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Metals and Alloys as Catalytic Hosts of Sulfur Cathode for Lithium–Sulfur Batteries

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Abstract: Lithium–sulfur batteries are recognized as one of the most promising next-generation energy storage devices, owing to the high theoretical energy density of 2600 Wh·kg^{-1}. However, their application is seriously hindered by the sluggish electrochemical reaction kinetics of elemental sulfur and discharged products (Li_2S_2/Li_2S), and the notorious "shuttle effect" of soluble intermediate lithium polysulfide species, leading to poor cycle stability, low sulfur utilization and inferior coulombic efficiency. Introducing catalytic hosts into sulfur cathode is an efficient path to propel the conversion of sulfur-contained species, thus preventing the dissolution and loss of active-sulfur material in lithium–sulfur batteries. In this review, we summarize recent progresses on the use of metals and alloys as the core catalytic host of sulfur and demonstrate the catalytic mechanism in the conversion process of sulfur species with the help of metal and alloy hosts. Finally, future outlooks are proposed on the construction of catalytic hosts and the development of high-energy lithium–sulfur batteries.

Key words: lithium–sulfur batteries; metals/alloys; catalytic hosts

1 Introduction

High-energy secondary batteries provide the prerequisite for developing large-scale energy storage devices, 3C (computers, communications and consumer electronics) products and electric vehicles. In terms of energy density, according to the road maps from Made in China 2025, US

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Battery 500 and Japan RISING II, the recent key goal of the high-energy power source is 500 Wh·kg^{-1}[1]. Lithium-ion (Li-ion) batteries based on the reversible intercalation-deintercalation mechanism have made great achievement, with their energy density upgraded triply from 100 to 300 Wh·kg^{-1} in the past few decades. However, the development of Li-ion batteries has almost approached their upper limit (350 Wh·kg^{-1}), and the improving space is extremely restricted[2]. Contrastively, lithium–sulfur (Li–S) batteries possess high theoretical energy density of 2600 Wh·kg^{-1} and the practical value in the future could reach to 500–600 Wh·kg^{-1}, which is much higher than commercial Li-ion batteries with metal oxide cathode and graphite anode. Accompanied with high natural abundance, low cost and environmental friendliness of elemental sulfur, Li–S batteries are recognized as one of the most promising next-generation energy storage devices[3,4].

In contrast to Li-ion batteries, the charge–discharge process of Li–S batteries usually involves the multistep solid–liquid–solid phase transformation accompanied by a high theorical capacity of active-sulfur (1675 mAh·g^{-1}). The discharge curve exhibits two discharge-plateaus: the first high plateau appears between 2.3 and 2.4 V (vs. Li/Li$^+$), providing 25% capacity contribution with about 418 mAh·g^{-1}, and herein, elemental S_8 is reduced to soluble lithium polysulfides (Li_2S_n, $4 \leq n \leq 8$). The second discharge-plateau at around 2.1 V (vs. Li/Li$^+$) involves the liquid–solid conversion from intermediate lithium polysulfides (LiPS) to Li_2S, delivering the theoretical capacity of 1255 mAh·g^{-1}[5–10]. Electrochemical reaction equations of the discharge process are shown as follows[11]:

$$S_{8(s)} + 2e^- + 2Li^+ \rightarrow Li_2S_{8(l)} \qquad (1)$$

$$3Li_2S_{8(l)} + 2e^- + 2Li^+ \rightarrow 4Li_2S_{6(l)} \qquad (2)$$

$$2Li_2S_{6(l)} + 2e^- + 2Li^+ \rightarrow 3Li_2S_{4(l)} \qquad (3)$$

$$Li_2S_{4(l)} + 2e^- + 2Li^+ \rightarrow 2Li_2S_{2(s)} \qquad (4)$$

$$Li_2S_{2(l)} + 2e^- + 2Li^+ \rightarrow 2Li_2S_{(s)} \qquad (5)$$

When charging, electro-active materials exhibit the reversible multistep conversion of Li_2S → LiPS → S_8, which fabricates a complete loop together with the discharge process. What's more, elemental S_8 may undergo a transition of crystalline phase (from α to β phase) and a redistribution on electrode interface during the discharge–charge cycles[12].

Li–S batteries have been defined and researched in the 1960s, while their application continuously suffers from serious challenges by the inherent solid–liquid–solid phase conversion mechanism. On the one hand, resulting from the extremely low conductivity of active-sulfur and discharged product Li_2S (10^{-30} and 10^{-14} $S \cdot cm^{-1}$, respectively), the chemical/electrochemical reaction kinetics of Li–S batteries is inert, thus leading to the low utilization of sulfur and serious capacity fading of the cathode. On the other hand, the intermediate LiPS tend to dissolve into ether-electrolyte in the discharge process, detaching from sulfur-hosts and shuttling toward the Li anode side driving by potential difference and concentration gradient. A part of the dissolved LiPS is chemically reduced to Li_2S_2/Li_2S on the surface of Li metal, leading to the continuous loss of active-sulfur material and serious corrosion of anode. Another part would migrate back to the cathodic side during charging, cycling back and forth, and this key side reaction is called the "shuttle effect"[9,13]. For Li–S batteries, the sluggish electrochemical kinetics of sulfur and Li_2S results in the retention and shuttle of soluble intermediate LiPS in ether-based electrolyte, which further leads to the incomplete redox conversion of active-sulfur and the disordered deposition of discharged products on the conductive matrix. Finally, the sulfur cathode is gradually passivated by the inside unexploited sulfur and outside discharged products during repeated cycles (Fig. 1). This "positive feedback control" in Li–S batteries results in the low sulfur utilization, capacity attenuation and low coulomb efficiency.

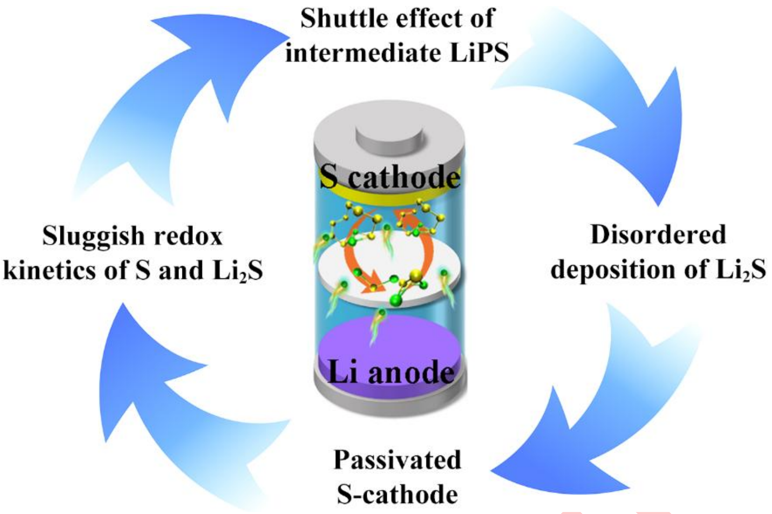

Fig. 1 Schematic illustration of the "positive feedback control" in Li–S batteries.

Deriving from the low proportion of active materials in the whole sulfur cathode and simultaneously a high electrolyte usage in battery, there exist a big gap in cell-level between the practical energy density and the theoretical standard of Li–S batteries. For the sake of realizing the practical implementation of Li–S batteries, it is significant to achieve high utilization of active-sulfur under the condition of increased sulfur loading, high sulfur content, and lean electrolyte usage[14,15]. Manthiram *et al.*[16] pointed out that Li–S pouch batteries should achieve the sulfur area-loading > 5 $mg\cdot cm^{-2}$ and carbon proportion < 5% in the sulfur cathode. Simultaneously, electrolyte/sulfur ratio (E/S) < 5 $\mu L\cdot mg^{-1}$ and negative/positive ratio (N/P) < 5 are also prerequisites. In addition, Tübke *et al.*[15] proposed that it was necessary to increase the sulfur loading to 6 $mg\cdot cm^{-2}$, the mass proportion of active materials to 70%, the sulfur utilization to 80%, and to decrease E/S lower than 3 $\mu L\cdot mg^{-1}$ for 18650 columnar Li–S batteries. However, it is hard to achieve the high discharge capacity and a stable cycle under all these harsh conditions. In the final analysis, the practical issues of Li–S batteries are mainly caused by the intrinsic phase conversion mechanism and the resulted inherent shortcomings of sulfur element.

2 Design and construction of sulfur cathodes

Elemental sulfur is usually incorporated with matrixes to drive the electrochemical kinetics of the sulfur electrode and inhibit shuttle effect of LiPS in Li–S batteries. Therefore, exploring efficient host materials and constructing desirable cathodic structures have always been the focus point. Toward the material selection and construction design of sulfur-hosts, following points must be taken into consideration systematically: (1) high electron conductivity and abundant ion-transfer channels; (2) moderate anchor ability toward intermediate LiPS, including physical confinement and chemical adsorption, to inhibit shuttle effect; (3) electrocatalytic activity toward the conversion of LiPS and Li_2S_2/Li_2S, thus to improve the reaction kinetics of the battery; (4) suitable specific surface area and pore size distribution to buffer the volume fluctuation of the sulfur cathode, and simultaneously to refrain unnecessary consumption of electrolyte.

Carbon nanomaterials usually possess high conductivity, large specific surface area, rich pore structure and flexible micro-morphology. Therefore, most of the building strategy toward sulfur cathodes are focused on incorporating sulfur element into nano-carbon materials. By accurately designing nanostructures and constructing three-dimensional (3D) networks, carbon-based hosts could enhance the electrochemical performance of Li–S batteries to some degree[17–20], nevertheless the weak Van der Waals interaction toward LiPS by non-polar carbon cannot effectively suppress the shuttle effect. Based on various carbonic nano-frameworks, heteroatomic-doping and single-atom-modification could improve the anchor/electrocactlytic capacity for LiPS and the cycle stability of sulfur electrodes, while the active site toward sulfur-contained species is still sterile[21–27]. With the deepened understanding for catalysis, polar catalytic sulfur-hosts, including mono-metals[3,28,29], alloys[30], metal oxides[4,31–33], sulfides[34–36] and nitrides[37–39], are introduced into Li–S batteries to accelerate the electrochemical conversion between solid sulfur and solid Li_2S/Li_2S_2 across soluble LiPS species. Today, the sulfur-host not only serves as the medium of electrons/ion-transfer and the inhibitor toward LiPS dissolution by physical/chemical interaction, but also gradually evolves into the participator and promoter in the conversion process of sulfur-contained species, which plays a very important role for the redox conversion of intermediate LiPS and the deposition behavior of solid discharged products, that is so called the “catalytic host”. Following issues must be taken into consideration when selecting and designing catalytic hosts: (1) strong chemical interaction toward polysulfides, which is the prerequisite for catalytic conversion; (2) efficient electron/ion transfer on the interface of catalyst/electrolyte/active-sulfur; (3) superb catalytic activity of the core catalyst (Fig. 2). Mono-metals and alloys share metal–metal bonds (M–M), and this bonding states endow metal/alloy materials with abundant compositions, various crystal structures, accessible electronic states and notable intrinsic features. Some mono-metal and transition metal-based alloys have shown great potential as catalysts, including the hydrogen evolution reactions and fuel cell reactions, due to their high activity and stability arising from good electronic and chemical properties toward oxygen element[40,41]. Given that the similar chemical property of oxygen and sulfur, metals and alloys also deliver a strong chemical interaction toward sulfur species, thus obviously decreasing the reaction barrier and accelerating their conversion in Li–S batteries, which has been widely reported in previous literature. Importantly, the high intrinsic conductivity avoids additional resistance and decreases electrochemical polarization on the sulfur cathode. Therefore, as compared to metal compounds with intrinsic semiconductor properties, metal/alloy hosts usually deliver natural instincts of stronger and more durable electrocatalytic activity toward LiPS, which are beneficial for the rapid redox conversion of sulfur species in Li–S batteries[42–45]. In addition, metal-based catalysts could exhibit high stability and compatibility in the charge-discharge voltage range and toward the electrolyte system of Li–S batteries, although some kind of electroactive metal/alloy hosts participate deeply in the conversion of sulfur-contained species[46–50]. Owing to these unique merits, metals and alloys as the catalytic hosts of sulfur cathode have drawn much attention and been expected to be a promising selection for Li–S batteries.

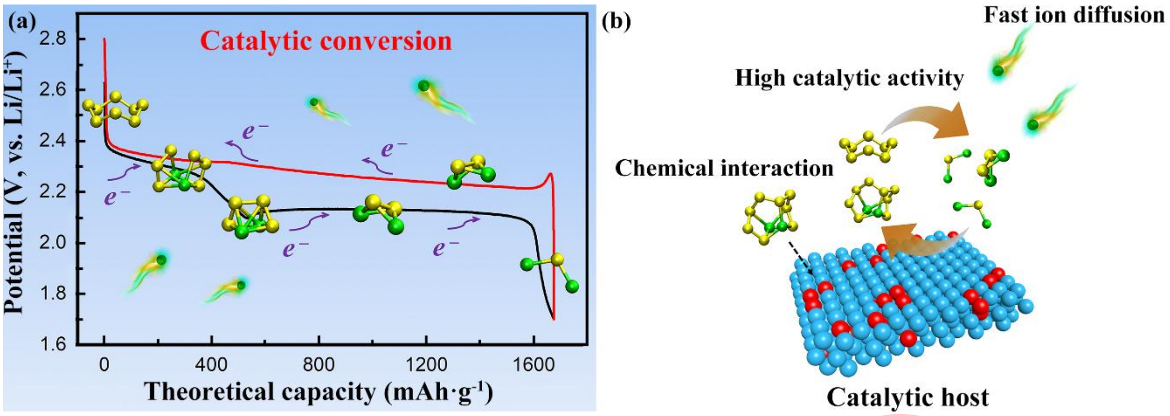

Fig. 2 Schematic of the working mechanism of sulfur cathode based on catalytic conversion in Li–S batteries.

This review mainly summarizes recent progresses on the use of metals and alloys as the core catalytic host of sulfur with a focus on the catalytic conversion and electrochemical performance of Li–S batteries.

3 Metal and alloy hosts for Li–S batteries

3.1 Metals as the core catalytic host of sulfur

Compared with various metal compounds, the inherent high conductivity of mono-metallic nanoparticles is helpful to decrease the additional interface resistance on the cathode of Li–S batteries during the charge–discharge process. Resulting from the unique orbital structure, some kind of precious metals and transition metals (TMs) could exhibit catalytic activity for the conversion of sulfur-contained species.

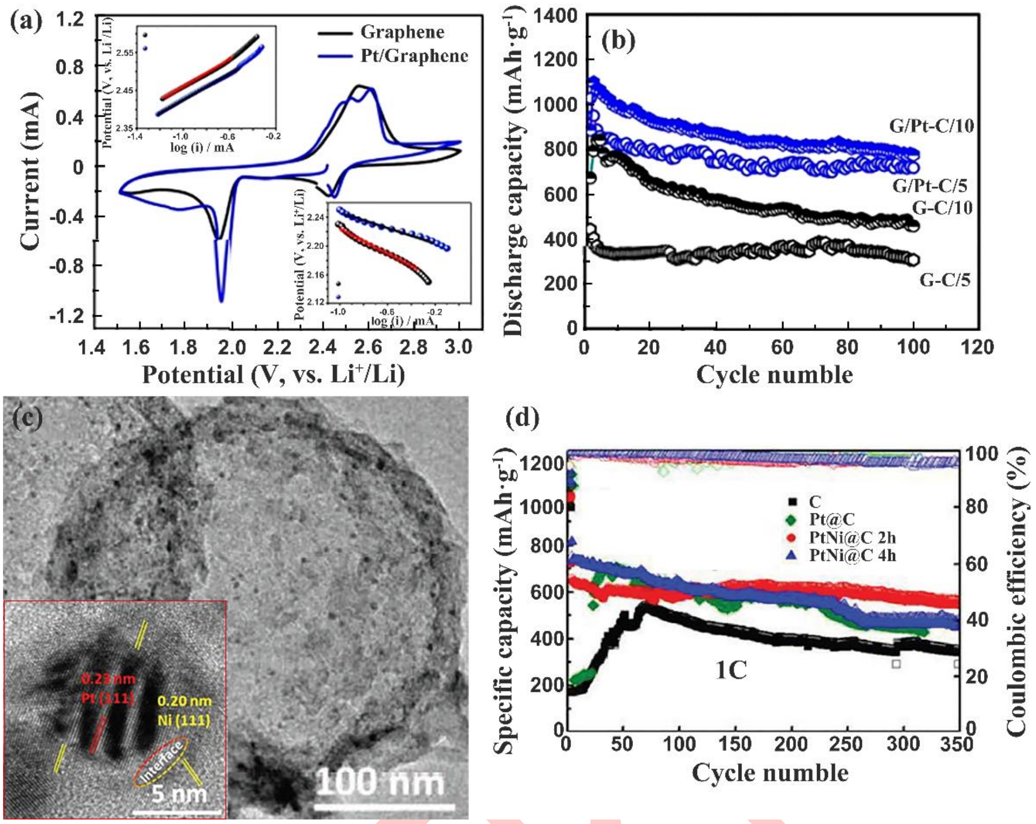

Fig. 3 (a) Cyclic voltammetry curves of graphene and Pt/graphene electrodes and the corresponding Tafel plots. (b) Cycle performance of Pt/graphene electrodes. (a, b) Reprinted from Al Salem H, Babu G, Rao C V, et al., *J Am Chem Soc*, 2015, 137(36): 11542–11545, Copyright 2015, with permission from American Chemical Society[46]; (c) TEM and HRTEM images of PtNi@C (2 h). (d) Cycle performance at 1C rate. (c, d) Reprinted from Liu Y, Kou W, Li X, et al., *Small*, 2019, 15(34): 1902431, Copyright 2019, with permission from Wiley-VCH Verlag GmbH & Co. KGaA[52].

Mono-metals can be prepared by many methods, which are classified mainly according to the requirement for morphology and particle size and different reductive conditions provided from $NaBH_4$ or $N_2H_4·H_2O$ toward metal salts. Shan's group[51] reported that Pt nanoparticles not only functioned as a static chemical absorber for LiPS, but also promoted the redox kinetic as an electrochemical catalyst, and the irreversible deposition of short-chain Li_2S_2/Li_2S was greatly gotten remission by the highly dispersed Pt particles on carbon substrate. The commercially available Pt/carbon (Pt/C) composite host enhances the electrochemical performance of the sulfur cathode efficiently. Furthermore, in order to stabilize the LiPS shuttle process and to enhance the redox reaction rate, Arava's group[46] introduced the concept of "electrocatalysis" into Li–S batteries for the first time. With H_2PtCl_6 and $NiCl_2$ solution as Pt precursor and Ni precursor, respectively, Pt and Ni nanoparticles are deposited on graphene substrates under a strong reductive condition endowed by $NaBH_4$, and the resulted Pt/graphene and Ni/graphene hosts exhibit reduced overpotential and excellent specific capacity over the pristine graphene, and more importantly, Pt nano-electrocatalysis demonstrates around 40% enhancement in the specific capacity (Fig. 3a and b). As shown in Fig. 3c, Liu *et al.*[52] prepared a Pt@Ni core–shell bimetallic catalyst with a patch-like Ni shell under the hydrothermal condition with $N_2H_4 \cdot H_2O$ as reducing agent, which was uniformed dispersed on porous carbon spheres (NiPt@C) to construct the sulfur cathode of Li–S batteries. The resulted bimetallic catalyst significantly enhances the transformation of insoluble products to soluble LiPSs in the charge process by accelerating electron transfer and reducing the energy barrier, achieving lower polarization and faster redox reaction kinetics. It is demonstrated that electronic migration from Ni to Pt activates the solid Li_2S_2/Li_2S by promoting the transformation of Li–S–Li to Ni–S–Li, consequently releasing Li-ion and free electrons, simultaneously enhancing protonic/electronic conductivity. With the synergic effect of the bimetallic catalyst, S/PtNi@C shows the discharge capacity of around 600 $mAh \cdot g^{-1}$ at 1C rate over 300 cycles without distinct fading (Fig. 3d). Zhou *et al.*[53] systematically investigated and correlated the sulfur evolution on various current collectors combining in situ optical microscopy, ex situ analyses and density functional theory (DFT) calculations. It is illuminated that different sulfur growth behaviors occur on different substrates during battery operation in real time: solid sulfur crystals are produced on the carbon surface, while supercooled liquid sulfur droplets are formed on the surface of Ni collector at room temperature. The battery with liquid sulfur droplets could deliver higher reversible capacity, faster reaction kinetics, and longer cycling life than solid sulfur crystals. On this basis, 3D Ni-based interconnected architectures are designed and achieve an enhanced electrochemical performance of Li–S batteries.

Furthermore, Xing *et al.*[54] synthesized a series of Li_2S/TM nanocomposites via a lithiothermic reduction reaction, and it was realized that the presence of TMs could transform electrochemical behaviors of Li_2S (Fig. 4). The introduction of W, Mo and Ti elements greatly increases the electronic and ionic conductivity of Li_2S/TM composites and effectively inhibits the polysulfide dissolution via TM–S interaction. While, Co, Mn and Zn elements can turn Li_2S into a prelithiation agent, forming metal sulfides rather than S_8 after the full charge. These findings have a guiding significance in fabricating novel Li_2S-based cathode materials.

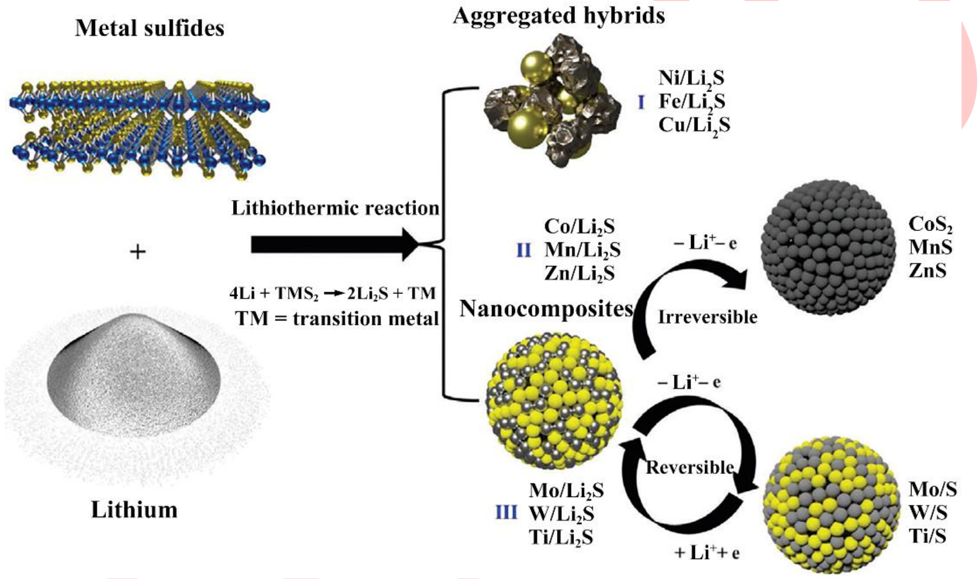

Fig. 4 Schematic of Li_2S/TMs synthesis and proposed electrochemical reaction mechanism. Reprinted from Xing Z, Tan G, Yuan Y, et al., *Adv Mater*, 2020, 32(31): 2002403, Copyright 2020, with permission from Wiley-VCH Verlag GmbH & Co. KGaA[54].

3.2 Binary alloys as the core catalytic host of sulfur

Alloy materials are synthesized by alloying several metal components or metal and non-metal components, which usually deliver metallic properties. As the core catalytic host of sulfur in Li–S batteries, alloys are mainly prepared by high-temperature calcination and hydrothermal treatment toward the mixture of metal sources under a reductive condition. Thereof, the morphology and microstructure of alloy hosts could be precisely regulated with the hydrothermal method, while to some degree, the residual hydroxyl/carbonyl on the surface might weaken their electrochemical activity toward LiPS and the electrical conductivity. Compared with the individual metal species, the alloy catalyst possesses an improved catalytic activity, which has been well proved in fields of water splitting and metal–air batteries[55,56]. For Li–S batteries, alloys could exhibit higher conductivity than that of TM compounds, thus reducing the charge-transfer resistance on the cathode surface. Due to the tuned electron cloud structure, alloy materials deliver stronger adsorption capacity and higher electrocatalytic ability toward polysulfide species than single-component metals. Among them, binary alloys possess the simplest constitution among various alloy materials. As compared to other non-noble metallic alloys, cobalt-based and nickel-based alloys usually exhibit higher electrocatalytic capacity toward the conversion reaction of sulfur species, and have archived a larger progress as the core catalytic hosts of sulfur cathodes, thus they are selected as representatives among numerous candidates in this section to illuminate the superiority of binary alloys for Li–S batteries[30,57,58].

3.2.1 Cobalt-based binary alloys

Li–S batteries with Co-based bimetallic alloy hosts could exhibit improved electrochemical performances. Wang's group[48] presented well-designed FeCo alloy catalysts anchored on porous carbon (FeCo–C) as the sulfur host to improve the discharge capacity and cycle stability by accelerating the conversion reactions. The FeCo alloy shows high catalytic effect and strong adsorption capability for LiPS, in which the potential polarization can be greatly decreased and the shuttle effect can be largely avoided. The obtained S/FeCo–C composite shows an initial specific capacity of 791.9 mAh·g^{-1} at 2C rate and maintains 502.5 mAh·g^{-1} even after 500 cycles. Combining DFT calculations, Zeng *et al.*[59] shown that the alloying of Fe into carbon-coated Co not only provided moderate chemical interaction with polysulfide species to hinder their diffusion but also served as an active catalyst in the successive lithiation of S_8 to Li_2S. Based on the fast migration of Li-ion and the spontaneous lithiation of Li_2S_2 on the carbon-coated Fe–Co alloy, the entrapping–conversion processes of polysulfides are both thermodynamically and kinetically promoted in redox cycles. Rationally designed Co_7Fe_3@porous graphite carbon–carbon nanotubes (Co_7Fe_3@PGC–CNT) electrocatalysts are introduced into Li–S batteries through separator functionalization, and the as-constructed Li–S batteries exhibit dramatically enhanced rate capacity of 788 and 631 $mAh \cdot g^{-1}$ at 10 and 15C rates, respectively (Fig. 5). Loaded on heteroatomic-doped carbon substrate, the catalytic activity of alloy hosts can be further enhanced by synergistic effect. As shown in Fig. 6a and b, Hu *et al.*[60] developed N-doped carbon-layer-enveloped CoFe alloy (CoFeCN@C) nanoparticles, which were employed to functionize the commercial polypropylene separators for Li–S batteries. In the hybrid structure, the N-doped carbon layer provides abundant conducting pathways for ion/electron transfer, while CoFe alloy offers sufficient polysulfide adsorptive and catalytic sites, which can simultaneously accelerate the multiphase conversion of sulfur–polysulfide–sulfide and suppress the polysulfide shuttling. A high initial areal capacity of 7.9 $mAh \cdot cm^{-2}$ is achieved even with a high sulfur loading up to 8.5 $mg \cdot cm^{-2}$.

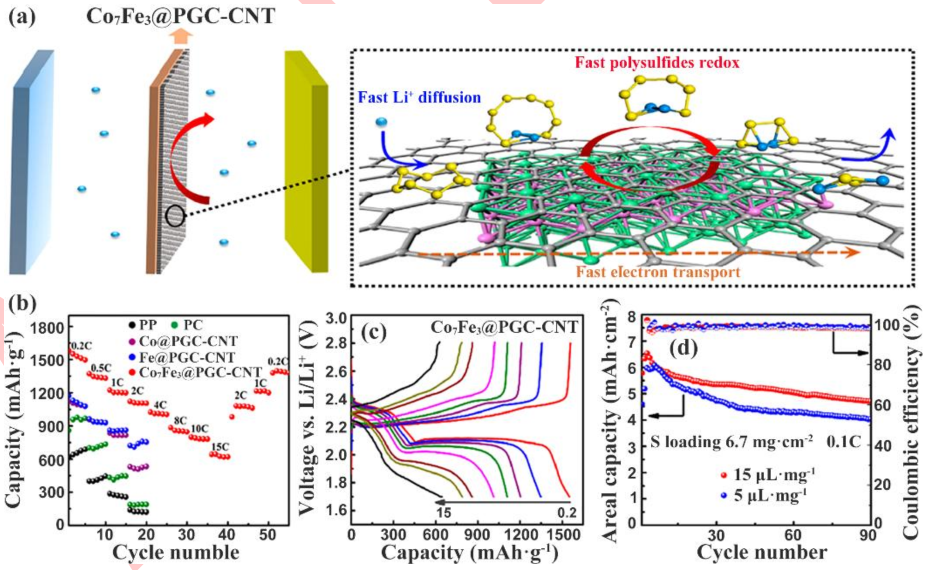

Fig. 5 (a) Schematic illustration of the shuttle suppression mechanism with the Co_7Fe_3@PGC–CNT modified separator. (b) Rate performance, (c) charge–discharge profile, and (d) cycle performance of Li–S batteries with Co_7Fe_3@PGC–CNT modified separator. (a–d) Reprinted from Zeng P, Liu C, Zhao X, et al., *ACS Nano*, 2020, 14(9): 11558–11569, Copyright 2020, with permission from American Chemical Society[59].

Nanotechnology offers the possibility of abundant active sites in host materials for high electrocatalytic ability. Therein, the accurate 3D structure-design toward sulfur-hosts is significant for exposing more adsorption/catalytic sites to improve the electrochemical performance of Li–S batteries. As shown in Fig. 6c and d, Co–Te alloy on hollow N-doped carbon spheres (Co–Te/NC) was synthesized via a tellurization process using hollow ZIF-67 spheres as the precursors by Zhang's group[49]. The obtained Co–Te alloy exhibits superior stability and catalytic activity to endow the Li–S battery with good rate performance and long cycle life. These excellent performances are attributed to the fine tuning of sulfur adsorption sites and binding energies, which enables the desirable adsorption and fast conversion of sulfur species on Co–Te alloy and avoids the electrode passivation. What's more, Qiao *et al.*[57] prepared a hollow Co_xSn_y modified N-doped carbon (E-Co_xSn_y/NC) as the host material for Li–S batteries through a stepwise coating-etching approach (Fig. 6e and f). The E-Co_xSn_y/NC composites not only show the strong chemisorption to anchor LiPS, but also have strong electrocatalytic effect to effectively accelerate the redox conversion activity of LiPS intermediates. Beneficial from the fast electrocatalytic conversion activity, strong chemisorption and the novel hollow carbon structure, a high specific capacity of 1006 mAh·g^{-1} at 0.2C after 100 cycles is obtained for the S/E-Co_xSn_y/NC cathode.

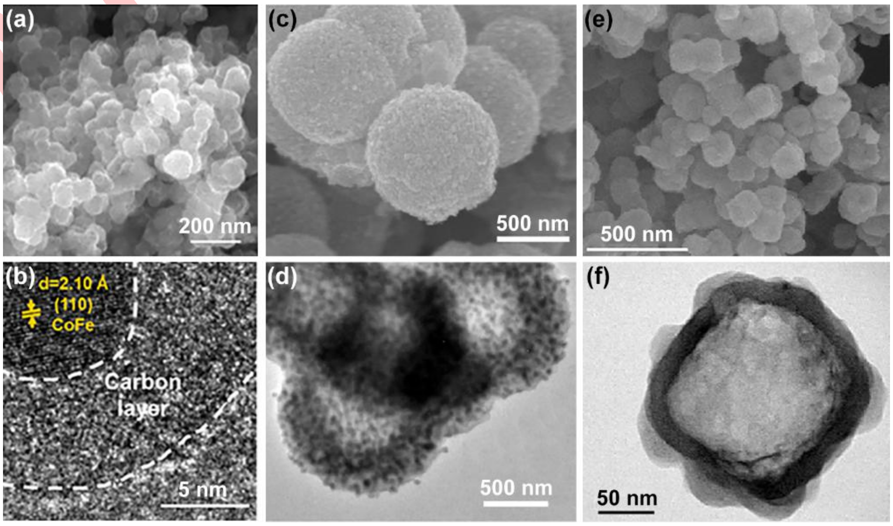

Fig. 6 (a, b) SEM and HRTEM images of CoFeCN@C. Reprinted from Hu Y, Cheng C, Yan T, et al., *Chem Eng J*, 2021, 421: 129997, Copyright 2021, with permission from Elsevier[60]. (c, d) SEM and

TEM images of Co–Te/NC. Reprinted from Song X, Tian D, Qiu Y, et al., *Energy Storage Mater*, 2021, 41: 248–254, Copyright 2021, with permission from Elsevier[49]. (e, f) SEM and STEM images of E-Co_xSn_y/NC composite. Reprinted from Qiao Z, Zhou F, Zhang Q, et al., *Energy Storage Mater*, 2019, 23: 62–71, Copyright 2019, with permission from Elsevier[57].

3.2.2 Nickel-based binary alloys

Compared with cobalt-based alloys, nickel-based alloys as the catalytic host of Li–S batteries have attracted more attention by its lower cost. For example, Ni–Fe intermetallic compound (Ni_3Fe) as a novel electrocatalyst could trigger the highly efficient polysulfide–involving surface reactions owing to the serious lattice distortion (Fig. 7a and b). Electrochemical kinetics of the sulfur–polysulfide–sulfide multiphase conversion reaction can be enhanced and Li-ion diffusion within the electrode is extremely promoted by Ni_3Fe catalyst[61]. Result, the Li–S batteries with Ni_3Fe modified separator deliver initial capacities of 1310.3 $mAh\cdot g^{-1}$ at 0.1C and 598.0 $mAh\cdot g^{-1}$ at 4C rate (Fig. 7c). Likewise, He *et al.*[47] shown a cost-effective hexagonal close-packed phase Fe–Ni alloy to serve as an efficient electrocatalyst to promote the LiPS conversion. The pouch cell fabricated with S/Fe–Ni composite achieves stable cycle performance under a realistic condition of a low electrolyte usage of 4.5 $\mu L\cdot mg^{-1}$. Furthermore, the electrocatalytic activity of alloy materials can be better activated via combined with 3D carbon substrates. As shown in Fig. 7d and e, Wang *et al.*[62] prepared Ni–B alloy nanoparticles dispersed uniformly on carbon nanotube microspheres (Ni–B/CNTMs) as the sulfur host, in which the loading of Ni–B alloy was about 20 wt%. On the one hand, Ni–B alloy nanoparticles can anchor polysulfides tightly through Ni–S and B–S bonds and exhibit high electrocatalytic capability toward the conversion of intermediate polysulfide species. On the other hand, the intertwined CNT microspheres provide an additional electron-conductive framework in response to the fast electrochemical reaction of the battery. The S/Ni–B/CNTM composite delivers high specific capacity and good cycle performance under both high sulfur loading of 8.3 $mg\cdot cm^{-2}$ and a lean electrolyte of 3 $\mu L\cdot mg^{-1}$ (Fig. 7f).

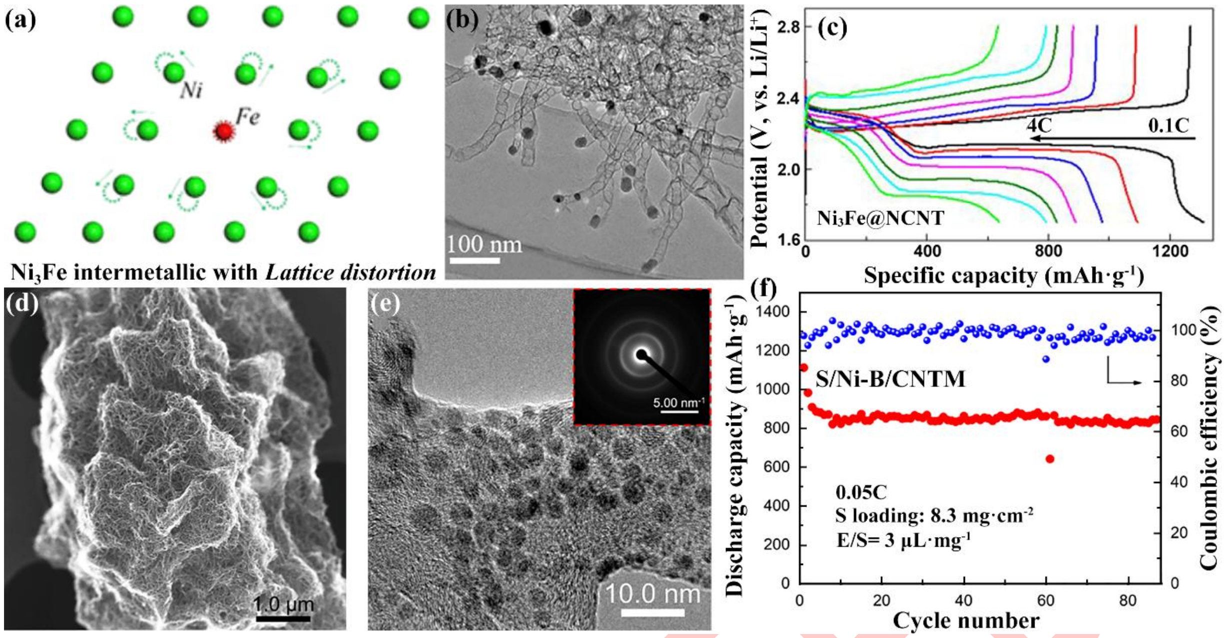

Fig. 7 Atomic structure model of Ni_3Fe intermetallic with lattice distortion. (b) TEM image of Ni_3Fe@NCNT. (c) Rate performance of Li–S batteries with Ni_3Fe@CNT modified separator. (a–c) Reprinted from Zhang Z, Shao A H, Xiong D G, et al., *ACS Appl Mater Interfaces*, 2020, 12(17): 19572–19580, Copyright 2020, with permission from American Chemical Society[61]. (d, e) TEM and HRTEM images of Ni−B/CNTM. (f) Cycle performances of high sulfur-loading electrodes under the lean electrolyte condition. (d–f) Reprinted from Wang Z Y, Wang H M, Liu S, et al., *ACS Appl Mater Interfaces*, 2021, 13(17): 20222–20232, Copyright 2021, with permission from American Chemical Society[62].

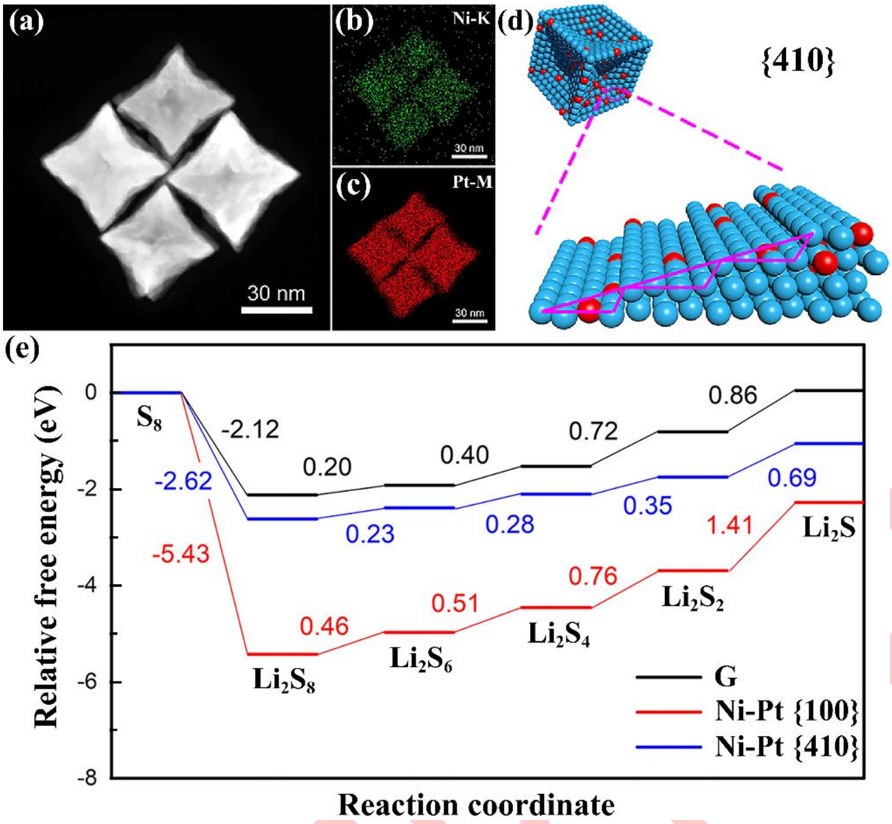

Fig. 8 (a–c) STEM image and the corresponding EDS mappings. (d) Atomic model of the CNC Ni–Pt alloy crystallite and the {410} facet. (e) Energy profiles for the sulfur reaction process. (a–e) Reprinted from Wang Z Y, Zhang B, Liu S, et al., *Adv Funct Mater*, 2022: 2200893, Copyright 2022, with permission from Wiley-VCH Verlag GmbH & Co. KGaA[50].

Catalytic property of the catalyst is strongly dependent on its surface atomic arrangement and configuration associated, thus the activity of catalytic sulfur-host could be effectively enhanced by the rational structural design. Especially, high-index facets (HIFs) possess high-density low-coordinated atoms, such as steps, edges and kinks, which usually deliver a much more superior activity than low-index facets (LIFs)[63–66]. In order to understand the superiority of HIFs of alloy catalysts, Wang *et al.*[50] prepared concave-nanocubic Ni–Pt (CNC Ni–Pt) alloys bounded by HIFs as the core catalyst of sulfur for Li–S batteries (Fig. 8a and b). Via kinetics studies and DFT calculations, it is demonstrated that CNC Ni–Pt alloy nanocrystallites with exposed HIFs not only exhibit the moderate chemical adsorption toward soluble LiPS but also accelerate the conversion of intermediate LiPS and solid discharged products more effectively than conventional nanocubic Ni–Pt nano-alloys with LIFs, thus enhancing the redox conversion of sulfur species (Fig. 8c). Benefiting from the accelerated kinetics by HIFs, the sulfur cathode delivers a high specific capacity of 783.3 mAh·g^{-1}$_{\text{-cathode}}$ with the whole cathode as active material at 0.1C rate, and a low capacity damping of 0.025% per cycle for 1000 cycles at 1C rate can be also obtained.

3.3 High-entropy alloys as the core catalytic host of sulfur

High-entropy alloys (HEAs) are fabricated by alloying five or more components into a single solid-solution phase, which possess the intrinsic high chemical complexity[67–69]. Compared with mono-metals and binary/ternary alloys, HEAs exhibit more serious lattice distortions and could deliver the superior activity on driving redox reactions owing to the atom-level high-disordered construction[70,71]. Actually, the enhanced catalytic activity of HEA materials is derived from the synergic effect associated with unique homogeneous solid-solution structure and high entropy, rather than the simple summation of components or the phase-separated heterostructures[72]. Xu *et al.*[73] prepared single-phase Fe–Co–Ni–Mn–Zn HEA nanoparticles via fast carbothermal reaction toward multimetal-MOF-74 precursor, which uniformly distributed on the porous carbon matrix and exhibited small size of about 7 nm. Owing to the optimized *d*-band center, nano-HEAs exhibit strong affinity and high catalytic activity toward LiPS. Li–S batteries assembled with nano-HEA modified separators could deliver outstanding capacity retention rates of 83.3% at 2C rate for 500 cycles. Gao's group[74] prepared Fe–Co–Ni–Cu–Mn HEAs with high mole mixing entropy (ΔS_{mix}) of 12.9 J·(K·mol)$^{-1}$, and introduced as the core catalytic host to activate the electrochemical performance of the sulfur cathode for Li–S batteries. As shown in Fig. 9a–h, HEA alloy nanocrystallites are distributed on nitrogen-doped carbon uniformly, and these nano-alloys exhibit high electrocatalytic activity toward the conversion of solid sulfur to solid discharged products across soluble intermediate LiPS, thus accelerating the redox reaction rate of the whole sulfur cathode. In addition, the HEA host plays a vital role in regulating the deposition behavior of discharged products, and boosts the conversion of Li_2S_2 to Li_2S and hindering the passivation of sulfur cathode. Conclusively, with the whole cathode as active material, the S/HEA−NC cathode delivers a high specific capacity of 1079.5 $mAh\cdot g^{-1}{}_{-cathode}$ at 0.1C rate, corresponding to the sulfur utilization of 90% (Fig. 9i). Under both lean electrolyte (3 $\mu L\cdot mg^{-1}$) and ultrahigh sulfur-loading (27.0 $mg\cdot cm^{-2}$) condition, a high initial capacity of 868.2 $mAh\cdot g^{-1}{}_{-cathode}$ can be also achieved.

In terms of HEA materials, the component-regulation and nano-sized preparation are extremely challenging topics due to their high complexity in atomic radius and electronegativity. Therefore, realizing constituent-adjustable and size-controllable HEAs is of great significance for the construction of high-performance sulfur cathode with the HEA core catalytic host.

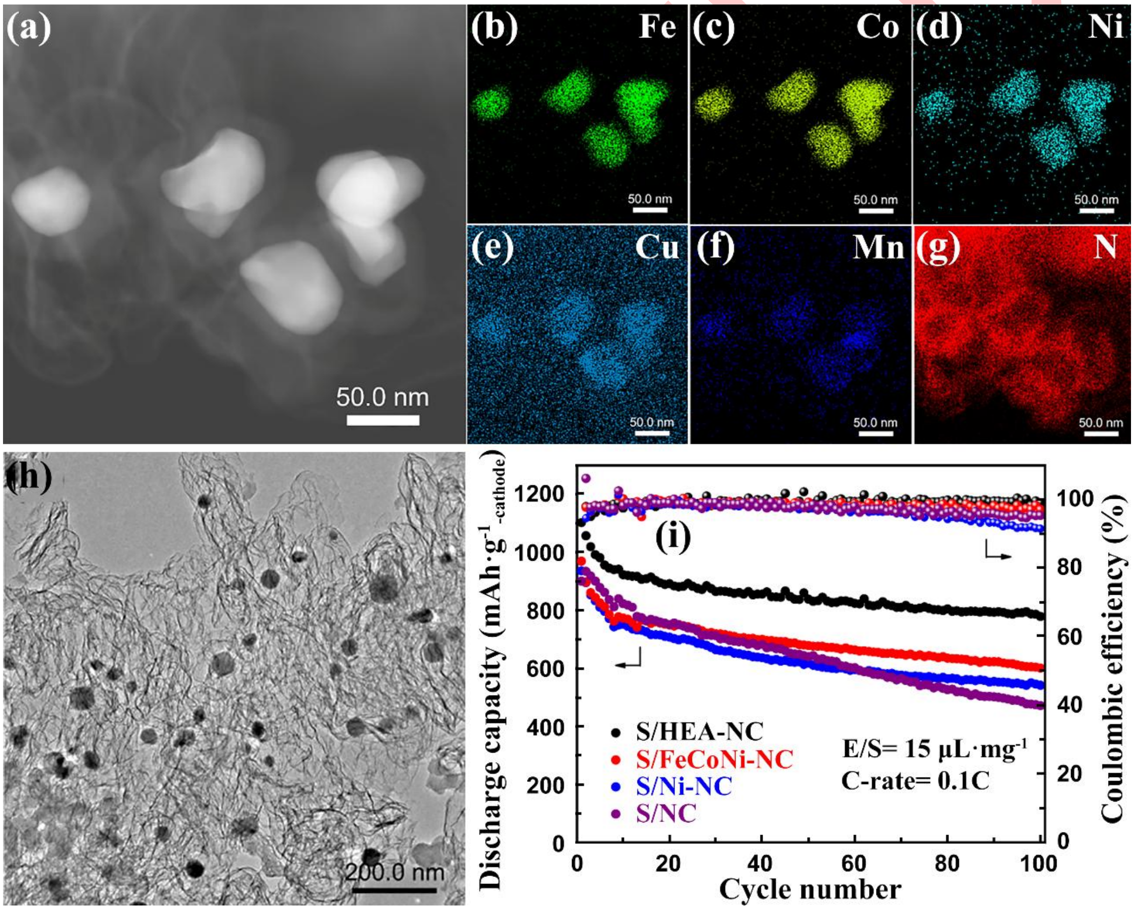

Fig. 9 (a–h) STEM image, corresponding EDS mappings and TEM image of the HEA–NC. (i) Cycle performance of the S/HEA–NC cathode. (a–i) Reprinted from Wang Z, Ge H, Liu S, et al., *Energy Environ Mater*, 2022, Copyright 2022, with permission from Wiley-VCH Verlag GmbH & Co. KGaA[74].

4. Conclusions and future outlook

Li–S batteries, constructed with sulfur element as the cathodic active material and lithium metal as the anode, possess high theoretical energy density of 2600 Wh·kg^{-1}, which are recognized as one of the most promising next-generation power source systems. In the past decades, researches for electrochemical mechanism and performances of Li–S batteries have witnessed tremendous progresses. However, controlled by the intrinsic multistep solid–liquid–solid phase transformation, their application and commercialization are still knotty. On the one hand, the electron/ion conductivity of sulfur and discharged products is low, and the sluggish electrochemical kinetics leads to low discharge capacity and short cycle life of the battery. On the other hand, uncontrolled dissolution and shuttle of intermediate LiPS in ether-based electrolyte not only seriously reduces the coulombic efficiency of the battery, but also destroys the interfacial stability of lithium metal anode.

Incorporating sulfur with desirable host materials is still an efficient path to circumvent the issues of Li–S batteries. In order to designing and constructing desirable sulfur-hosts, especially, the anchor ability toward sulfur-contained species, electrocatalytic activity and electron/ion conductivity must be systematically taken into consideration. Therein, metal/alloy hosts show good competitive potential. Therefore, this article systematically summarizes mono-metals and alloys as catalytic hosts for the sulfur cathode of high-performance Li–S batteries.

As the desirable catalytic hosts, mono-metals and alloys could not only exhibit inherent high conductivity to decrease the additional interface resistance on sulfur cathodes, but also provide superb adsorption/catalytic activity to drive the catalytic conversion of sulfur-contained species and suppress the notorious shuttle effect of LiPS. Among them, HEAs, possessing atom-level high-disordered construction, could provide a higher electrochemical activity on driving the redox kinetics of sulfur cathodes, especially under the condition of lean electrolyte and high sulfur-loading. Designing and employing high-entropy materials for the construction of catalytic hosts will bring advantages to the performance of Li–S batteries in the future.

Challenges still remain for the future development of Li–S batteries. In order to achieve the high energy density, it is vital to increase the content and loading of active-sulfur as high as possible in the whole sulfur cathode, and simultaneously decrease the electrolyte usage in the battery. In addition to constructing high-performance sulfur cathodes with catalytic hosts, other technology strategies, including functional design and modification toward separators and electrolyte, have been employed to boost the electrochemical activity and suppress the shuttle of LiPS under these harsh conditions. Importantly, Li–S batteries based on DME/DOL electrolyte system involve solid–liquid–solid phase conversion, and electrolyte is not only the medium for ion-transfer, but also the place in which electrochemical reactions occur. Based on this dissolution–deposition reaction mechanism, it is hard to reduce the usage of electrolyte in Li–S batteries. Therefore, using new electrolyte systems and simultaneously combining catalytic sulfur-hosts to finally achieve the accelerated solid–solid or quasi-solid phase conversion of sulfur-contained species may be an effective way to reduce electrolyte usage for high-energy Li–S batteries.

Quasi-solid-state and all-solid-state electrolyte bring new hopes to address the stability of Li–S batteries. By fabricating Li–S batteries based on solid-state electrolyte, the direct conversion from solid elemental sulfur to solid Li_2S could fundamentally avoid the notorious shuttle effect of intermediate LiPS. However, derived from the sluggish redox kinetics and extremely complex interface reactions, the study toward practical quasi/all-solid-state Li–S batteries still have a long way to go. Therefore, catalytic host materials with high electrochemical activity and conductivity are such indispensable for effective and complete conversion of sulfur cathodes in solid-state Li–S batteries. Especially, some alloy hosts could propel the solid–solid conversion of sulfur-contained species in Li–S batteries with liquid-state electrolyte to regulate the nucleation and growth of discharged products and increase the deposition capacity[50,62,74]. Based on the aforementioned discussion toward metal/alloy-based core sulfur-hosts in this review, it could be audaciously anticipated that introducing well-designed catalytic mono-metal or alloy materials to build effective hosts will activate electrochemical performances of the sulfur cathode for solid-state Li–S batteries in the future.

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金属和合金作为锂-硫电池硫正极催化载体

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摘要: 锂-硫电池具有 2600 Wh·kg^{-1} 的理论能量密度，被认为是最具发展潜力的下一代能量存储体系之一. 然而，锂-硫电池的应用严重受制于单质硫和放电产物（Li_2S_2/Li_2S）迟滞的电化学反应动力学以及可溶性多硫化锂中间体的“穿梭效应”，这些问题导致电池的循环稳定性差、硫利用率以及库伦效率低下. 将催化载体引入硫正极可加快锂-硫电池中含硫物种反应速率，进而抑制活性物质溶解流失的一种有效方法.在这篇综述中，简要总结了金属和合金材料作为硫正极核心催化载体的最新研究进展，同时阐明了金属及合金载体对含硫物种的催化转换机理. 最后，对催化载体的构筑以及高能锂-硫电池的发展进行了展望.

关键词：锂-硫电池；金属/合金；催化载体