂. (B) Cyclic voltammetry (CV) curves of symmetric cell. Reproduced, with permission, from [59]. (C) Illustration of ZnS-mediated redox reaction. Potentiostatic discharge curves with (D) carbon black (CB) and (E) ZnS-CB electrodes. Reproduced, with permission, from [60]. (F) Illustration of built-in catalysis in a nanoreactor. (G) Rate and cycle performances of S-C@MoS₂ and S-C cathodes. Reproduced, with permission, from [61]. (H) Schematic of the synthesis of Co₉S_{8-x}/CNT with a Co₉S₈ core and S-deficient shell and the conversion of lithium polysulfides (LiPSs) on its surface. Reproduced, with permission, from [62]. (I) Schematic illustration of confinement and catalytic conversion of LiPSs by the VS@CNT host in a Li-S cell model. Reproduced, with permission, from [63].

Overall, metal sulfides have the unique intrinsic advantage of strong sulphiphilicity to sulfur-containing species, thus providing effective immobilization for LiPSs. Although metal sulfides have better conductivity than their oxides, they are also usually coupled with carbon materials to further improve the overall conductivity for facilitating charge transfer during the redox reactions.

Transition-Metal Nitrides

Metal nitrides have been applied as catalysts for Li-S batteries due to their higher electrical conductivity compared with their metal oxide and metal sulfide counterparts. Ding and coworkers found that TiN can effectively reduce the potential barrier for Li₂S oxidation (Figure 5A) [64]. It was also found that TiN can efficiently catalyze the reduction of LiPSs. DFT calculations revealed that the faster polysulfide conversion on TiN surfaces is mainly ascribed to its stronger chemical interaction with LiPSs (Figure 5B). Li and coworkers reported that VN can also trap LiPSs and catalyze their conversion [65]. The positive shift of reduction peaks together with the negative shift of oxidation peaks of the VN nanoribbon/graphene (VN/G) electrodes confirm the much enhanced polysulfide redox kinetics by VN (Figure 5C). When used as the current collectors for Li-S batteries, the VN/G electrode exhibited much improved electrochemical performance compared with that of the reduced graphene oxide (RGO) electrode.



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Figure 5. Transition-Metal Nitrides as Catalysts for Li-S Batteries. (A) First-cycle charge profiles of C@TiO₂-Li₂S and C@TiN-Li₂S electrodes. (B) Schematic of polysulfide trapping and conversion on TiO₂ and TiN. Reproduced, with permission, from [64]. (C) Cyclic voltammetry (CV) curves of Li-S cells with VN nanoribbon/graphene (VN/G) and reduced graphene oxide (RGO) as sulfur hosts. Reproduced, with permission, from [65]. (D) CV curves of Li-S cells with InN-modified separator and pristine separator. (E) Cycling performances of Li-S cells with different separators at 1 C. (F) Schematic of polysulfide adsorption and conversion on InN. Reproduced, with permission, from [66].

Recently, Zhang and colleagues reported that InN nanowire-modified separators can promote the adsorption and conversion of LiPSs to inhibit the shuttle effect (Figure 5F) [66]. It was found that the In cation and electron-rich N anion in InN can effectively bond with the polysulfide anion and lithium cation, respectively, through the strong chemical affinity. Moreover, benefitting from the facilitated electron transfer on the surface of InN nanowires, Li-S cells with InN-modified separators exhibited enhanced electrochemical reaction kinetics compared with the electrodes with the pristine separators (Figure 5D). Consequently, the cells with InN-modified separators demonstrated stable cycling performance over 1000 cycles with an ultralow capacity fading rate of only 0.015% per cycle (Figure 5E).

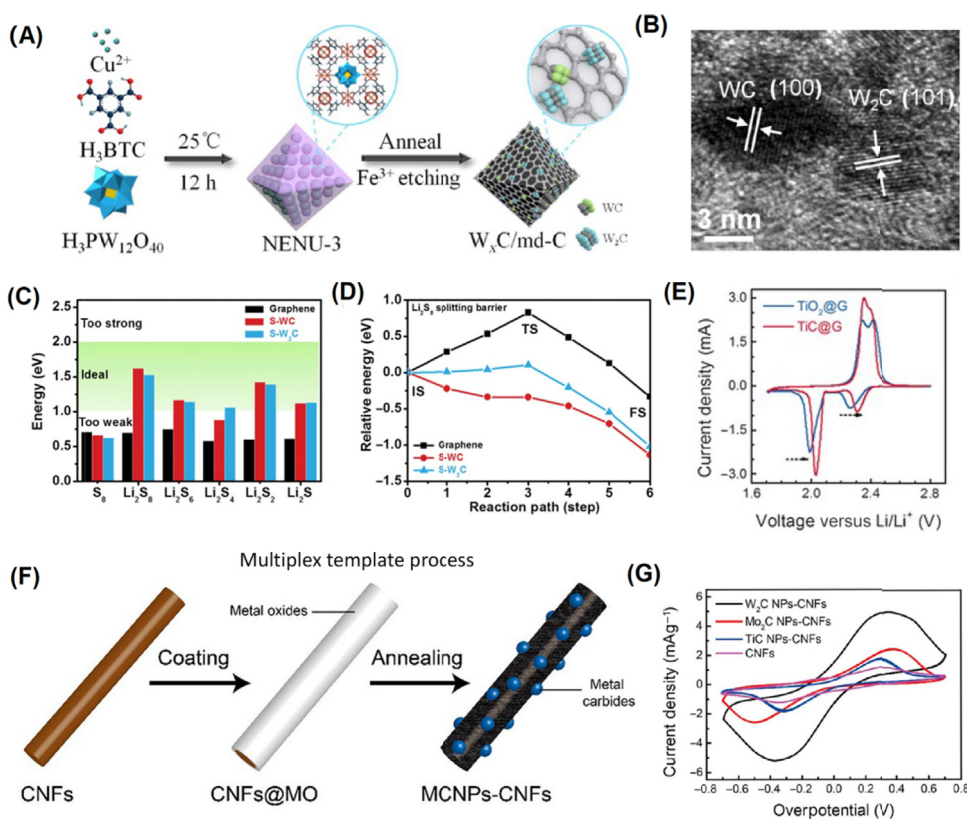
Metal nitrides combine the advantages of both high conductivity and abundant polar active sites for boosting polysulfide redox kinetics. However, the preparation of metal nitrides usually requires high temperature annealing with NH₃, which may limit their large-scale practical applications. To this end, exploring low cost and facile synthesis method is in great need for future research.

Transition-Metal Carbides

Transition-metal carbides have been explored as efficient redox mediators for the conversion between S and Li₂S [67–72]. Recently, Wu and coworkers reported tungsten carbide materials embedded in a metal-organic framework (MOF)-derived carbon (W_xC/md-C) via the pyrolysis

of phosphotungstic acid (PTA)-functionalized MOFs (Figure 6A) [70]. The *in situ* formed precursors not only suppress the vaporization of the carbon source, but also favor the generation of WC and W_2C heterostructure (Figure 6B). Compared with nonpolarized graphene, both WC and W_2C show strong affinity to adsorb LiPSs and barrierless cleavage energy of $Li_4S_8 \rightarrow 2Li_2S_4$ and $Li_4S_4 \rightarrow 2Li_2S_2$ (Figure 6C,D). Peng and coworkers claimed that TiC is superior to TiO_2 for facilitating the lateral growth of Li_2S due to its magnitudes higher electronic conductivity [67]. Thus, they achieve an enhanced battery capacity and low electrochemical polarization in TiC@G (Figure 6E,G indicates graphene).

Yu and coworkers systematically investigated performances of a series of metal carbide (W_2C , Mo_2C , TiC) nanoparticles on the surface of carbon nanofibers (MCNPs-CNFs) (Figure 6F) [72]. The charge transfer and mechanical robustness of MCNPs-CNF electrodes were significantly enhanced, owing to conductive and flexible 3D CNF networks. It was found that W_2C exhibited the best catalytic activity as seen from the highest redox current density in Li_2S_6 - Li_2S_6 symmetrical cells (Figure 6G).



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Figure 6. Transition-Metal Carbides as Catalysts for Li-S Batteries. (A) Schematic of synthesis procedure for $W_xC/md-C$. (B) Transmission electron microscopy images of $W_xC/md-C$. (C) Binding energies of S_8 and different lithiated polysulfides (LiPSs) on S- W_2C , S-WC, and graphene. (D) Energy profiles for the splitting of lithiated Li_4S_8 to Li_2S_4 on S- W_2C , S-WC, and graphene. Reproduced, with permission, from [70]. (E) Galvanostatic discharge-charge profiles of $TiO_2@G$ and TiC@G at a current density of 0.2 C. Reproduced, with permission, from [67]. (F) Schematic of synthetic procedure for metal carbide (MC) nanoparticles on the surface of carbon nanofibers (NPs-CNFs). (G) Cyclic voltammetry (CV) curves of symmetric Li_2S_6 cells with different metal carbides. Reproduced, with permission, from [72].

Metal carbides have the benefits of high conductivity and chemical stability. However, the preparation of metal carbides requires high temperature treatment between metal/metal oxide and carbon. In addition, most of the prepared metal carbides form irregular particles due to the inhomogeneous carburization and inevitable aggregation at high reaction temperatures. This limits the utilization of electroactive sites of metal carbides for use as catalysts for Li-S batteries. Thus, the development of a facile method to prepare metal carbides with tailored morphology and dimension may provide more opportunity to maximize the catalytic capability.

Transition-Metal Phosphides

Compared with the above-mentioned metallic compounds, transition-metal phosphides have the merits of metallic character and facile synthesis [73]. Moreover, metal phosphides feature both high LiPS absorption ability and low Li_2S dissociation energies, which are regarded as the most important factors to facilitate the redox kinetics of Li-S batteries [74]. In an early study, Tao and colleagues reported a facile synthetic approach to prepare metal phosphides (Ni_2P , Co_2P , Fe_2P) simply by annealing the chelated products of ethylene diamine tetraacetic acid, sodium phosphate, melamine, and metallic nitrates [75]. They found that Ni_2P -based cathodes exhibited the highest capacity retention of 90.3% after 400 cycles at 0.5 C, even with a high sulfur mass loading of 3.4 mg cm^{-2} . This can be ascribed to the Ni_2P having an optimized LiPS binding energy of -3.7 eV and appropriate Li_2S dissociation energy (0.74 eV). It should be noted that extremely high values of LiPS binding energy will result in LiPS accumulation and hinder subsequent migration and transfer processes (Figure 7A–F).

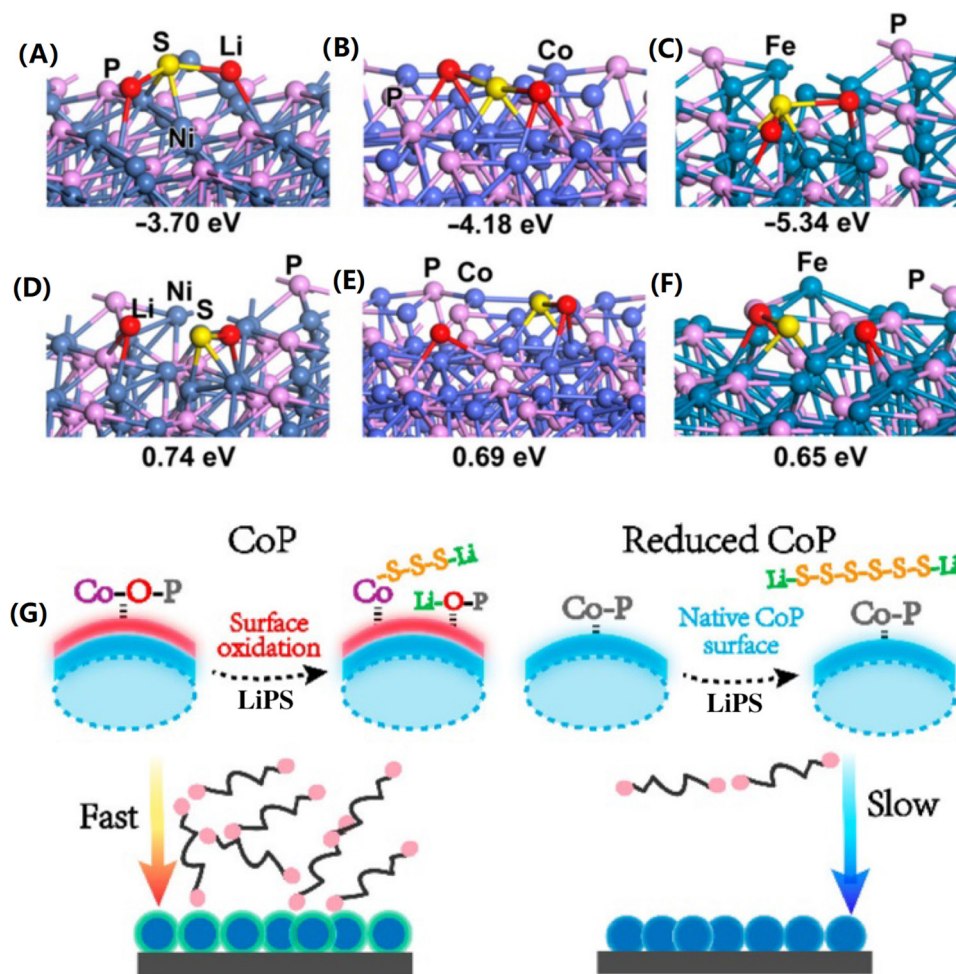
Recently, Wang and colleagues reported that the natural oxidation layer on CoP plays a vital role in adsorbing LiPSs via Co–O–P bonding and activating the surface Co sites for binding LiPSs via strong Co–S bonding (Figure 7G) [76]. As a result, the CoP/S electrodes demonstrated a high areal capacity of 5.6 mA h cm^{-2} with an ultra-high mass loading of 7 mg cm^{-2} .

Overall, metal phosphides have high conductivity, an abundant polar surface, and exhibit a superior catalytic effect. Moreover, the preparation of metal phosphides is quite moderate and does not require ultra-high temperature treatment, like their nitrides and carbides. As metal phosphides are readily oxidized under ambient conditions, the catalytically active sites need to be further studied in order to provide rational principles for designing metal phosphide catalysts for Li-S batteries.

Metal Nanoparticles, Clusters, and Single Atoms

Recently, metal nanoparticles, clusters, and single atoms have drawn extensive attention in the research field of electrocatalysis for applications such as water splitting [77], CO_2 reduction [78,79], N_2 fixation [80], and fuel cells [81,82]. This concept has also been introduced to Li-S batteries. Salem and coworkers first reported that the uniform distribution of Pt nanoparticles on graphene can reduce LiPS redox overpotential and deliver a 40% enhancement in the specific capacity over pristine graphene electrodes [83]. However, the employment of noble metals increases the overall cost of the material and lowers the energy density of Li-S batteries. To this regard, Wang's group proposed an N-doped porous carbon with uniformly dispersed Co clusters (N-PC@uCo) sulfur host via annealing a mixture of ZnCo-ZIF and glucose (Figure 8A) [84]. Apart from structural merits, Co clusters can also promote lithium-ion kinetics, interfacial charge transfer processes, redox of Li_2S_n , and LiPS immobilization. Consequently, N-PC@uCo@S showed superior cycling and rate performance.

Transition-metal single atoms such as Ni, Fe, and Co have been extensively explored for Li-S batteries [84–88]. Du and colleagues presented a cathode material comprising Co atoms

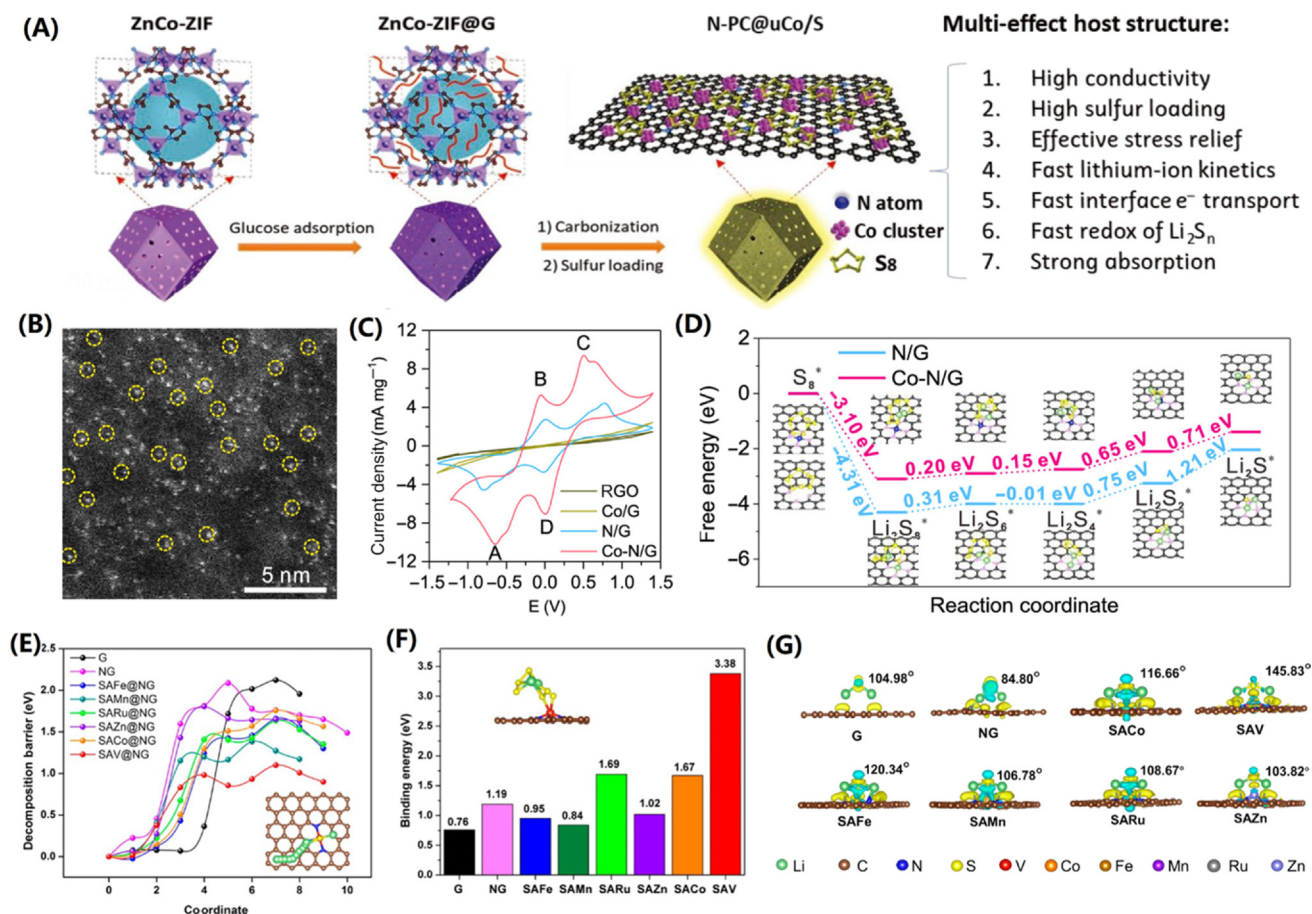


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Figure 7. Transition-Metal Phosphides as Catalysts for Li-S Batteries. The adsorption energy of Li_2S on (A) Ni_2P (111), (B) Co_2P (121), and (C) Fe_2P (111) surfaces. The dissociation energy of Li_2S on the surface of (D) Ni_2P (111), (E) Co_2P (121), and (F) Fe_2P (111) [75]. (G) Proposed binding schemes of lithium polysulfides (LiPSs) on CoP and reduced CoP (CoP-R) surfaces. Reproduced, with permission, from [76].

embedded in a nitrogen-doped graphene framework (Co-N/G, Figure 8B) [85]. They found that the Co-N-C coordination significantly enhanced the redox peaks in Li_2S_6 symmetric cells (Figure 8C). The Co single atoms serve as an electrocatalyst for Li_2S formation, as predicted from the reduced free Gibbs free energy during the whole S_8 reduction reaction (Figure 8D). Specifically, DFT calculations evidenced that Fe, Mn, Ru, Zn, Co, and V single atom-loaded substrates are ultra-stable after Li_2S and LiS adsorption, while Cu or Ag-derived substrates show a distorted atomic lattice [86]. Among those stable single atoms, V atoms exhibited the lowest Li_2S decomposition barrier of 1.1 eV, longest Li-S bond length of 2.28 Å, and largest bond angle (145.83°), indicating its superior LiPS/ Li_2S catalytic effect in Li-S batteries (Figure 8E–G). As a result, single atom V loaded N-doped graphene (SAV@NG) displayed a higher capacity and rate performance than the widely investigated Co-decorated sample.

Overall, metal catalysts have the advantages of both high catalytic activity and excellent electronic conductivity, which leads to the facilitated redox kinetics and high sulfur utilization. However,



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Figure 8. Metal Nanoparticles, Clusters, and Single Atoms as Catalysts for Li-S Batteries. (A) Schematic diagram of synthetic route for N-PC@uCo/S cathode with multiple effects. Reproduced, with permission, from [84]. (B) High-angle annular dark field scanning transmission electron microscopy (high-angle annular dark-field imaging-scanning electron emission microscopy) of Co atoms embedded in a nitrogen-doped graphene framework (Co-N/G). (C) Cyclic voltammetry (CV) scans of Co-N/G, Co/G, and reduced graphene oxide (RGO) electrodes. (D) Energy profiles of the reduction of lithium polysulfides (LiPSs) on N/G and Co-N/G. Reproduced, with permission, from [85]. (E) Decomposition barriers of Li_2S , (F) binding energy of Li_2S_6 , and (G) charge density difference of Li_2S adsorption on different substrates including graphene, NG, SACo@NG, SAV@NG, SAFe@NG, SAMn@NG, SARu@NG, and SAZn@NG (SA indicates single atom, NG indicates N-doped graphene). Reproduced, with permission, from [86].

these metal catalysts are either noble metals or heavy metals, which may not be suitable for practical applications. Thus, more effort is needed to develop metal catalysts with abundance and lightness.

Other Metal-Based Catalysts

Besides the typical metal-based catalysts discussed earlier, some metal borides and MOFs also show potential catalytic activity for the redox reactions in Li-S batteries. Nazar and coworkers reported that the lightweight superconductor MgB_2 can serve as a metallic sulfur host with both high conductivity and superior LiPS confinement [89]. By using DFT calculations, they found that the borides are unique in that both B- and Mg-terminated surfaces bond exclusively with the S_x^{2-} anions and not the Li^+ cations, which facilitates the electron transfer to the active S_x^{2-} anions. This surface-mediated polysulfide redox process leads to the larger exchange current and higher sulfur utilization compared with the MgO and carbon. The Li-S cell with MgB_2 shows superior electrochemical performance with stable cycling at a high sulfur loading of $9.3\ mg\ cm^{-2}$.

Wang and colleagues reported that a Ce-MOF-2/CNT-decorated Celgard separator can improve the electrochemical performance of Li-S batteries [90]. The cell with the Ce-MOF-2/CNT-modified separator showed stable cycling performance over 800 cycles. It was found that the coordination-unsaturated Ce(IV)-cluster nodes can efficiently capture LiPSs and catalyze their conversion process, which contributed to the superior electrochemical performance.

Concluding Remarks

Over the past 5 years, the efforts devoted to improving sluggish LiPS redox kinetics have generated rich knowledge on how to design catalysts for Li-S batteries. In this review, we highlighted recent significant progress on materials with both strong LiPS absorption ability and boosted catalytic effect, including metal-free polar materials, transition-metal compounds, and metals. An ideal catalyst for Li-S batteries should satisfy the following prerequisites:

- (i) Favorable electrical conductivity for fast electron transport.
- (ii) Optimized LiPS affinity. Too weak a trapping ability would result in severe shuttling effect, while too strong absorption ability leads to surface sulfuration or sluggish LiPS diffusion processes.
- (iii) Abundant exposure of active sites to accelerate the redox reactions.
- (iv) Low Li_2S formation and decomposition barriers. Li_2S redox reactions are the dominating steps that cause low sulfur utilization, inferior rate performance, and fast capacity fading in Li-S battery system.

Despite the substantial progress made in recent years, the use of catalytic materials for Li-S batteries is still in its infancy, with many remaining challenges in developing ideal catalysts for Li-S batteries (see Outstanding Questions). Advanced *in operando* measurements employing X-ray photoelectron spectroscopy (XPS), Raman, and synchrotron radiation are needed to further elucidate active sites and intermediates during catalytic LiPS redox reactions. Moreover, designing architectures with appreciable flexibility to relieve the mechanical stress originating from Li_2S deposition and dissolution should be considered, particularly under extra-high sulfur loading. One important strategy is to develop light element-derived catalysts over heavy or noble metallic compounds/metals to improve overall battery energy density, lower the battery cost, and reduce environmental pollutions. With synergetic efforts from research fields of electrochemical catalysis, theoretical calculations, and nanoscience, more breakthroughs on Li-S batteries can be achieved and Li-S batteries can contribute to rapidly expanding commercial applications.

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Outstanding Questions

What is the in-depth lithium polysulfide (LiPS) regulation mechanism on the catalytic host?

For metal-free catalytic materials such as heteroatom-doped carbon, what is the intrinsically active site for boosting LiPS conversion (i.e., heteroatom-doped sites or defective sites)?

Can the active sites of catalytic host remain stable during the repetitive discharge-charge process?

Which factor dominates the performance of a host material, the LiPS trapping ability, the surface reactivity, the diffusivity of lithium ions and LiPSs, or the electrical conductivity?

Can we identify the accurate active crystalline planes of metallic compounds/metals as current researches only choose several crystalline planes into DFT calculations?

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