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REVIEW

Recent Advances of Functional Electrolyte Additives for Lithium-Sulfur Batteries

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Abstract

Lithium-sulfur (Li-S) batteries have become one of the most promising next-generation battery systems due to their high energy density and low cost. However, the application of Li-S batteries still faces critical challenges, such as the low conductivities of S and Li_2S, shuttle effect of polysulfides and dendrite growth of Li, etc. The optimization of the electrolyte can ameliorate the electrolyte|electrode interphase, conveniently regulating the parasitic reaction and improving the performance of the resultant batteries. The functional additives in electrolytes provide chances to tune the interphase and even the redox mechanism to improve the performance of the batteries. In this review, we systematically summarize the latest progresses of additives for Li-S batteries. The additives are classified according to the category that lies on the protection of Li metal anode or the stabilization of S cathode. The functions of additives on the S cathode such as the inhibitions of dissolution and shuttle of the polysulfides, the redox mediators, and the activation of Li_2S deposits are discussed in detail. Finally, the prospects of additives for Li-S batteries are supplied in brief. We hope that the review can provide a guidance in the design of electrolyte for high-performance Li-S batteries.

Keywords: Lithium-sulfur batteries; Additives; Shuttle effect; Polysulfides; Electrolyte

1. Introduction

With the depletion of fossil fuels and the growing severity of environmental pollution, it is critical to develop renewable energy to meet the rising energy demand [1]. Because of the high energy density and long cycle life, lithium-ion batteries have dominated the portable energy storage market [2]. However, practical lithium-ion batteries are restricted by the theoretical capacity of electrode materials, and their energy density can no longer be significantly enhanced, falling well short of satisfying the actual needs of technological growth [3]. As a result, it is necessary to develop novel electrochemical energy storage devices with high energy density, low cost, and environmental friendliness. The lithium-sulfur (Li-S) battery, which uses metallic lithium as the anode and elemental sulfur as the cathode, has a high theoretical specific capacity and energy density of 1672 $mAh\cdot g^{-1}$ and 2600 $Wh\cdot kg^{-1}$, respectively. It is much higher than that of typical lithium-ion batteries [4]. Furthermore, sulfur as an abundant, inexpensive, and non-polluting element, also promotes Li-S battery one of the most promising energy storage devices [5].

Li-S batteries still face some critical challenges despite the advantage of high energy density. Firstly, the highly soluble lithium polysulfides (LiPSs) will diffuse from the cathode into the electrolyte under the concentration gradient, resulting in "shuttle effect" and the loss of active materials [6]. Secondly, the final discharge products, Li_2S_2 and Li_2S, have extremely low solubility in the electrolyte, and it is difficult to be completely electrochemically oxidized back to soluble LiPSs. The low conductivities of elemental S and Li_2S_2/Li_2S also reduce the utilization of active materials [7]. In addition, there is a large density difference between S and the discharge product Li_2S. The severe volume expansion (ca. 80%) could affect the integrity and stability of the cathode material [8].

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Finally, highly reactive lithium metal easily reacts with electrolyte to generate unstable solid-electrolyte interphase (SEI), resulting in continuous electrolyte loss, and the shuttled LiPSs will further aggravate interfacial side reactions [9]. Furthermore, uneven lithium deposition can lead to the dendrite growth of lithium, which may penetrate the separator and cause a short circuit, reducing the safety of battery [10].

In response to the above problems, many strategies have been proposed to improve the performance of Li-S batteries. Designing host materials for S species can improve the conductivity of the S cathode and adsorb the polysulfides, such as various C/S composite structures [11], functional inorganic compounds [12] or heterojunction doping [13] etc. Functional separator can hinder the shuttle effect by the adsorption or the size effect of nano-sized channels such as the metal organic frameworks (MOFs) [14]. Some artificial interphase [15] and three-dimensional design [16] of the Li metal anode can regulate plating/stripping behaviors of Li and improve the reversibility of the Li-S batteries. The electrolyte optimization and improvement, in addition to electrode materials and separator, is a convenient way to improve the performance of Li-S batteries. The electrolyte is not only capable of transporting Li^+ but also can provide the high solubility for polysulfides, promoting the electrochemical reaction process of the S cathode [17]. Moreover, the electrolyte also has a crucial impact on the safety, cycling stability, and wide-temperature performance of the battery [18].

Compared to regulating electrolyte solvents and salts or the development of new electrolytes, introducing additives is a more economical, convenient and efficient way to improve the battery performance. A small amount of electrolyte additives may significantly change the property of electrolyte (typically a concentration of less than 10%), and slightly increase the cost of the battery [19]. Apart from effectively improving the physicochemical behaviors of the electrolyte, additives can also relieve the shuttle effect of LiPSs, reduce the activation energy of Li_2S oxidation, accelerate the reaction kinetics, and protect the Li metal anode [20]. At present, the main additives include organic molecules, inorganic compounds, ionic liquids, and salts etc.

In this review, the latest research progress of electrolyte additives for Li-S batteries is summarized and categorized. The work principle, advantages and disadvantages of various additives are discussed based on their functionality. Meanwhile, the impact of additives on the overall performance of batteries is analyzed. Finally, prospects about further development and application for additives of Li-S batteries are discussed to provide reference for the design and development of Li-S batteries in the future.

2. Additives for protection of lithium anode

Li metal anode faces both the severe issues originated from the dendrite growth and the parasitic reaction with the soluble LiPSs. Solid Li_2S and Li_2S_2 are generated when LiPSs shuttle to the anode and are reduced by metallic Li, resulting in the loss of active sulfur species and irreversible Li consumption [21]. The heterogeneous SEI layer formed on Li surface would obstruct Li^+ ion diffusion, result in nonuniform ionic flux and uncontrollable Li dendritic growth, and eventually cause the poor cycle performance and safety risks [21]. Therefore, it is required to mitigate the interfacial reaction between LiPSs and Li, and the uneven Li deposition, which can be effectively achieved by the interface engineering. In this section we summarize the corresponding strategies based on the *in situ* facile construction of functional SEI via electrolyte additives.

2.1. Nitrate additives

Metal nitrate additives have brought a breakthrough in the development of Li-S batteries. In addition to the most widely adopted $LiNO_3$, other cation nitrates, such as $CsNO_3$, KNO_3, $ZrO(NO_3)_2$, $LaNO_3$ and $NaNO_3$, have also been developed successively. $LiNO_3$, first proposed by Aurbach, has been proven to be the most effective additive for stabilization of Li plating [22]. The NO_3^- anion can be reduced by metallic Li to generate a stable LiN_xO_y-containing SEI, which can protect the Li metal anode and suppress the shuttle effect of LiPSs. As shown in Fig. 1a, Hong et al. demonstrated that the SEI layer, consisting of inorganic species (LiN_xO_y) and organic species (ROLi and $ROCO_2Li$, R represents the alkyl groups), can induce uniform Li deposition as well as prevent the parasitic reaction between Li anode and LiPSs or electrolyte [23]. Brezesinski et al. found that the CH_4 and H_2 evolution resulting from the slight decomposition of ether solvents, could be noticeably suppressed because of the stable SEI, although the electrolyte with $LiNO_3$ facilitates a small amount of N_2 and N_2O [24].

Zhang et al. further discovered that $LiNO_3$ also has synergistic interaction with the S cathode [25]. They reported that NO_3^- can boost a complete conversion of polysulfide to elemental S at the end of charge, improving the utilization of S

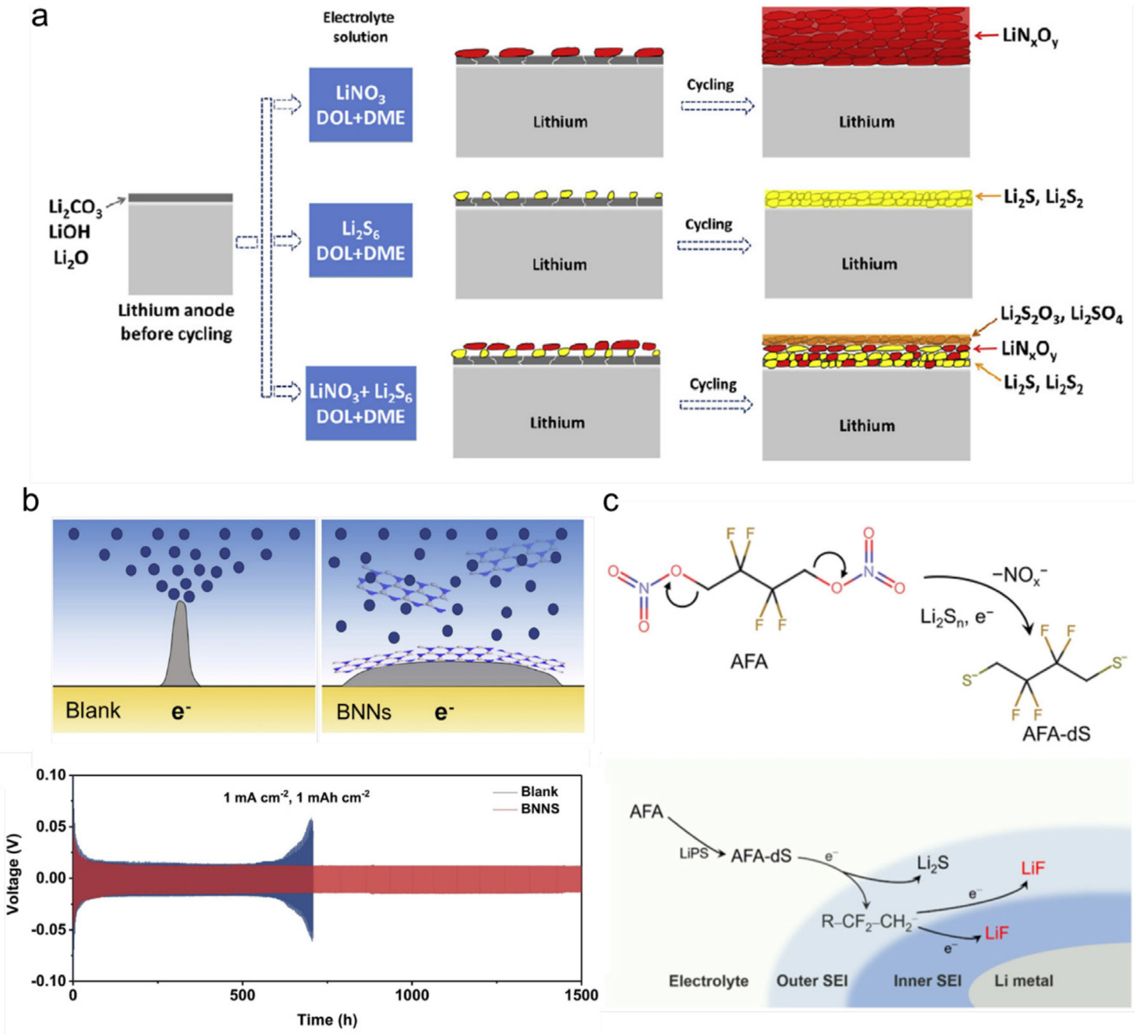

Fig. 1. (a) Scheme of the surface components for the Li metal anode in different electrolytes [23]. Reproduced with permission of Ref. [23], copyright 2014 Elsevier. (b) Illustration of Li deposition regulated by BNNs and the corresponding voltage profiles of the Li-Li symmetric cells cycled in electrolytes with and without BNNs [34]. Reproduced with permission of Ref. [34], copyright 2020 Elsevier. (c) Activation mechanism of polysulfides by the AFA additive during the first discharge process and the reaction mechanism for formation of the fluorinated SEI [35]. Reproduced with permission of Ref. [35], copyright 2022 Wiley-VCH.

cathode. With the presences of dissolved polysulfides and $LiNO_3$ additive in electrolyte, a multi-layered stable SEI can be formed. The inner layer is obtained from the direct reduction reaction of them with Li metal mainly consisting of Li_2S, Li_2S_2, and LiN_xO_y. Meanwhile, the surface layer contains Li_2SO_4 and $Li_2S_2O_3$ species from the oxidation of polysulfides by $LiNO_3$. In addition to the catalysis and film-forming effect, the self-discharge of Li-S battery can also be relieved by the addition of $LiNO_3$ [26]. Beside the function of NO_3^- anion, the role of cations in nitrate has also been explored. Lai et al. indicated that the $ZrO(NO_3)_2$ electrolyte has a strong repulsion to polysulfides via its negatively charged states due to the coordination between the ZrO^{2+} and anions, which can effectively prevent the dissolution and diffusion of polysulfides [27]. For the other aspects, the strong affinity between ZrO^{2+} and S also can promote the reaction from polysulfides to element S. Jia et al. verified that the growth of Li dendrites can be effective delayed by the electrostatic attraction of K^+ cations from the KNO_3 additive, which gather and surround the Li dendrites surface [28]. Similar approaches by regulating the deposition behavior of Li and by electrostatic shielding mechanism of cations are also reflected in other nitrates such as $CsNO_3$ [29] and $NaNO_3$ [28]. Liu [30] and Jin [31] et al. designed an *in situ* formed protection film on the surfaces of both Li and S electrodes by introducing $La(NO_3)_2$ additive, which can exist as lanthanum sulfides, to facilitate a smooth Li deposition and a chemical adsorption of LiPSs.

2.2. N-containing molecular additives

The N-containing SEI is an effective interfacial layer for protecting Li metal anodes, which is generally constructed by N-containing compounds. Baloch et al. adopted azido-trimethylsilane $(CH_3)_3SiN_3$ as an electrolyte additive in Li-S battery to form the protective interphase with the exceptionally high Li-ion conductivity and high-molar-volume Li_3N on metallic Li, which has similar passivation effect to $LiNO_3$ but a more controllable thickness [32]. Eshetu et al. directly used lithium azide (LiN_3) additive for all-solid-state Li-S batteries, and the result showed that the SEI formed by LiN_3 has uniform and compact surface morphology, avoiding the dendrite growth and LiPSs corrosion [33]. Compared with the $LiNO_3$, the SEI in the presence of LiN_3 additive is richer in Li_3N, leading to a higher ionic conductivity and thus lower overpotential in the plating process. Then, Wu et al. reported an additive of boron nitride nanosheet (BNNs), one of the graphene analogs with chemically inert and high modulus feature, which can mechanically and continuously flatten Li deposits and accommodate volume changes of Li metal anode during cycling [34]. Moreover, BNNs with the Lewis acid sites of B can trap anions in electrolyte, leading to uniform Li^+ flux on Li surface to guarantee a dendrite-free Li metal anode (Fig. 1b). As a result, the Li|Li symmetric cell with BNNs achieves a long cycle stability of 1500 h under the conditions of 1 $mA\cdot cm^{-2}$ and 1 $mAh\cdot cm^{-2}$. Even in a deep plating/stripping capacity of 35 $mAh\cdot cm^{-2}$, the symmetric cell also displays an excellent lifespan up to 400 h.

Besides inorganic nitrides, organic N-containing compounds can also build a stable and effective SEI layer. Zhang and coworkers designed a novel N-containing fluorinated molecule, 2,2,3,3-tetraflurobutane-1,4-diol dinitrate (AFA), as an additive to construct a fluorinated SEI on Li metal anodes [35]. AFA molecule, $-NO_3$ acts as an active ending group on each β-site of fluoroalkyl chain, has strong leaving tendency in electrochemical reduction process. The leaving of β-site group facilitates defluorination of the C—F bond and then generates abundant LiF component, which has been regarded as a promising interphase that benefits transport of Li^+ in SEI and uniform plating/stripping of Li. In addition, $-NO_3$ in AFA serves as another effective additive composition that can replace $LiNO_3$ in general electrolyte and further enhances the stability of SEI (Fig. 1c). Besides, our research group used nitrogen-rich azoles including triazole (Ta) and tetrazole (Tta) as multifunctional additives to enhance the cycling performances of Li-S and Li-organosulfide batteries [36]. The azoles boost a dendrite-free morphology of the Li anode because of the increased Li transference number. Moreover, azoles molecule can alleviate the shuttle effect via the formation of Li bonds between nitrogen-containing heterocycles and LiPSs, which will be carefully discussed hereafter.

2.3. Sulfides additives

Sulfides and related S-containing compounds are another important member of the additive group for Li-S battery. Lithium polysulfides Li_2S_n ($4 \leq n \leq 8$) as functional additives can reduce the dissolution of active sulfur through the common ion effect, and compensate for the loss of active sulfur in electrolytes, thereby, improving the specific capacity of Li-S batteries. It is noteworthy that Li_2S_n can also form a relatively stable SEI layer mainly composed of insulating Li_2S and Li_2S_2. The synergistic effect of SEI with Li_2S_n and LiN_xO_y promotes the smooth and compact plating of Li. Zhang et al. illustrated that a compact SEI layer is formed with the help of LiTFSI-$LiNO_3$-Li_2S_5, which can render the dendrite-free anode and improve Coulombic efficiencies [37]. As illustrated in Fig. 2a, the similar effect also exists with other LiPSs additives like Li_2S_8 [38] and Li_2S_6 [39]. But the amount of LiPSs needs to be carefully controlled because the high concentration of polysulfides in organic electrolyte will lead to the increases of viscosity and impedance. It is also reported carbon disulfide (CS_2) as an accessory SEI-formed additive combined with $LiNO_3$ facilitates a thiosulfate-containing protective layer on Li anode [40]. The resultant Li-S cell exhibits high Coulombic efficiency (>99%) and a capacity retention of 88% over 300 cycles.

Compared with simple inorganic sulfides, organic sulfides have more obvious stabilizing effect on SEI layer. Kim et al. discovered that alpha-lipoic acid (ALA) can produce stable passivation layer on Li anode as well as a polymer-based protective layer on the cathode surface, which effectively prevents its side reaction with metallic Li and the dissolution of LiPSs [41]. Then, Wang et al. reported an *in situ* formed robust SEI with a high S-containing polymers poly (sulfur-random-triallylamine) (PST) additive through co-deposition of organosulfides, Li_2S_n and LiTFSI salt (Fig. 2b) [42]. The S-containing components (organosulfide/organopolysulfide) act as “plasticizer” in the

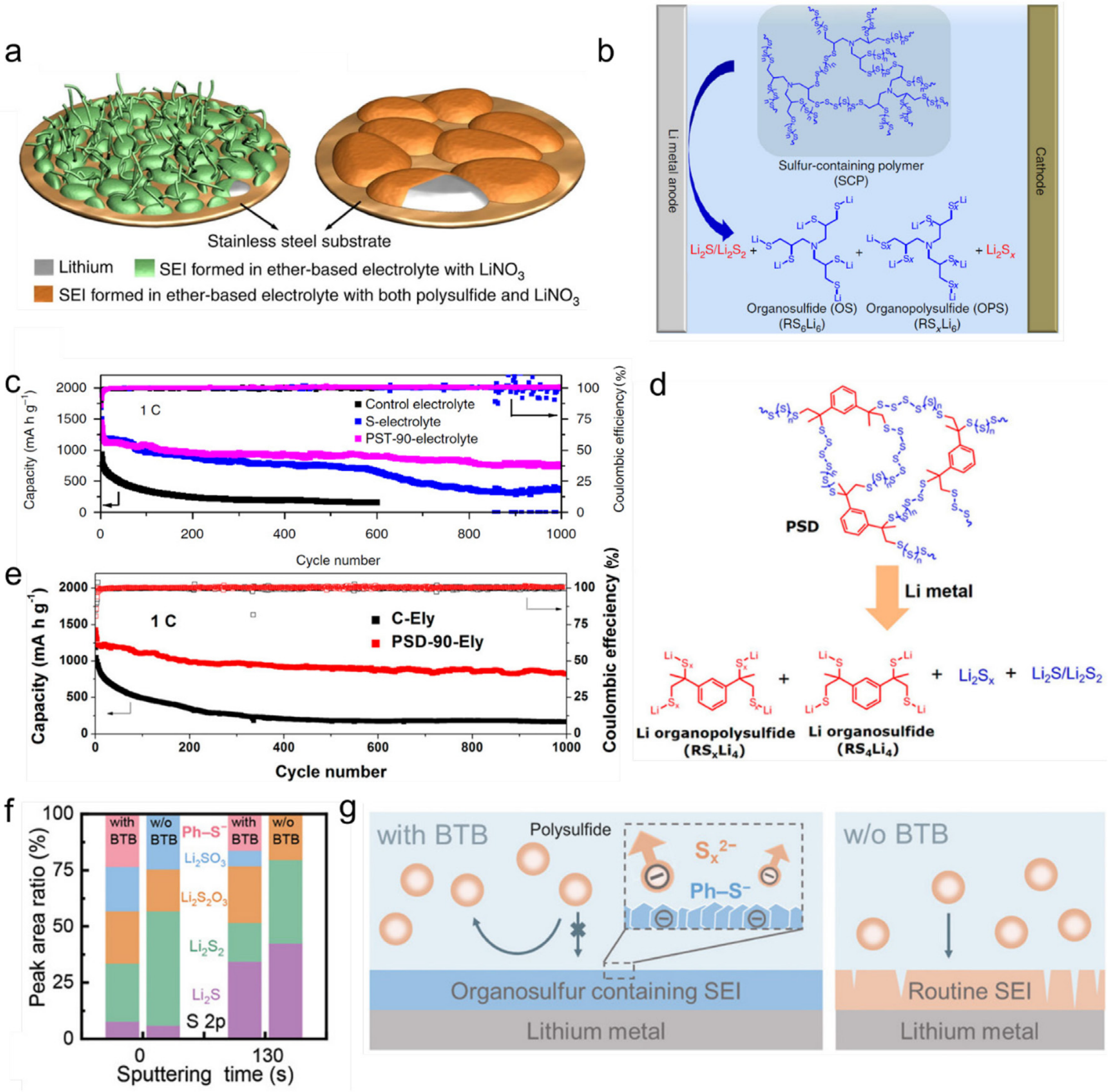

Fig. 2. (a) Schematic showing the morphologies of Li deposited on the substrate in different electrolytes [38]. Reproduced with permission of Ref. [38], copyright 2015 Springer Nature. (b) Schematic illustration of formation of the stable inorganic/organic hybrid SEI layer with SCP and (c) the corresponding electrochemical performances of Li-S cells [42]. Reproduced with permission of Ref. [42], copyright 2017 Springer Nature. (d) Mechanism of the spontaneous formation of the hybrid SEI layer and (e) cycling performance of the Li-S cells with PSD [43]. Reproduced with permission of Ref. [43], copyright 2018 American Chemical Society. (f) The peak area ratio of the X-ray photoelectron spectroscopic (XPS) spectra for sulfur-containing components in the SEI formed with and without BTB additives after different sputtering time. (g) The schematics of the formation and the function of SEIs in electrolytes with and without BTB [45]. Reproduced with permission of Ref. [45], copyright 2020 Wiley-VCH.

inorganic phase (Li_2S/Li_2S_2) to make the SEI layer more flexible and tougher, which is capable of accommodating the large volume change and suppressing the Li dendrites for Li anode. As illustrated in Fig. 2c, the Coulombic efficiency of 99% over 400 cycles of Li plating/stripping was achieved and a 1000-time cycle life with good capacity retention of Li-S battery was obtained based on this additive. Lately, as exhibited in Fig. 2d, Wang et al. proposed another approach to fabricate a stable hybrid SEI layer with a new organosulfide-based polymer poly (sulfur-random-1,3-diisopropenylbenzene) (PSD) [43]. The aromatic-based organic components with planar backbone conformation and π-π interaction promote uniform Li deposition and flexible interface formation. The co-deposition of inorganic Li salts and Li_2S/Li_2S_2 on anode, provides necessary Li^+ transport pathways and mechanical hardness. The Li-S battery exhibits an initial capacity of 1427 $mAh\cdot g^{-1}$ and relatively steady cycling performance with the capacity of 817 $mAh\cdot g^{-1}$ after 1000 cycles, corresponding to a slow capacity decay and a high Coulombic efficiency of ca. 99.9% (Fig. 2e).

Recently, molecular organosulfides are also used as the additives in Li-S batteries due to their excellent film-forming ability. Gewirth et al. proposed a kind of thiol-based additives, biphenyl-4,4′-dithiol (BPD), to bring a smooth and thin SEI/Li entangled phase, enhancing the performance of Li-S batteries [44]. Huang et al. introduced 3,5-bis(trifluoromethyl) thiophenol (BTB) as an additive for optimization of the SEI components [45]. Through verifying the composition of this SEI by XPS, they found that the electrolyte with BTB can generate the SEI layer containing more organosulfide components, which origins from the reaction between BTB and the Li metal (Fig. 2f). The resultant PhS^- anions can repel LiPSs via electrostatic repulsion, decreasing the continuous side reactions between LiPSs and fresh Li, and significant weakening the depletion of electrolyte. In contrast, the SEI formed in the controlled electrolyte mainly consists of inorganic sulfites, thiosulfates, and Li sulfides, causing continuously decomposition reactions of active material and Li, and the corrosion of the Li anode and rapid failure of the battery (Fig. 2g).

Based on the excellent action of organosulfide, our group has successively designed organic thiol-based molecules as additives, such as 1,4-benzenedithiols (1,4-BDT) [46], 1,3,5-benzenetrithiol (BTT) [47] and benzoselenol (PhSeH) [48], for Li-S batteries and achieved outstanding results. The 1,4-BDT in the electrolyte increases the Young's modulus of the SEI from 774 to 2556 MPa, and thus the robust SEI layer is able to suppress the growth of Li dendrites. The SEI layer is thinner (31.5 μm) than that in ordinary Li-S battery (41.4 μm), which is beneficial to the migration of Li^+ at the electrolyte/electrode interphase. Analogously, the BTT containing three thiol groups reacts with Li metal to form a lithiated 1,3,5-BTT layer, possessing the self-healing ability like the "skin" on the Li metal anode, and thus enabling a fast Li^+ conductivity and uniform Li deposition. In addition, it is worth noting that these thiol-based molecules also have a greater impact on the sulfur cathode, and the relevant details will be discussed in the subsequent part.

2.4. Halide-based additives

Not only sulfides, halides also can help to reinforce the *in situ* formed SEI, the representatives of which are various metal halides (MX, M = In, Li; X = Br, Cl, I). Liu et al. employed LiI as an additive in Li-S batteries for smooth Li deposition, because the additive could induce the polymerization of ether-based electrolyte and form an elastic polymer interphase [49]. Moreover, the LiI component in electrolyte, enhances the Li^+ migration in SEI layer, forming a net-like porous structured interphase on the surface of metallic Li. The Li|Li symmetrical cell with LiI-added electrolyte displays a long-term cycling stability of 2000 h with a small hysteresis voltage of 57 mV at 0.5 $mA\cdot cm^{-2}$. Jiang et al. chose indium (III) iodide (InI_3) as a bifunctional additive for Li-S batteries to improve the performance of the Li anode and S cathode [50]. The indium (In) in InI_3 will preferentially be electrodeposited on Li metal during the initial charging process, resulting in a passivation alloy layer to prevent the anode from corrosion by LiPSs. The same effect can be obtained in SnO_2/Li_2S full battery with InI_3 additive [51]. Thus, in terms of optimizing composition of the SEI, LiF [52], LiCl [53], and LiBr [54] species are all considered as stable SEI components, commonly generated through chemical or electrochemical reactions between Li metal and halide-containing additives. For instance, Archer et al. have reported that $SiCl_4$ was adopted as an additive to form an organic/inorganic hybrid SEI composed of Si-interlinked −OOCOR organic oligomer film [55]. LiCl is also formed in the SEI (Fig. 3a). This SEI exhibits lower charge-transfer resistance and thus faster electrodeposition kinetics of alkali metals, which has been confirmed to enable good performance of the Li-S and Li-$Li_4Ti_5O_{12}$ batteries.

Lately, it is found that thionyl chloride ($SOCl_2$) can react with Li metal, *in situ* constructing a stable LiCl-rich SEI layer to prevent the dendrite growth and hinder the direct contact between the electrolyte and Li metal [56]. The Li-S battery with $SOCl_2$ additive presents an ultrahigh initial discharge capacity and a high reversible capacity of 1021 $mAh\cdot g^{-1}$ after 500 cycles. Besides, the extra active S can be generated by decomposition of $SOCl_2$, compensate the loss of origin S cathode and contribute to improving the active capacity. Then, Tu et al. *in situ* constructed a highly Li^+ conductive SEI with a mosaic-like and dendrite-free morphology via the additive of tetrapotassiumheptaiodobismuthate (K_4BiI_7), and the modified electrolyte with the K_4BiI_7 improved electrochemical performance in Li-Li, Li-Cu as well as Li-S battery [57]. The Li plating/stripping process still maintains a stable and low voltage hysteresis over 800 h under the conditions of 5.0 $mA\cdot cm^{-2}$ and 5.0 $mAh\cdot cm^{-2}$.

2.5. Other additives for lithium anode protection

Nitrofullerene (Nitro-C_{60}) is employed as a bifunctional additive with a smoothing and stable effect on Li metal anodes [58]. Insoluble C_{60} can fill in the Li pits to make it smoother, leading to a

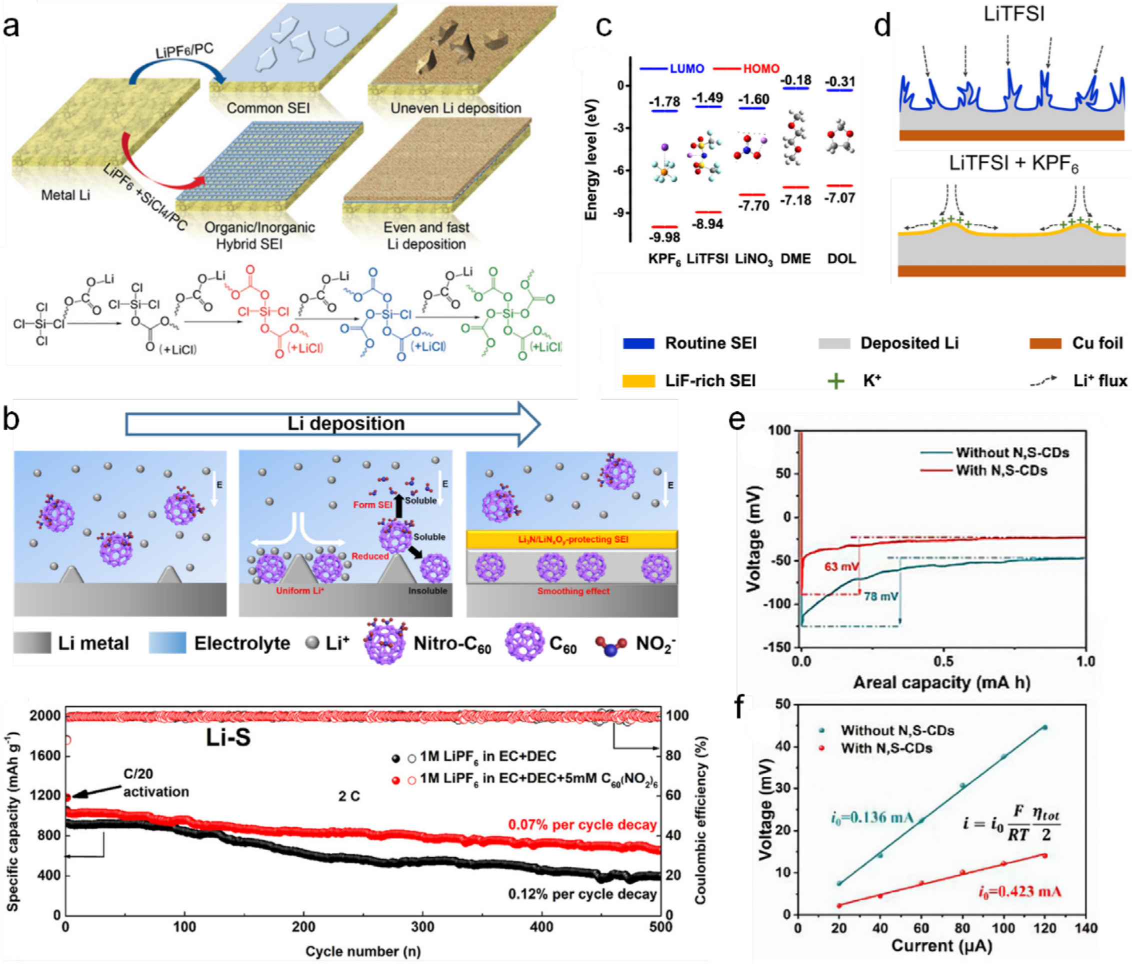

Fig. 3. (a) The reaction mechanism for the formation process of $SiCl_4$ cross-linked hybrid SEI and the corresponding deposition scheme of Li [55]. Reproduced with permission of Ref. [55], copyright 2017 Wiley-VCH. (b) The scheme showing the effects on Li deposition and the cycling performance of Li-S batteries at 2 C with and without nitro-C60 [58]. Reproduced with permission of Ref. [58], copyright 2019 American Chemical Society. (c) Molecular orbital energies of the different solutes and solvents as well as the schematic illustration (d) of Li plating process in electrolytes with and without KPF_6 [59]. Reproduced with permission of Ref. [59], copyright 2020 American Chemical Society. (e) The initial voltage profile of Li deposition process of the Li|Cu half cell and (f) the overpotential as a function of the current for the Li|Li symmetric cell with and without N,S-CDs additives [62]. Reproduced with permission of Ref. [62], copyright 2021 Elsevier.

uniform distribution of the Li^+ flux. The NO_2^- anions further react with Li metal forming a compact and robust SEI with high ion transport. With 5 $mmol \cdot L^{-1}$ nitro-C_{60} additives, the Li-Li symmetric cells display stable voltage profiles in both carbonate and ether electrolytes, and the Li-S battery presents an improved capacity retention of 63.2% over 100 cycles under a high S loading of 10.6 $mg \cdot cm^{-2}$ (Fig. 3b). Then, Tu et al. proposed 0.01 $mol \cdot L^{-1}$ potassium hexafluorophosphate (KPF_6) in ether electrolyte to improve the performance of Li metal anode [59]. Due to the lower LUMO energy level of PF_6^- than $TFSI^-$ anion (Fig. 3c), the former will give priority to reduction and decomposition on Li and a trace amount of KPF_6 enables a LiF-rich SEI. Moreover, the electrostatic shield of K^+ causes the self-healing effect to stabilize the interphase and mitigate the tip effect of Li deposition (Fig. 3d), enabling an enhanced capacity retention with only 0.25% decay per cycle for the Li-S full cell.

Carbon Quantum Dots (CQDs) have numerous advantages, including superior physical and chemical properties, environmental friendliness and low cost, and have promising applications in analytical chemistry, catalytic chemistry, and energy storage fields. Recently, CQDs have emerged as a functional additive for stabilizing Li metal anodes [60]. Xiong et al. introduced graphene quantum dots (GQDs) into the electrolyte, which have average lateral size of ca. 2 nm and thickness of 1—3 layers, serving as the heterogeneous seeds for the uniform Li nucleation [61]. Moreover, enriched GQDs on Li metal surface can regulate a uniform electric field and Li^+ flux, causing a dendrite-free anode. So that the Li-Li symmetrical cell exhibits stable cycling performance with the GQDs-added electrolyte for more than 500 h with a lower overpotential of only 20 mV at both 3 mA·cm^{-2} and 3 mAh·cm^{-2}. The Li-S battery using the GQDs modified electrolyte displays the Coulombic efficiency of 99% over 200 cycles under a high S loading of 4 mg·cm^{-2}. After that, Ji et al. employed nitrogen, sulfur-codoped carbon dots (N,S-CDs) as additives to regulate homogeneous deposition of Li^{+} ion [62]. N,S-CDs with numerous lithiophilic sites can be adsorbed surrounding Li^{+} ions on their surface by the ultrahigh Li adsorption energy, resulting in a homogeneous and dense Li deposition. As illustrated in Fig. 3e and f, the Li anode in electrolyte with N,S-CDs shows a lower initial nucleation overpotential of 63 mV and a higher exchange current density. It suggests that N,S-CDs can act as nucleation sites for Li and significantly reduce the energy barriers of nucleation process in Li|Cu half cell, and the presence of N,S-CDs is also beneficial for charge transfer in Li|Li symmetric cell. Therefore, with 0.3 mg·mL^{-1} N,S-CDs in electrolyte, the Li|Cu half cells achieve stable Coulombic efficiency more than 200 cycles at 0.5 mA·cm^{-2}, and the Li|Li symmetric cell exhibits long-term cycling performance over 1200 h at 1.0 mA·cm^{-2} and 1.0 mAh·cm^{-2}.

3. Additives for stabilization of sulfur cathode

In comparison to the Li anode, there are more comprehensive studies on functional additives for the S cathode. The additives may affect the conversion process, and thus the thermodynamics and kinetics of the S cathode in Li-S batteries. Thus, it is of decisive significance, in terms of introducing additives, to improve the overall performance of the battery through interaction between additives and sulfur species. Some representative functions of the additives for S cathode can be mainly categorized into redox mediation, kinetic acceleration, inhibitions of the dissolution and shuttle of polysulfides, as well as improvement of the utilization of sulfur species.

3.1. Inhibitions of the dissolution and shuttle of polysulfides

Dissolution and diffusion of polysulfides are the critical challenges for Li-S batteries. Many strategies have been proposed to address this issue [63]. Zhuo et al. found that CS_2 not only can form stable SEI on Li metal anode, but also can suppress the diffusion of long-chain polysulfides by generation of complexes with polysulfides and passivate electrode surfaces by the formation of thiosulfate-containing protective layers [40]. Moreover, insulated "dead" S in cathode could be partially activated by CS_2 through its strong solubility to the elemental S. As shown in Fig. 4a, the pyrrole (Py) additive is proposed to form a polypyrrole protective layer on cathode through electrochemical oxidative polymerization during cycling, which not only acts as an effective conductive agent to promote electron conduction but also an adsorbing agent and a barrier layer to inhibit the migration of LiPSs [64]. In addition, triphenylphosphine (TPP) was reported to spontaneously react with S_8 and sulfides species, and *in situ* produce a triphenylphosphine sulfide (TPS) wrapped layer on the surface of C/S (or C/S@PAN) particles (Fig. 4b) [65]. By addition of 2 wt% TPP in electrolyte, the CMK-3/S@PANS@TPS complex cathode shows the reversible capacities of 698 and 598 mAh·g^{-1} during 1000 cycles at 1 C and 2 C, respectively. Similar effects also exist in the electrolyte with LiBr additive as illustrated in Fig. 4c. During pre-cycling of S cathode at high potential, Br^{-} anion in LiBr will be oxidized, accompanied by the decomposition of 1,2-dimethoxyethane (DME) and subsequent formation of DME (-H) radicals. The polymerized protective layer on S cathode is formed through polymerization of two DME (-H) (triplet) radicals into a singlet oligomer, which effectively inhibits the dissolution of polysulfides [54].

Another strategy to effectively suppress the shuttle effect is to reduce the generation and accumulation of soluble polysulfides, mainly through the reaction of additives with polysulfides to produce insoluble solid intermediates. Following this strategy, Goodenough et al. found that the soluble lithium polysulfides could react with bis(4-nitrophenyl) carbonate (BNC) to generate insoluble polysulfides species and lithium 4-nitrophenolate (LiNPH) as displayed in Fig. 4d and e [66]. Meanwhile, the lithiated LiNPH will react with the Li metal anode and create a dense passivating SEI, which has a high Li^{+} conductivity and lowers the interfacial impedance. It is worth noting that the Li-S battery using the BNC-added electrolyte shows a high Coulombic efficiency of above 99.1% with various sulfur loadings from 1.4 to 6.7 mg·cm^{-2}, and the battery achieves the reversible capacity of 778.7 mAh·g^{-1} over 300 cycles at the rate of 1 C (Fig. 4f and g). Later, Dong et al. found that the reaction between quinhydrone (QH) and Li metal can *in situ* yield a dual-terminal

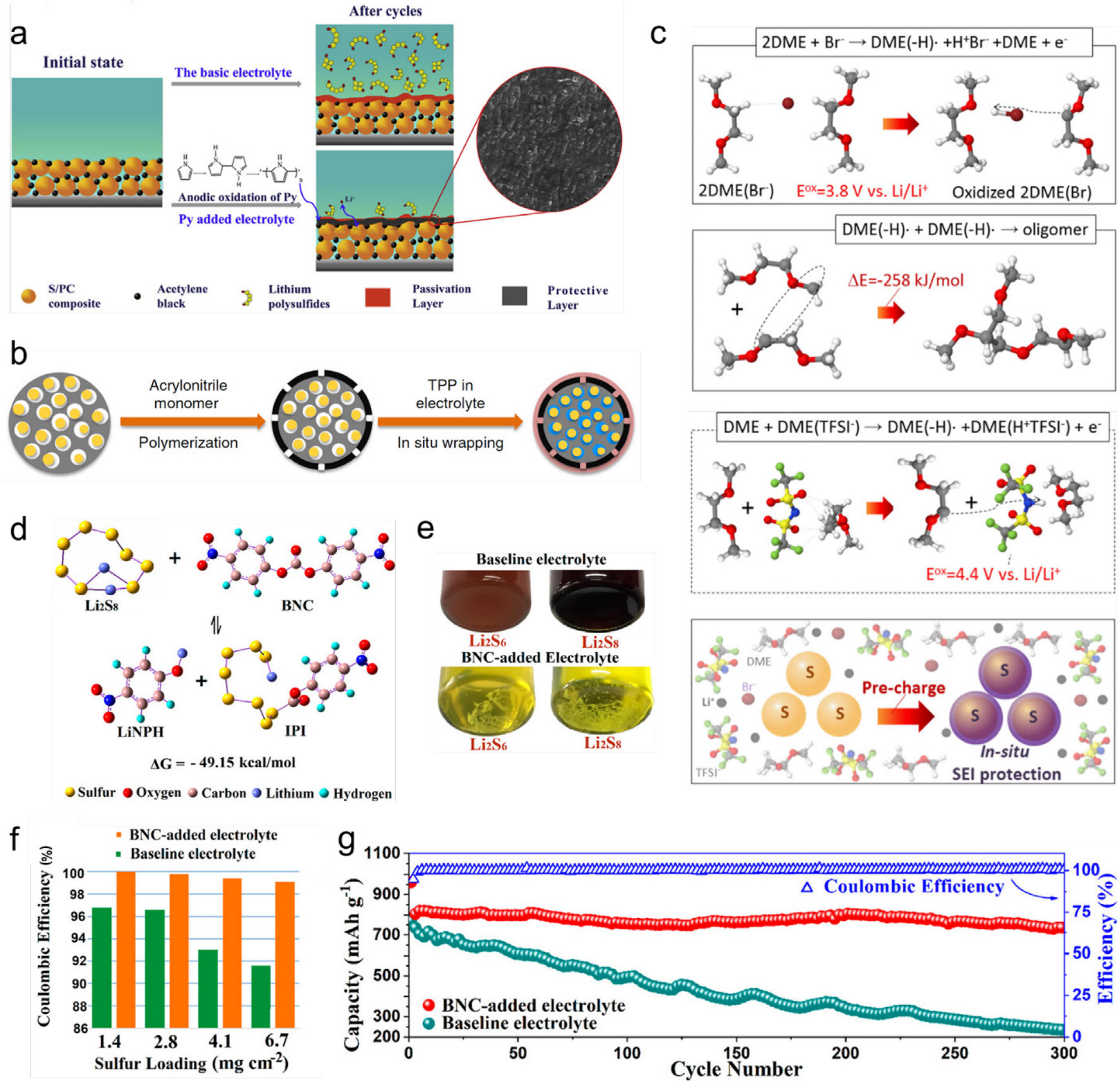

Fig. 4. (a) Schematic illustration of the protective layer on sulfur cathode with the pyrrole additive [64]. Reproduced with permission of Ref. [64], copyright 2017 Elsevier. (b) Schematic illustration of the in situ wrapping process on C-S@PANs particles by TPP [65]. Reproduced with permission of Ref. [65], copyright 2017 Springer Nature. (c) Mechanism inference for the generation of in situ SEI protection on S cathodes with LiBr by calculations of quantum chemistry. The initial step is the electrolyte decomposition due to the electrochemical oxidation of DME with Br^- anion, producing DME (-H)·radicals. Then two DME (-H) radicals polymerize into a singlet oligomer and is coated on the surface of cathode [54]. Reproduced with permission of Ref. [54], copyright 2017 Elsevier. (d) DFT calculations of the interaction between the Li_2S_8 cluster and BNC. (e) Visual comparison of Li_2S_6 and Li_2S_8 with blank and BNC-containing electrolyte. (f) Comparison of the average Coulombic efficiency with different sulfur loadings at 1 C and (g) the long-term cycling performance of the Li-S batteries with different electrolytes [66]. Reproduced with permission of Ref. [66], copyright 2019 American Chemical Society.

coupling functional molecule binder (MB), which is able to anchor soluble polysulfides by reversible chemical coordination and form the solid-state −[MB-Li_2S_n]−complexes (Fig. 5a) [67]. Besides, −[MB-Li_2S_n]− has faster redox conversion kinetics through the copolymerization of bonded polysulfide compared with simple Li_2S_n. The Li-S battery displays a high initial capacity of 1347 mAh·g^{-1} at 0.1 C and an ultrastable long-term performance at 1 C, which has no obvious fade over 400 cycles (Fig. 5b).

As mentioned above, carbon dots (CDs) can be used for the protection of Li anode, and are able to improve the performance of S cathode as well. Lu et al. constructed an electrochemically recoverable protective layer to suppress the dissolved polysulfides by introducing the additive of nitrogen-doped carbon dots (N-CDs) [68]. N-CDs have a high reaction activity with polysulfides and can form an insoluble polysulfide-encapsulating layer at the cathode|electrolyte interphase (Fig. 5c). The strong binding ability with polysulfides derived

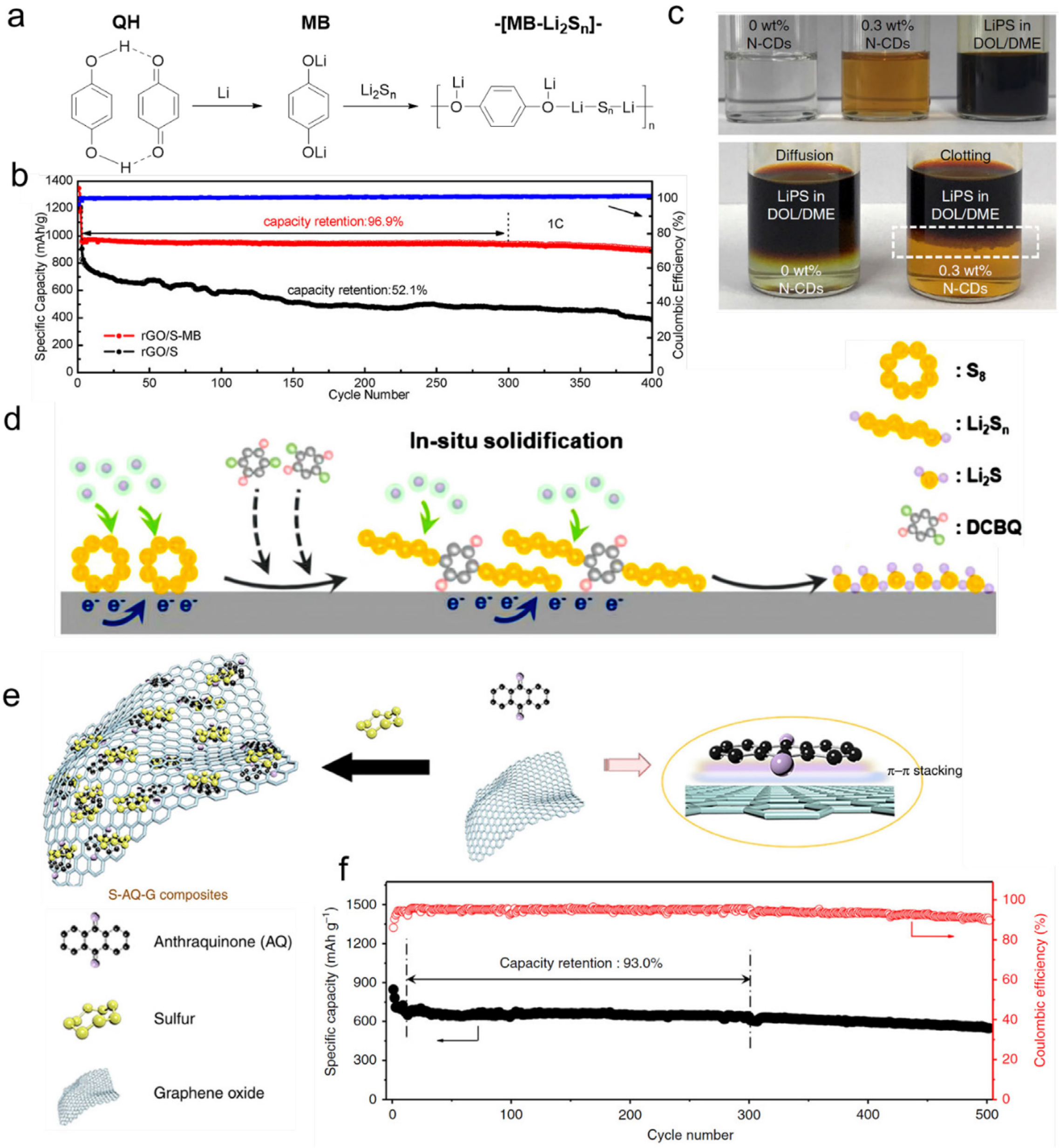

Fig. 5. (a) Formation mechanism of the -[MB-Li_2S_n]- and (b) cycling performance of rGO/S||Li cells with and without MB at 1 C [67]. Reproduced with permission of Ref. [67], copyright 2020 American Chemical Society. (c) The optical photos showing the interaction between LiPSs and electrolyte with and without N-CDs. The white dashed box indicates the formed protective layer at the LiPSs|electrolyte interface [68]. Reproduced with permission of Ref. [68], copyright 2020 Springer Nature. (d) The in situ solidification process of S-DCBQ and the schematic of the following discharge process [69]. Reproduced with permission of Ref. [69], copyright 2021 Elsevier. (e) Schematic illustration of the formation of S-AQ-G composites. (f) The long-term cycling performance of Li-S battery at 0.5 C with AQ [71]. Reproduced with permission of Ref. [71], copyright 2018 Springer Nature.

from the abundant N atoms and oxygen-containing groups on N-CDs, is confirmed by the binding energies in different binding configurations between Li_2S_4 and oxygen-containing groups (mainly $-C{=}O$ on the N-CDs) and pyridinic N (doped at the center/edge of the N-CDs). This optimized approach results in a high sulfur utilization and long cycle performance for Li-S batteries. The reversible capacity of 891 $mAh\cdot g^{-1}$ at 0.5 C with the Coulombic efficiency of 99.5% is achieved.

Quinones with high solubilities and high theoretical capacities, possess advantages of resources and adjustable structures, and have been widely studied as electrode materials in batteries. Li et al. utilized the *in situ* solidification strategy to obstruct polysulfide through nucleophilic substitution reaction between polysulfide and 2,5-dichloro-1,4-

benzoquinone (DCBQ) [69]. The polysulfide with the strong nucleophilicity (Fig. 5d) can react with organic halides and subsequently polymerize to form an insoluble organosulfur polymer (S-DCBQ). Therefore, the solid S species can be confined firmly, and the benzoquinonyl groups in S-DCBQ are capable of accelerating the Li^+ transport as well as facilitating the conversion kinetics. The cell exhibits a capacity retention rate of 92% after 100 cycles, much higher than that of 55% for the cell without DCBQ.

In the study of cathode optimization for Li-S batteries, the direct adsorption and catalysis of polysulfides have been proved to be a mature approach to address the dissolution of polysulfides. This strategy can also be applied in electrolytes by appropriate additives. Villevieille et al. demonstrated the adsorption of SiO_2 for polysulfides by *in situ* X-ray diffraction, which can effectively hinder the shuttle effect [70]. The strategy by introducing fumed silica additives significantly enhances the reversible capacity from 870 to 1080 $mAh\cdot g^{-1}$ of Li-S battery. Benefiting from the advantages of quinones molecules mentioned above, Chen et al. reported an innovative strategy to suppress dissolution and diffusion of LiPSs by enabling redox reactions of organic compounds anthraquinone (AQ) [71]. AQ has a strong Lewis acid-base interaction with LiPSs and can be linked with rGO through π-π stacking to improve the conductivity (Fig. 5e). Furthermore, AQ as small organic molecules can be easily dispersed throughout the whole electrode. Therefore, under S loading of 73% in the composite cathode, the Li-S battery achieves a reversible capacity of 550 $mAh\cdot g^{-1}$ after 500 cycles (Fig. 5f).

Inspired by catalysis for accelerating the reaction rates in cathode, Yu group adopted a biological reagent of dithiothreitol (DTT) as the novel additive to mitigate the shuttle effect [72]. DTT can fast slice the —S—S— bond in polysulfides at room temperature, facilitating the reaction kinetic of conversion from S_8 to Li_2S_2/Li_2S, and thus eliminate accumulation of LiPSs. The Li-S battery with DTT provides a high rate performance and a high capacity retention of 87.5% is achieved with a reversible capacity of 594 $mAh\cdot g^{-1}$after 500 cycles. Lately, Wang et al. used 1,3,5-triformylphloroglucinol (TFP) additive to accelerate the redox kinetics and suppress the dissolved LiPSs through the reaction between TFP and LiPSs, which could *in situ* produce insoluble organopolysulfides instead of simple polysulfides [73]. Furthermore, the aggregated organopolysulfides are able to adsorb untransformed polysulfides and also act as active redox mediators to facilitate the fast conversion of S species. As a result, the Li-S battery with the TFP additive exhibits a higher initial capacity of 1219 $mAh\cdot g^{-1}$ and the capacity retention of 69.7% after 280 cycles at 0.2 C.

In addition to the approaches mentioned above, some new concepts have also been proposed recently. He et al. introduced the glutamate additive, a kind of biomass-based molecules to suppress the shuttle effect [74]. The glutamate can efficiently inhibit the diffusion of LiPSs due to the strong repulsive interaction of negatively charged hydroxyl groups without affecting the transportation of Li^+ ions. Accompanied with discharge process, the appearance of characteristic Raman signals for long-chain polysulfides Li_2S_8 and short-chain polysulfides Li_2S_4/Li_2S_6 suggests that serious shuttle effect occurs in the control electrolyte. In contrast, for the glutamate-containing electrolyte, only Raman peaks of glutamate can be observed, indicating the weakened formation of soluble polysulfides. The capacity retention of 60% after 1000 cycles of the Li-S batteries is achieved with the glutamate-added electrolyte. Then, Zhang et al. innovatively put forward the concept of sulfur container to regulate the polysulfides [75]. They used di (tri)sulfide polyethylene glycol (PES_n) to directly modify the LiPSs in the cathode. PES_n with the grafted (di/tri) sulfide bonds at each side of the polyether chains can reversibly store and release sulfur species by lengthening and shortening the sulfur chains, respectively. The soluble polysulfides in electrolyte are transformed into larger organosulfur species by S container, suppressing the dissolution and migration of polysulfides. Therefore, the initial capacity of the Li-S cells was enhanced from 833 to 1009 $mAh\cdot g^{-1}$ at 0.5 C with PES_n, and a high capacity of 748 $mAh\cdot g^{-1}$ is achieved after 100 cycles.

3.2. Redox mediators

Redox mediators (RMs) play a key role in ameliorating the performance of electrochemical energy storage and conversion systems. When incorporated as electrolyte additives, RMs can serve as the reversible redox couples, accelerating the reaction kinetics and improving the utilization of active species [76]. For the S cathode, the role of redox mediators is mainly reflected in the activation of insoluble sulfur species such as Li_2S_2 and Li_2S. In this case, rational selection of redox mediators has an important impact on the performance improvement of Li-S batteries.

Wang et al. first reported utilizing organosulfides serving as intermediates in Li-S battery to change

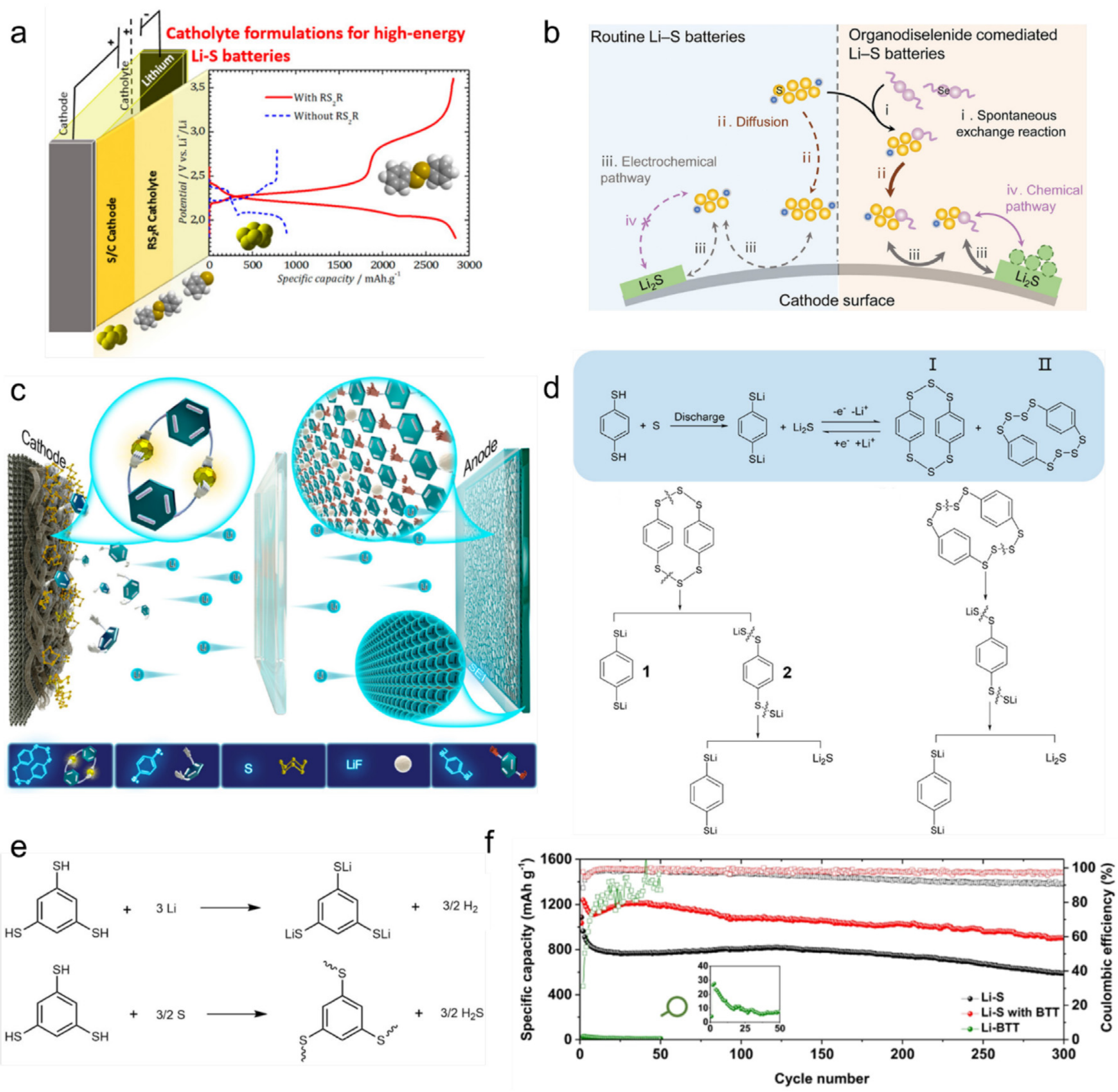

Fig. 6. (a) Schematic of the effect of RS_2R redox mediators on the Li-S cell [78]. Reproduced with permission of Ref. [78], copyright 2017 American Chemical Society. (b) Difference of routine and organodiselenide-comediated reaction pathway for Li-S batteries [80]. Reproduced with permission of Ref. [80], copyright 2021 Wiley-VCH. (c) Schematic diagram and (d) redox mechanism for the Li-S battery with 1,4-BDT [46]. Reproduced with permission of Ref. [46], copyright 2021 American Chemical Society. (e) The pathways of BTT reacting with Li and S. (f) Long-cycling performance of the Li-S cells with and without BTT at 1 C [47]. Reproduced with permission of Ref. [47], copyright 2021 Springer Nature.

the redox pathway of S species [77]. The introduction of dimethyl disulfide (DMDS) in electrolyte reacts with sulfur and generates soluble methyl polysulfide intermediates, improving the electrochemical reversibility of S cathode and supplying the extra capacity. Then, based on the similar molecular structures, Anouti et al. indicated that aromatic organic disulfides also have a beneficial effect on evolution of S species [78]. They used diphenyl disulfides (PhS_2Ph) as the electrolyte additive, which undergo an electrochemical process analogous to that of DMDS, catalyzing the redox reaction between S, Li_2S_n and Li_2S_2/Li_2S directly via an alternative route (Fig. 6a). Moreover, the diversity of R functional group in the R-S_n-R structure enriches the design, regulation, and selection of such additives. According to this design principle, Lai and coworkers studied a series of thiuram-type 'vulcanization accelerators' as electrolyte additives to react with LiPSs, in which dipentamethylenethiuram tetrasulfide (DPTT) achieves the best performance [79]. It can be observed that the color of electrolyte containing LiPSs rapidly faded with the addition of DPTT, indicating that DPTT goes through a rapid and spontaneous reaction with LiPSs, accelerating the transformation of Li_2S_2 and elemental S and thus mitigating the shuttle effect.

Motivated by the similar mechanisms in the electrochemical processes of sulfur and selenium, Huang et al. used diphenyl diselenide (DPDSe) as the redox comediator to modify the polysulfides and promote the kinetics [80]. Fig. 6b indicates that the DPDSe in electrolyte can spontaneously react with LiPSs, generating active lithium phenylseleno polysulfides and participating in the redox reaction process of the S cathode. The as-generated organoselenosulfide intermediator provides a faster redox rate of S species and higher-degree deposition of Li_2S, significantly reducing the overpotential. Hence, the DPDSe additive enables an excellent capacity of 817 $mAh \cdot g^{-1}$ at 2 C and superior cycling performance under finite lithium source for the Li-S battery.

Based on the reports above, it is clear that the introduction of organodisulfides (organodiselenides) is a feasible strategy for the direct chemical regulation in the electrochemical behavior of LiPSs via binding sulfur covalently. In addition, another organosulfur molecule with thiol-groups, organothiols, can effectively improve the performance of the S cathode. The biphenyl-4,4′-dithiol (BPD) was successfully used to enhance the capacity retention of Li-S batteries by Gewirth et al. [44]. They found that the sulfhydryl in thiol has the high reactivity with the S element that can *in situ* form the oligomers with multiple S—S bonds via condensation reactions. Following this view, an additional sulfur reduction process is obtained at 2.1 V with BPD corresponding to the reduction of the combined BPD and short polysulfides, and thus the formation of soluble LiPSs is alleviated.

Recently, the author group introduced different isomeric benzenedithiols (BDT) as the additives [46]. Among them, 1,4-BDT presents the best effect on Li-S battery because of the strong bonding ability with more sulfur atoms. Fig. 6c and d suggests that the thiol groups in 1,4-BDT could react with sulfur and form the intermolecular S—S bond, and produce cyclic organosulfur oligomers, changing the redox pathway of S sulfur and thereby suppressing the formation of LiPSs. In addition, 1,4-BDT can create a compact and robust SEI on the surface of the anode, which has been discussed in the previous section. With this scheme, the Li-Li symmetric cell exhibits an extremely low overpotential of 0.08 V at 5 $mA \cdot cm^{-2}$ for over 300 h. And the Li-S cell also achieves excellent performance, with a high initial capacity of 1548.5 $mAh \cdot g^{-1}$ and a reversible capacity of 909.3 $mAh \cdot g^{-1}$ after 500 cycles at 0.5 C.

Furthermore, the author group introduced another organosulfur of 1,3,5-benzenetrithiol (BTT) as additives in Li-S battery, which can *in situ* construct stable protective layers on both cathode and anode through the reaction of BTT with S and Li respectively (Fig. 6e) [47]. Because of the oligomer/polymer-based cathode electrolyte interphase (CEI) layer covered on the sulfur cathode, the dissolution and diffusion of LiPSs are obviously inhibited. Consequently, the Li-S battery with BTT additives exhibits a capacity of 1239 $mAh \cdot g^{-1}$ and stable cycling for more than 300 times (Fig. 6f).

Following that, the effect of benzeneselenol (PhSeH) additive in Li-S battery is further explored based on the S-Se covalent bonds [48]. Similar to the interaction between DPDSe and LiPSs, the —SeH group in PhSeH will react with S to generate phenyl selenosulfide via breaking the S—S bond and then results in formation of the S—Se bond. With the optimized electrolyte with PhSeH additive, Li-S battery delivers the lower discharge overpotential and high capacity of 1436 $mAh \cdot g^{-1}$ with eximious capacity retention rate of 92.86% after 200 cycles.

3.3. Activation of Li_2S

The S cathode generally suffers from the low utilization mainly due to the insulating nature of Li_2S. The Li_2S particles are electrically isolated and only the ones at the electrode/electrolyte interface can be oxidized. Thus, the oxidation of Li_2S usually experiences a huge overpotential and the limited reaction reversibility leads to a lowered capacity retention. Most importantly, insulating deposits of Li_2S via the dissolution-precipitation route passivate the electrode architecture and thereby aggravate the battery performance. Fortunately, introduction of RMs in the electrolyte alters the original electrochemical oxidation route by chemically oxidation, which can occur at the entire surface of the active materials [81]. The additional charge transfer pathway renders a holistic and complete oxidation of Li_2S with a lower overpotential (Fig. 7a).

In earlier studies, the metallocene has been demonstrated being able to promote the Li_2S oxidation with the reduced charge potential of Li_2S. Aurbach et al. investigated a series of metallocenes as additives for the activation of Li_2S [82]. Among the tested RMs, decamethylferrocene significantly reduces the charging potential of Li_2S oxidation to 2.9 V in an Li/Li_2S cell which is far below the typical potentials (>4 V) in the control electrolyte, enabling the highest reversible capacity in the first activation process.

Recently, Bao et al. used quinone-based compounds as additives to realize efficient and

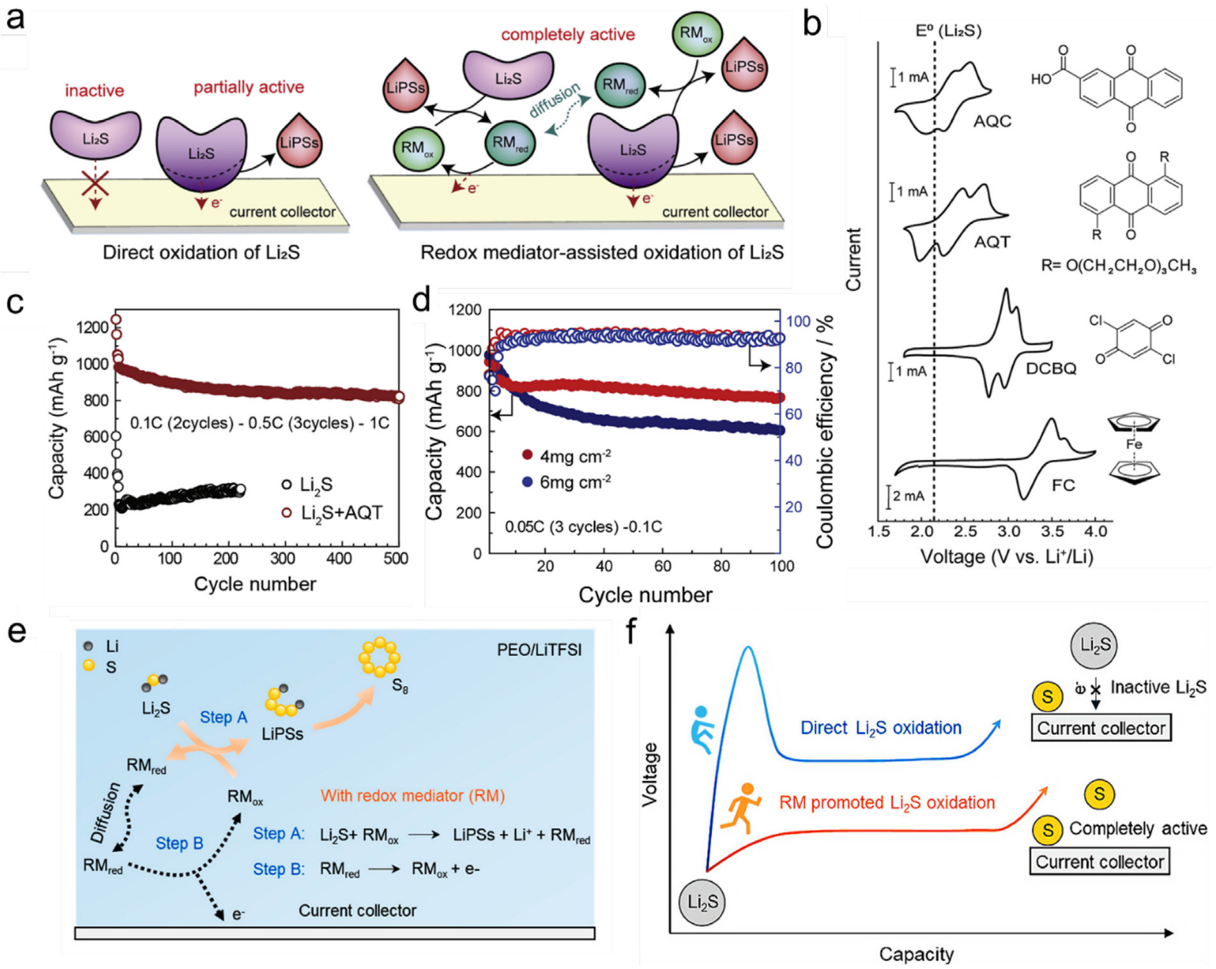

Fig. 7. (a) Schematic illustration of Li_2S oxidation with and without RMs in Li-S batteries. (b) Cyclic voltammograms of different RMs of 20 mmol·L^{-1}. (c) Capacity retention of the Li_2S cathodes cycled with and without AQT. (d) Cycling performance of high-mass-loading Li_2S cathodes using AQT [81]. Reproduced with permission of Ref. [81], copyright 2018 Elsevier. (e) Reaction scheme of RMs for all-solid-state Li-S batteries. (f) The scheme of the charge profiles with and without RMs [83]. Reproduced with permission of Ref. [83], copyright 2021 American Chemical Society.

utilization of Li_2S material [81]. By appropriately regulating the characteristics such as the redox potential, stability, and solubility of quinones with different functional groups, the initial charge potential of Li_2S first decreases to below 2.5 V at 0.5 C (Fig. 7b). Notably, the minimal polarization exists throughout the cycling of the battery, and the Li_2S electrode maintains the original morphology during the process. Therefore, as shown in Fig. 7c, the first discharge capacity of Li/Li_2S cell improves to as high as 1300 mAh·g^{-1}. The reversible capacity of 952 mAh·g^{-1} is achieved with the active S loading of 6 mg·cm^{-2} S (Fig. 7d). Moreover, Bao et al. applied the same strategy to the all-solid-state Li-S batteries [83]. The RMs of the soluble quinone-based 1,5-bis(2-(2-(2-methoxyethoxy) ethoxy)ethoxy) anthra-9,10-quinone (AQT) are confirmed to possess the appropriate redox potential and reversibility to facilitate the oxidation of Li_2S in polyethylene oxide (PEO) polymer electrolytes at 60 °C. Li_2S cathodes with AQT display a remarkable decreased oxidation potential of 2.4 V at initial charge process and subsequently exhibit a discharge capacity of 1133 mAh·g^{-1}. *In situ* X-ray absorption spectra reveal a solid-polysulfide-solid reaction with AQT dissolved in PEO electrolyte during the first charging, instead of solid-solid Li_2S-S transformation for the bare Li_2S cathode. It offers a low energy barrier for activation of the S cathode (Fig. 7e and f).

Organic molecules with the diverse functional groups have been proved to have a good mediated effect for oxidation of Li_2S. In addition, other types of inorganic compounds can also improve the electrochemical conversion process of Li_2S and S. The previous part has illustrated the good stabilizing effect of InI_3 on Li anode by preferential electrodeposition [50]. Meanwhile, as a bifunctional electrolyte additive, the I_3^- in InI_3 can serve as a redox mediator for spontaneously oxidizing the insoluble product (Li_2S/Li_2S_2) because the anodic peak of I^-/I_3^- redox reaction (ca. 3.0 V) is considerably higher than the anodic peaks for Li_2S oxidation (ca. 2.4 V). Through charging the batteries to the potential of I^-/I_3^- redox reaction, insulated Li_2S/Li_2S_2 could be chemically converted to the long-chain Li_2S_n and regain the electrochemical activity.

It is reported that the high donor number solvents are more favorable for Li_2S deposition compared to commonly used ether-based solvents. Liu et al. proposed an approach to tune Li_2S dissolution through the addition of NH_4NO_3 in dimethyl sulfoxide (DMSO) [84]. The high electronegativity of the N atom will attract electrons from the H atom, resulting in the strong polarity of N—H and the enrichment of the positive charge on the H atom. The polar effect of N—H groups promotes the dissolution of Li_2S through the powerfully hydrogen bond interaction between NH_4^+ and S^{2-} ($N—H\cdots S^{2-}$). Hydrogen bond interaction, synergistically with the solvating ability of high-dielectric-constant DMSO, significantly facilitates the oxidation kinetics of Li_2S.

Another approach to enhance the utilization of Li_2S is to construct a conductive and protective layer on the surface of Li_2S, to effectively confine LiPSs species. LiI has been proved to not only generate a stable SEI layer on anode, but also form an effective protective coating on the surface of cathode particles via the *in situ* polymerization of DME induced by the iodine radicals. Due to the modification function of Li_2S surfaces, the LiI additive reduced the overpotential of first charge process to 2.75 V, which is near the oxidation equilibrium potential of Li_2S. Manthiram et al. built a transition-metal sulfide layer coated the surface of micrometer-sized Li_2S particles through surface chemical reaction between Li_2S and the electrolyte containing the transition-metal salts additive (Fig. 8a) [85]. It is demonstrated that manganese (II) acetylacetonate could generate a fairly stable encapsulation layer of MnS among the mostly explored additives. It should be electrochemically inactive within the cycling voltage window. The *in situ* formed protection layer distinctively reduces the activation overpotential and enhances the utilization of Li_2S.

Recently, the catalytic host materials, such as transition metal sulfides and oxides, as well as single-atom catalysts, have been applied in Li-S batteries. These catalytic hosts usually are able to promote the redox kinetics of S species as well as adsorb LiPSs to mitigate the LiPSs diffusion. However, the solid-state Li_2S will cover on the active sites of catalyst and prevents the contacts with active species, leading to the deactivation of the catalyst. Based on this, introducing the catalysts into electrolyte could be an effective way to address the issues above. Yang et al. empolyed soluble cobalt phthalocyanine (CoPc) and cobalt hexadecachlorophthalocyanine (CoPcCl) as the additive in Li-S battery to promote the conversion and utilization of S species [86]. The results show that the catalyst in liquid phase is more effective than that in host materials, efficiently avoiding the failure of the catalyst activity.

3.4. Regulation for the deposition of Li_2S

Beside the large overpotential of electrochemical oxidation of Li_2S, the sluggish deposition kinetics process and the thin two-dimensional (2D) layer growth of insulating Li_2S lead to the severe irreversible loss of the active sulfur and the rapid capacity decay [87]. The electrochemical behavior of Li_2S is regulated by redox process of soluble LiPSs in the general battery system, which act as the inherent RM, directly affecting the deposition rate and growth morphology of Li_2S [88]. Unfortunately, intrinsically slow kinetics of LiPSs fail to guide the Li_2S growth. Thus, it is critical to tune the deposition behavior of Li_2S by introducing extrinsic effective RMs to obtain the high-performance S cathode. The key to choosing RMs is that the equilibrium potential of RMs should be slightly lower than that of Li_2S_4 to Li_2S. In this case, RMs will be reduced in prior and thus further facilitate the dissolved polysulfides being reduced to Li_2S.

Helms et al. found that micron-sized, porous 3D deposits of Li_2S can be obtained with benzo [ghi] peryleneimide (BPI) presented in the electrolyte [89]. In their concept, BPI serves as “capillaries” to mediate the short-range ionic transport and electron transfer between the active materials and the conductive carbon, providing a new route for Li_2S nucleation and growth. Therefore, the addition of BPI enables the deposition of Li_2S on the deposited Li_2S, not just on the carbon surface. As illustrated in Fig. 8b, such BPI additive creates a 3D growth of Li_2S and avoids the isolation of conductive carbon by insulating discharge product, resulting in a 6-fold increase in Li_2S formation and consequently 220% improvement in sulfur utilization. This means that less conductive carbon is required in cathode under a given amount of Li_2S generation during discharging, enabling a higher percentage of active materials in battery.

Organometallic complexes consisting of organic ligands and metal active moieties, possess variable structures, rich porosities, active sites and

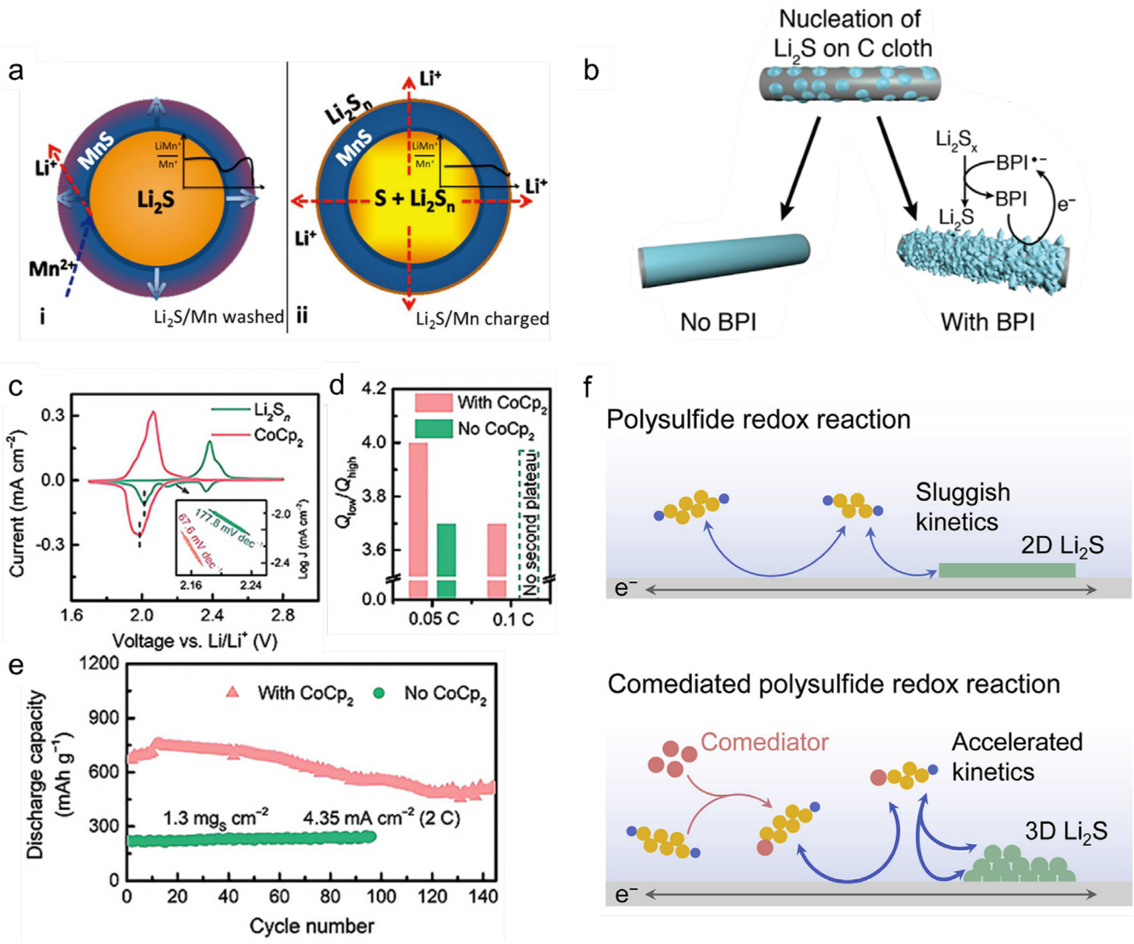

Fig. 8. (a) Schematic of reaction mechanism and resultant particle morphology for the Li_2S/Mn cathode before and after charge [85]. Reproduced with permission of Ref. [85], copyright 2017 Wiley-VCH. (b) The electrodeposition of Li_2S onto C cloth in the absence or presence of BPI RMs [89]. Reproduced with permission of Ref. [89], copyright 2015 American Chemical Society. (c) CVs of Li|Li_2S_4 and Li|$CoCp_2$ cells with isoelectronic quantities at 0.1 mV·s^{-1}, and the insets are the Tafel plots for reduction reactions of Li_2S_n and $CoCp_2$. (d) The Q_{low}/Q_{high} ratios of the Li-S cell at different rates and (e) the cycling performance of the Li-S cell with/without $CoCp_2$ [91]. Reproduced with permission of Ref. [91], copyright 2019 Wiley-VCH. (f) Schematic illustration of LiPS-mediated and external redox comediated reaction pathway of Li-S batteries [87]. Reproduced with permission of Ref. [87], copyright 2020 Elsevier.

distinctive charge centers, which have been demonstrated the considerable potential for application in various battery systems. Sung et al. first reported the application of cobaltocene ($Co(\eta\text{-}5C_5H_5)_2$) in Li-S batteries [90]. The cobaltocene in electrolyte act as a redox mediator and play a role of a charge transfer agent between the conductive surface and the polysulfides. The effective conductivity increase of cathode by the cobaltocene additive boosts the transformation of polysulfides to Li_2S, and the nucleation and growth of Li_2S. Then, Zhang et al. used cobaltocene ($CoCp_2$) as an extrinsic RM to change reduction pathway of LiPSs toward a 3D Li_2S deposition, immensely improving the discharge capacity for more than several times under harsh conditions [91]. The result confirms that the dissolved $CoCp_2$ in electrolyte will chemically reduce polysulfides because of the more negative reduction peak of $CoCp_2$ than the formation potential of Li_2S, and it is oxidized to $CoCp_2^+$ concurrently. Then, $CoCp_2^+$ will in turn be electrochemically reduced back to $CoCp_2$ in the discharge process, and thereby participate in the reduction of polysulfides again until polysulfides are completely reduced. The highly reversible $CoCp_2$ reduction/oxidation minimizes the huge gap between these reductive/oxidative peaks of Li_2S formation/oxidation. The smaller Tafel slope of $CoCp_2/CoCp_2^+$ redox couple also means a faster electrochemical conversion kinetics than that of intrinsic polysulfides. (Fig. 8c). The cell with $CoCp_2$ has a higher Q_{low}/Q_{high} value than the control cell, suggesting a more complete Li_2S transformation with $CoCp_2$ (Fig. 8d). Importantly, the redox couple of $CoCp_2/CoCp_2^+$ can always be presented in the electrolyte and maintains a certain concentration, and thereby ensures the persistence of the Li_2S growth. As shown in Fig. 8e, the $CoCp_2$-containing

Table 1. The summarized electrolyte additives and performances for Li-S batteries in literatures.

Additive	Electrolyte	Initial capacity ($mAh\cdot g^{-1}$)/ C rate	Sulfur loading ($mg\cdot cm^{-2}$)	Final capacity ($mAh\cdot g^{-1}$)/ cycle number	Ref.
2 wt% $ZrO(NO_3)_2$	Li-S electrolyte[a]	1226/0.5	1.5	398/280	[27]
2 wt% $LaNO_3$	Li-S electrolyte	1280/0.2	0.9	807/300	[31]
2 wt% LiN_3 (70 °C)	LiTFSI PEO (EO:Li 20:1)	0.1	1.0	800/30	[33]
7 $mg\cdot mL^{-1}$ boron nitride nanosheet (BNNS)	Li-S electrolyte	1223/0.1	1.5	881/200	[34]
0.2 $mol\cdot L^{-1}$ triazole (Ta) and tetrazole (Tta)	Li-S electrolyte	(1425)1322/0.2	1	704 (780)/200	[36]
40 wt% CS_2	Li-S electrolyte	962/0.5	1	747/300	[40]
4 wt% Alpha-lipoic acid (ALA)	Li-S electrolyte	1005/0.2	1.2	787/200	[41]
8 wt% Poly (sulfur-random-triallylamine) (PST)	Li-S electrolyte	1431/1	1.5	735/1000	[42]
50 $mmol\cdot L^{-1}$ biphenyl-4,4′-dithiol (BPD)	1 $mol\cdot L^{-1}$ LiTFSI G4/DOL	900/0.1	0.7−1.2	650/100	[44]
80 $mmol\cdot L^{-1}$ 3,5-bis(trifluoromethyl) thiophenol (BTB)	Li-S electrolyte	950/0.1	4.5	700/82	[45]
0.15 $mol\cdot L^{-1}$ 1,4-benzenedithiols (1,4-BDT)	Li-S electrolyte	1347/0.5	1	909/500	[46]
0.15 $mol\cdot L^{-1}$ 1,3,5-benzenetrithiol (BTT)	Li-S electrolyte	1036/1	1	907/300	[47]
0.7 $mol\cdot L^{-1}$ benzoselenol (PhSeH)	Li-S electrolyte	1436/0.5	1.1	1300/200	[48]
0.1 $mol\cdot L^{-1}$ $SiCl_4$	1 $mol\cdot L^{-1}$ $LiPF_6$/PC	ca. 1350/1	1	751/200	[55]
5 $mmol\cdot L^{-1}$ nitrofullerene (Nitro-C_{60})	1 $mol\cdot L^{-1}$ $LiPF_6$ in EC:DEC	ca. 2000/0.05	1.5	ca. 630/500	[58]
2 mg 4 mL^{-1} graphene quantum dots (GQDs)	Li-S electrolyte	830/0.5	4	498/200	[61]
N, S-codoped carbon dots (N,S-CDs)	Li-S electrolyte	915/0.5	1	600/300	[62]
5 wt% pyrrole	Li-S electrolyte	1649/0.2	1	908/100	[64]
2 wt% triphenylphosphine (TPP)	Li-S electrolyte	994/1	2.1	698/1000	[65]
0.11 $mol\cdot L^{-1}$ Bis(4-nitrophenyl) Carbonate (BNC)	Li-S electrolyte	841/1	1.49	778/300	[66]
20 $mmol\cdot L^{-1}$ Quinhydrone (QH)	0.5 $mol\cdot L^{-1}$ LiOTf and 0.5 $mol\cdot L^{-1}$ $LiNO_3$ in DME/DOL	963/1	1.5	933/300	[67]
0.5 wt% nitrogen-doped carbon dots (N-CD)	Li-S electrolyte	891/0.5	2	589/500	[68]
10 $g\cdot L^{-1}$ dithiothreitol (DTT)	Li-S electrolyte	808/0.5	1.8−2	471/500	[72]
4% glutamate	Li-S electrolyte	605/2	1.5	363/1000	[74]
Diphenyl diselenide (DPDSe)	Li-S electrolyte	1056/0.5	1.2	720/350	[80]
80 $mmol\cdot L^{-1}$ 1,5-bis(2-(2-(2-methoxyethoxy) ethoxy)ethoxy) anthra-9,10-quinone	Li-S electrolyte	1300/0.1	0.7 (Li_2S)	850/500	[81]
20 $mmol\cdot L^{-1}$ cobaltocene ($CoCp_2$)	Li-S electrolyte	757/2	1.3	552/100	[91]
100 $mmol\cdot L^{-1}$ di-*t*-butyl disulfide (DtbDS)	Li-S electrolyte	ca. 1000/0.5	1.2	600/300	[87]

[a] The Li-S electrolyte represents 1 $mol\cdot L^{-1}$ LiTFSI in DME:DOL (V:V = 1:1) with or without $LiNO_3$.

Li-S cell can reach the maximum capacity of 757 $mAh\cdot g^{-1}$ and stable cycling for 100 times at 2 C.

Huang et al. reported an organopolysulfide as a comediator in electrolyte to modulate the evolution of polysulfides, especially promoting the rapid conversion of LiPSs to Li_2S via a more kinetically favorable redox pathway [87]. The introduced di-*t*-butyl disulfide (DtbDS) additive can spontaneously react with LiPSs and produce lithium organopolysulfides, resulting in a faster redox-mediated process compared with intrinsic LiPSs. Moreover, DtbDS transforms the deposition morphology of Li_2S from film-like 2D to three-dimensional (3D) by a more beneficial reaction pathway (Fig. 8f). They found that the presence of LitbDS alters the electrochemical equilibrium and promotes the kinetics of the liquid-solid conversion for both Li_2S deposition and dissolution. Either discharge or charge process with LitDS exhibits a higher specific capacity than the control battery, and the corresponding interfacial charge transfer impedances decreases and the redox currents in CV profiles obviously increases. As a result, with the significant improvement of the redox kinetics, the Li-S battery with the DtbDS additive displays the high specific capacity of 863 $mAh\cdot g^{-1}$ at 0.5 C and the reversible capacity of 600 $mAh\cdot g^{-1}$ maintained after 300 cycles.

4. Additives for safe Li-S batteries

In addition to the risk of short circuits due to the formation of metallic Li dendrites, Li-S batteries also face the serious safety concerns derived from the volatile and flammable organic electrolytes as well as the highly reactive Li metal. Therefore, addressing the safety issues of Li-S system is necessary before used in practical applications. Generally, the widely studied electrolyte with the flame retardant mainly involves phosphorus-

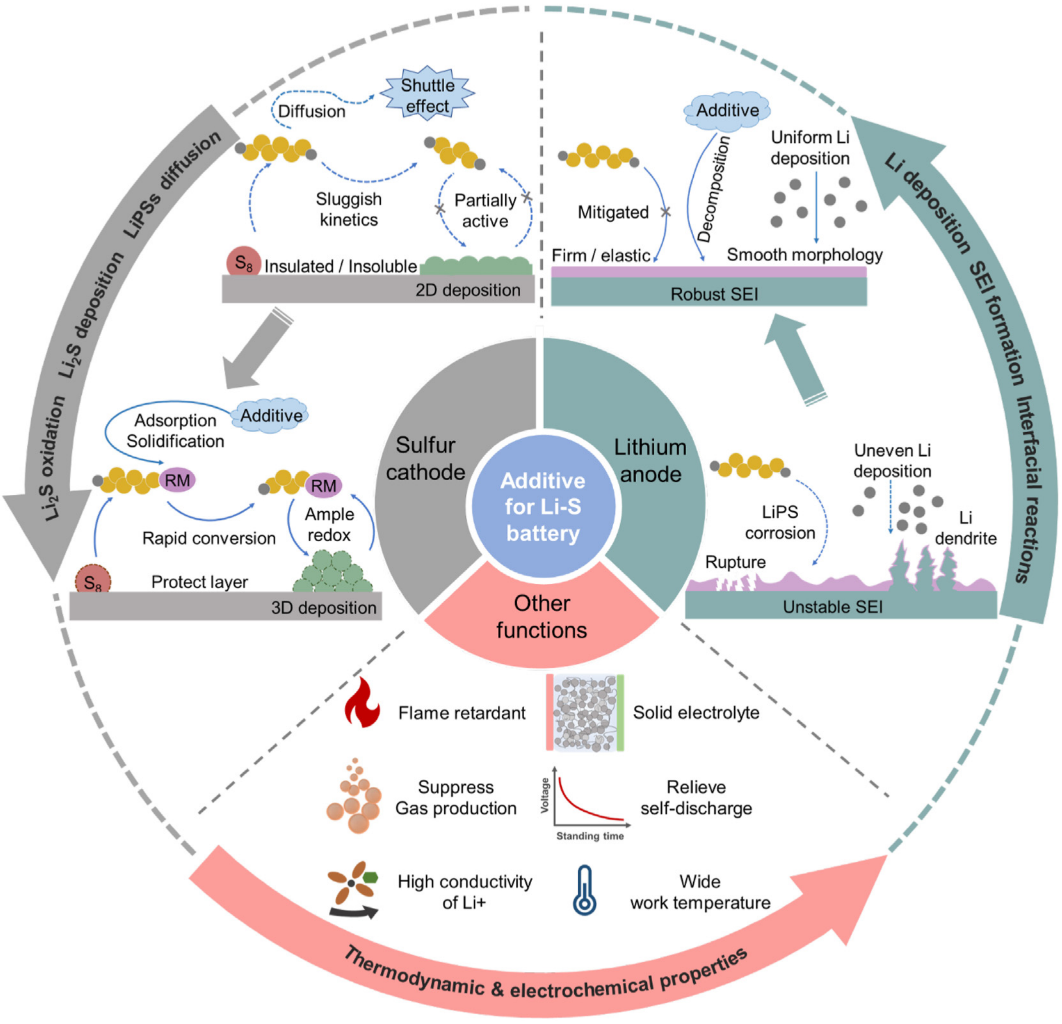

Fig. 9. Challenges and perspectives in advanced additives of electrolytes for high-performance Li-S batteries.

containing compounds and ionic liquids. Sulfurized polyacrylonitrile (S@PAN) as a substitute for sulfur cathode, with limited oxygen index value has excellent flame-retardant properties. Moreover, S@PAN is compatible with the carbonate-based electrolyte and thus the flame retardant in the lithium ion batteries can be used to enhance the safety. Based on this, NuLi and co-workers successively reported the dimethyl methylphosphonate (DMMP) [92], tris(2,2,2-trifluoroethyl) phosphite (TTFP) [93] and triphenyl phosphite (TPPi) [94] as additives and applied in flame-retardant Li-S@PAN batteries. The nonflammability and thermal stabilities of the electrolyte are greatly improved with these additives, but has little side effect on the cycling performance. The Li-S cell with 10 wt% TTFP achieves a reversible capacity of 1500 $mAh\cdot g^{-1}$ in the first cycle and a stable cycling for more than 400 cycles with no remarkable fading [93].

It is generally believed that the main function of the flame retardant is because of the chemical radical termination in the combustion process. Once the retardants are heated above their pyrolysis temperatures, phosphorous compounds yield free radicals (such as PO· and F·), which can capture other free radicals released by the burning electrolyte (usually H· and HO·) to suppress the combustion reaction of the long-chain organics. Huang et al. develop a novel flame-retardant polymerized 1,3-dioxolane electrolyte by a tris(-pentafluorophenyl) borane (TB) additive [95]. TB is introduced not only as an initiator for *in situ* polymerization of DOL, but also as a multifunctional additive. A small amount of TB molecules serves as a high-efficient flame retardant through producing fluorine radicals, achieving a flame-retardant polymer electrolyte. Moreover, a highly stable LiF-rich SEI is obtained by fluorinated TB additive with high fluorine content. As a result, the solid Li-S battery without $LiNO_3$ displays excellent performance with an initial capacity of 1060 $mAh \cdot g^{-1}$ at 0.2 C and the reversible capacity of 660 $mAh \cdot g^{-1}$ is maintained after 500 cycles. Meanwhile, the Li-S cell with the polymer electrolyte achieves a high reversible capacity of 700 $mAh \cdot g^{-1}$ at -20 °C.

5. Summary and perspectives

As a potential alternative to commercial Li-ion batteries, Li-S batteries with such advantages as high theoretical specific capacities and energy densities have attractive prospects. After the unremitting efforts of researchers in the past few decades, Li-S batteries have achieved considerable progress. However, before reaching practical application, Li-S batteries still face many scientific and technical problems. At present, the exploration of electrolyte additives with different functions has become one of the main ideas for the development of high-efficiency electrolyte systems, and is also the mainstream way to improve the comprehensive performance of Li-S batteries. The reported performances of Li-S batteries with different additives in literatures are summarized in Table 1.

In addition, the review briefly classifies the current challenges of Li-S batteries and the corresponding solutions in terms of electrolyte additives (Fig. 9). The main conclusions and perspectives are given as follows.

(1) To achieve the high energy density, the problems of polysulfide shuttle and low sulfur utilization will be further amplified under conditions of high sulfur loadings and low E/S (electrolyte/sulfur) ratios. In addition, the insulating properties of S/Li_2S and the sluggish conversion kinetics of sulfur species still need to be improved. For the Li metal anode, the formation of Li dendrites poses a serious safety hazard, and the unstable SEI layer and consistent side reactions also lead to poor electrochemical performances. Moreover, the inherent obstacles such as thermal stability and safety of the electrolyte still need to be solved by further designs. In this context, the regulation of the overall performances of Li-S batteries by rational additives has shown its great potential.

(2) To overcome the problems described above, in-depth research on electrolyte additives is urgently required. Generally, the function of additives mainly depends on functional groups. Therefore, it is necessary to guide the designs of molecular structure and functional groups of functional additives combined with theoretical calculations. Adjustment and optimization of additive components through molecular engineering can effectively reduce or eliminate adverse effects on battery performance such as the polarization, cycling stability and safety. The various functions can be achieved including building the stable SEI, stabilizing polysulfides through various mechanisms (absorption, oxidation, complexation, anchoring, etc.), promoting oxidation of Li_2S, and improving the kinetics. In addition, it is also important to adopt various advanced *in situ* characterization technologies to analyze the working mechanism and interaction principle of additives. Moreover, environmental friendliness, compatibility, cost, and mass production of additives also need to be carefully considered.

In conclusion, as a convenient and effective way to promote the practical Li-S batteries, electrolyte additives need to be continuously improved to eliminate their drawbacks and enhance the performance of Li-S batteries. It is promising to see that electrolyte additives will play a crucial role in high-performance and safe Li-S batteries.

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锂硫电池电解液功能性添加剂研究进展

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摘要

由于具有能量密度高、成本低等优点，锂硫电池成为最有前景的下一代电池体系之一。然而，锂硫电池的实际应用仍面临着严峻挑战，如硫和硫化锂的低电导率、多硫化物的穿梭效应和锂枝晶的生长等。通过电解液的优化，可以改善电极|电解质界面，减弱副反应，提高电池性能。其中，电解液中的功能添加剂能有效调节电极界面和电池的氧化还原机制。本文系统性总结了锂硫电池添加剂的最新研究进展，并根据添加剂对锂金属负极的保护作用和对硫正极的稳定作用进行了分类。另外，本文详细讨论了添加剂在硫正极的作用，如抑制多硫化物的溶解和穿梭、充当氧化还原介质、激活硫化锂的沉积与溶解等。最后，本文展望了锂硫电池添加剂的发展前景，希望能对高性能锂硫电池电解液的设计提供借鉴。

关键词： 锂硫电池；添加剂；穿梭效应；多硫化物；电解液