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# Revitalizing Li–S batteries: the power of electrolyte additives

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Lithium–sulfur (Li–S) batteries have garnered significant attention as promising next-generation energy storage solutions due to their high energy density and cost efficiency. However, the broad adoption of Li–S batteries is impeded by several critical issues. These include the intrinsically low conductivities of sulfur (S) and lithium sulfide (Li<sub>2</sub>S), the polysulfide shuttle effect, and dendrite formation on the lithium (Li) electrode, among other challenges. Overcoming these obstacles is crucial to realizing the full potential of Li–S batteries. A key step towards improving Li–S battery performance is the optimization of electrolytes, with a particular focus on enhancing cell cyclability, rate capability, safety, and lifespan. This review examines the current advancements in various electrolyte additive options, including their concepts, designs, and materials, and how the electrolyte's final chemical and physical properties influence the overall performance of Li–S batteries. The aim is to provide a comprehensive framework for the rational selection of future electrolyte additives for Li–S batteries, based on the available concepts, and to evaluate the existing electrolyte additives.

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## 1. Introduction

Elemental sulfur, as a cathode material for lithium batteries, boasts a high specific capacity of 1672 mA h g<sup>−1</sup> and is both inexpensive and widely available, with the added benefit of being non-toxic.<sup>1,2</sup> With theoretical gravimetric and volumetric energy densities reaching up to 2600 W h kg<sup>−1</sup> and 2800 W h L<sup>−1</sup>, respectively, the combination of lithium and sulfur offers the highest potential energy density among solid elemental pairs. Compared to lithium-ion batteries, lithium–sulfur (Li–S) batteries can achieve energy densities three to five times greater. In Li–S batteries, the interaction between a sulfur-based cathode and a lithium metal anode leads to the generation of a series of lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, where 3 ≤ x ≤ 8), with the final reduction product being solid lithium sulfide (Li<sub>2</sub>S).<sup>3,4</sup> Specifically, longer-chain lithium polysulfides (LiPSs) are soluble in typical electrolytes and can migrate to and from the lithium (Li) electrode through a phenomenon known as “polysulfide shuttling”. During this process, these compounds undergo continuous reduction and oxidation at the electrodes, yet they do not contribute to the overall battery capacity.<sup>5</sup> In recent decades, considerable efforts have been made to address the inherent challenges associated with Li–S batteries. These

include, but are not limited to, issues such as the instability of lithium metal anodes, the polysulfide shuttle effect, and fluctuations in electrode volume,<sup>6,7</sup> additional focus has been placed on optimizing cathode architecture,<sup>8–15</sup> functionalization of separators,<sup>16–19</sup> stabilization of the lithium metal surface,<sup>20–23</sup> and most pertinent to this review, modification of the electrolyte solution.<sup>24–28</sup> When combined with sulfur's advantageous properties—such as non-toxicity, affordability, and natural abundance—Li–S batteries emerge as one of the most promising energy storage technologies for the next generation of high-energy power systems.<sup>29–31</sup>

The primary electrochemical characteristics of a Li–S cell are predominantly influenced by the choice of electrolyte. Unfortunately, there is currently no established electrolyte that consistently allows for high electrochemical utilization under realistic conditions. The electrolyte's ability to form a stable interface with the Li-metal anode may not necessarily be chemically optimal when paired with the sulfur-active material, and *vice versa*. These conflicting trade-offs lie at the heart of this challenge. Additives can alter not only the dissolution of polysulfides but also the electrolyte/electrode interface on Li anodes. Consequently, additives hold significant potential for enhancing the cycle life of Li–S batteries. Ether-based electrolytes have been a primary focus of research due to their ability to initiate the solid-to-liquid transition in the sulfur cathode during discharge while maintaining a reasonably stable interface with the Li-metal anode, particularly in the presence of lithium nitrate (LiNO<sub>3</sub>) in the electrolyte. However, due to its continuous consumption at both anodes and cathodes and the presence of flaws in the solid electrolyte interface (SEI) layer,

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LiNO<sub>3</sub> often fails to provide long-term protection to Li anodes.<sup>32–34</sup> To achieve high specific capacity relative to the amount of sulfur in the cathode, a surplus of electrolyte is required because the commonly used ether-based formulation cannot fully achieve lithiation depth with limited quantities. This limitation in reaction kinetics necessitates a high electrolyte-to-sulfur (E/S) ratio, significantly reducing the achievable energy density in a cell and thus compromising the primary potential of Li–S technology. In practical terms, only a small fraction of sulfur's theoretical capacity is accessible when Li–S cells employing ether-based electrolytes are operated under commercially relevant lean E/S conditions.

A critical factor influencing the sulfur reaction pathway is the solvation of polysulfides. In traditional ether-based solutions—such as 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.2 M LiNO<sub>3</sub> in an equal-volume mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), referred to as DOL/DME throughout this review—effective polysulfide solvation enhances sulfur utilization and reaction kinetics. However, it also induces the notorious “shuttle effect”, which impedes the recharging process to elemental sulfur. This effect diminishes the practical specific capacity of the sulfur cathode and increases lithium corrosion, leading to low coulombic efficiency and shortened cycle life due to the degradation of the corroded Li anode.<sup>35,36</sup> Besides ether-based electrolytes, carbonates can also be utilized in Li–S batteries. However, their use requires restructuring the sulfur cathode due to the interaction of carbonates with soluble polysulfides *via* nucleophilic reactions.<sup>37–39</sup> Recent advancements in microporous and ultra-microporous carbon–sulfur composites have enabled the adoption of carbonate-based electrolytes in next-generation Li–S batteries.<sup>40,41</sup> Using commercial liquid carbonate electrolytes in Li–S batteries provides significant advantages: it enhances cycle life by eliminating the polysulfide shuttle mechanism and requires less electrolyte due to minimal dissolution of sulfur/polysulfides.

This review paper provides an overview of various functional electrolyte additives in Li–S batteries. It summarizes and categorizes recent developments in electrolyte additive research for Li–S batteries, discussing their functionalities, working principles, benefits, and drawbacks. The analysis also examines how additives impact the overall performance of batteries. Lastly, the paper explores prospects for further developing and utilizing additives in Li–S batteries, aiming to guide future design and development efforts in this field.

## 2. Additives for Li–S battery electrolytes

It is widely acknowledged that functional additives are as crucial as solvents and salts in the electrolyte of Li–S batteries, which are considered highly cost-effective and efficient for enhancing cell performance. The use of additives in Li–S batteries is more constrained compared to those in LIBs, primarily due to the stringent requirements posed by this specific and challenging battery system. These include issues

such as polysulfide dissolution and shuttle effects, lithium metal anode with dendrite growth, electrolyte instability, and safety concerns.<sup>42</sup> These additives can interact with polysulfides through different mechanisms, such as chemical adsorption, complexation, or redox reactions, to suppress their migration and enhance battery performance. The efficacy of these additives is supported by a combination of experimental techniques and theoretical calculations. Electrochemical tests demonstrate improved cycling stability, higher capacity retention, and enhanced rate performance in Li–S batteries with these additives. Spectroscopic techniques, such as NMR and Raman spectroscopy, provide insights into the interactions between additives and polysulfides. Theoretical calculations, such as density functional theory (DFT), can reveal the binding energies and electronic structures of additive-polysulfide complexes.<sup>43</sup>

Among these electrolyte additives, Lewis acidic additives such as metal ions (*e.g.*, Al<sup>3+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>) and metal-organic frameworks (MOFs) are particularly effective. Metal ions can form complexes with polysulfides, reducing their solubility and mobility in the electrolyte, which stabilizes the battery.<sup>44</sup> For instance, adding AlCl<sub>3</sub> forms stable Al–S complexes that have shown to significantly enhance cycling stability.<sup>45</sup> MOFs with Lewis acidic sites, like those based on titanium dioxide,<sup>46</sup> can also trap polysulfides, further preventing their migration. Redox mediators/catalysts including and organic compounds like dithiothreitol (DTT)<sup>47</sup> and tetrathiafulvalene (TTF), facilitate the conversion of polysulfides into less soluble forms, shuttling electrons between the electrodes to support redox reactions. Inorganic catalysts like Fe–N/Co–N@C reported by Ye *et al.*<sup>48</sup> and transition metal sulfides, sulfur dioxide (SO<sub>2</sub>), selenium dioxide (SeO<sub>2</sub>) and ammonium thiosulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) catalyze similar conversions, enhancing performance.<sup>49</sup> Lewis base additives such as nitrogen-doped carbon materials with nitrogen-functional groups, or organic compounds like thio-urea,<sup>50</sup> interact with polysulfides to reduce their mobility. Likewise, polymer-based additives like poly(ethylene oxide) (PEO) and poly(acrylonitrile) (PAN) form complexes with polysulfides, lowering their solubility and preventing diffusion.<sup>51,52</sup> Together, these diverse additive types provide effective strategies for suppressing the shuttle effect, thus extending Li–S battery life and performance. The following additive concepts, outlined in Table 1, represent diverse approaches aimed at tackling the key challenges associated with Li–S batteries, and they currently constitute significant areas of research and development in the field (Fig. 1).

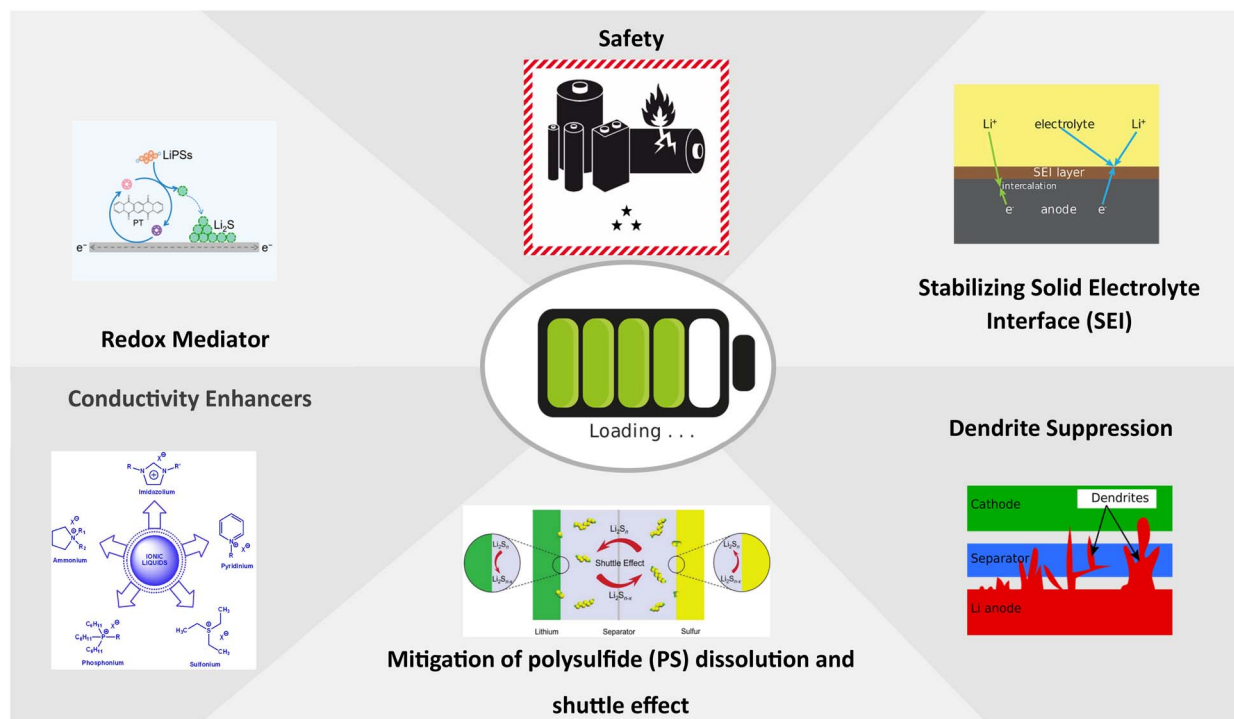
### 2.1. Enhancing stability of solid electrolyte interface (SEI) formation

New additives are being developed to address limitations with lithium metal anodes in batteries. These additives aim to create a stable solid layer (SEI) on the lithium surface. This SEI layer acts like a protective shield, preventing unwanted reactions between the lithium and the electrolyte, ultimately improving the battery's lifespan. However, lithium metal anodes still face challenges. One major issue is the formation of needle-like structures called dendrites. Additionally, soluble sulfur



**Table 1** Analysis of electrochemical performances of various electrolyte additives for lithium–sulfur batteries as documented in this review

| Additive                                                       | Concentration                                            | Mechanism                      | Ref. |
|----------------------------------------------------------------|----------------------------------------------------------|--------------------------------|------|
| LiNO <sub>3</sub>                                              | 2 wt%                                                    | SEI modification               | 42   |
| CsNO <sub>3</sub>                                              | 0.05 M                                                   | SEI modification               | 53   |
| KNO <sub>3</sub>                                               | 0.1 M                                                    | SEI modification               | 54   |
| La(NO <sub>3</sub> ) <sub>3</sub>                              | 2 wt%                                                    | SEI modification               | 55   |
| LiI                                                            | 0.5 M                                                    | SEI modification               | 56   |
| LiBr                                                           | 0.15 M                                                   | SEI modification               | 57   |
| InI <sub>3</sub>                                               | 0.05 M                                                   | SEI modification               | 58   |
| Li <sub>2</sub> S <sub>5</sub>                                 | 1.0 wt%                                                  | SEI modification               | 59   |
| Biphenyl-4,4'-dithiol (BPD)                                    | 50 mmol L <sup>-1</sup>                                  | SEI modification               | 60   |
| 3,5-Bis(trifluoromethyl)thiophenol (BTB)                       | 80 mmol L <sup>-1</sup>                                  | SEI modification               | 61   |
| 1,3,5-Benzenetrithiol (BTT)                                    | 0.15 mmol L <sup>-1</sup>                                | SEI modification               | 62   |
| P <sub>2</sub> S <sub>5</sub>                                  | 5 wt% of Li <sub>2</sub> S/P <sub>2</sub> S <sub>5</sub> | SEI modification               | 63   |
| H <sub>2</sub> O                                               | 250 ppm                                                  | SEI modification               | 64   |
| Lithium difluoro(oxalato)borate (LiODFB)                       | 2 wt%                                                    | SEI modification               | 65   |
| Boron nitride nanosheets (BNNS)                                | 7 mg mL <sup>-1</sup>                                    | SEI modification               | 66   |
| 1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) | 2 wt%                                                    | SEI modification               | 67   |
| LiN <sub>3</sub>                                               | 2 wt%                                                    | SEI modification               | 68   |
| Cu(CH <sub>3</sub> COO) <sub>2</sub>                           | 0.03 M                                                   | SEI modification               | 69   |
| Di(tri)sulfide polyethylene glycol (PES <sub>n</sub> )         | 0.002 mmol                                               | SEI modification               | 70   |
| Bis(4-nitrophenyl)carbonate (BNC)                              | 0.11 M                                                   | Tackling polysulfide shuttling | 71   |
| Aluminium phosphate (AlPO <sub>4</sub> )                       | 0.5–1.0 wt%                                              | Tackling polysulfide shuttling | 72   |
| Dithiothreitol (DTT)                                           | 10 g L <sup>-1</sup>                                     | Tackling polysulfide shuttling | 73   |
| Carbon disulfide (CS <sub>2</sub> )                            | 40 wt%                                                   | Multifunctional                | 74   |
| Pyrrole (Py)                                                   | 5 wt%                                                    | Multifunctional                | 75   |
| Trifluoromethane sulfonamide (TFMSA)                           | 1 wt%                                                    | Multifunctional                | 76   |
| Hexadecyltriethylammonium iodide (HTOA-I)                      | 0.5 M                                                    | Multifunctional                | 77   |
| Triphenyl phosphite (TPPi)                                     | 5 wt%                                                    | Safety                         | 78   |
| Dimethyl methylphosphonate (DMMP)                              | 7–11 wt%                                                 | Safety                         | 79   |
| Tris(pentafluorophenyl)borane (TB)                             | 1–5 wt%                                                  | Safety                         | 80   |

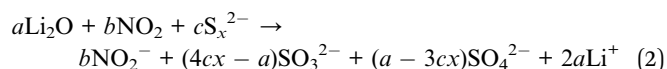
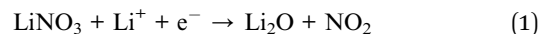
**Fig. 1** The major groups of electrolyte additives discussed in this review.<sup>81,82</sup>

components in the battery can dissolve and travel to the anode, reacting with the lithium metal. This reaction creates unwanted solid lithium sulfide compounds, which reduces the amount of useable sulfur and consumes lithium metal irreversibly.<sup>83</sup> Furthermore, the formation of a patchy or uneven SEI layer (heterogeneous SEI) can cause problems. This uneven layer can hinder the movement of lithium ions (Li ion diffusion) within the battery. This uneven flow of ions can lead to several issues: nonuniform ionic flux (uneven distribution of ions), unregulated growth of lithium dendrites, poor performance over charging and discharging cycles (cycle performance), and potential safety hazards.

**2.1.1. Lithium nitrate (LiNO<sub>3</sub>).** One effective solution to address the issue of soluble sulfur comes in the form of electrolyte additives like lithium nitrate (LiNO<sub>3</sub>). Pioneered by Aurbach,<sup>84</sup> LiNO<sub>3</sub> has become widely used in lithium–sulfur (Li–S) batteries. This additive helps to reduce the “polysulfide shuttle effect”. The polysulfide shuttle effect occurs when soluble sulfur components dissolve and travel to the anode, reacting with the lithium metal. This reaction creates unwanted solid lithium sulfide compounds, which reduces the amount of useable sulfur and consumes lithium metal irreversibly. LiNO<sub>3</sub> helps to mitigate this issue, leading to improved battery performance and cycle life. The mechanism behind this enhancement has been increasingly understood. It's believed that when LiNO<sub>3</sub> is reduced, it creates species containing nitrogen, such as nitrite groups (NO<sub>2</sub><sup>−</sup>), R-NO<sub>2</sub> (organic nitrites), Li<sub>2</sub>O, and LiNO<sub>2</sub>. These species then contribute to the formation of a stable solid electrolyte interphase (SEI) rich in nitrogen and oxygen (LiN<sub>x</sub>O<sub>y</sub>). This improved SEI layer effectively shields the lithium metal anode from detrimental reactions and dampens the shuttle effect of lithium polysulfides (LiPSs).

According to Zhang *et al.*'s research<sup>85</sup> (illustrated in Fig. 2), the addition of LiNO<sub>3</sub> to the electrolyte specifically influences the SEI formation process during the first discharge. They propose that LiNO<sub>3</sub> can oxidize the shuttled polysulfides to

more stable lithium sulfates (Li<sub>2</sub>SO<sub>3</sub> and Li<sub>2</sub>SO<sub>4</sub>), while being reduced to LiNO, itself. This two-step redox reaction helps create a compact and stable SEI layer on the lithium anode, further enhancing its performance. They explained the redox reaction between LiNO<sub>3</sub> and the shuttled polysulfides through a two-step reaction:



As the concentration of Li<sub>2</sub>SO<sub>3</sub> and Li<sub>2</sub>SO<sub>4</sub> increases, a stable layer forms on the lithium anode, further hindering the reaction between polysulfides and lithium metal. This passivation layer effectively reduces the impact of the polysulfide shuttle effect and consequently improves cycling performance. Interestingly, research by Brezesinski *et al.* found that a stable SEI formed in the presence of LiNO<sub>3</sub> inhibits the unwanted evolution of gases like methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) during the decomposition of ether-based solvents commonly used in electrolytes. However, this LiNO<sub>3</sub>-containing electrolyte can still lead to the production of small amounts of nitrogen gas (N<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). This presents a trade-off, as these nitrogen-containing gases may have both positive and negative effects (illustrated in Fig. 3(a)).<sup>86</sup> Zhang *et al.* further revealed that LiNO<sub>3</sub> interacts beneficially with the sulfur cathode. They discovered that the NO<sub>3</sub><sup>−</sup> anions can catalyse the transformation of highly soluble lithium polysulfides (Li<sub>2</sub>S<sub>n</sub>) into less soluble elemental sulfur (S<sub>8</sub>). This reduces the impact of the shuttle effect. Additionally, the presence of both dissolved polysulfides and LiNO<sub>3</sub> in the electrolyte can lead to the formation of a multi-layered stable SEI. The inner layer, formed by the direct reduction of these species with lithium metal, is primarily composed of Li<sub>2</sub>S, Li<sub>2</sub>S<sub>2</sub>, and LiN<sub>x</sub>O<sub>y</sub>. The outer layer consists of Li<sub>2</sub>SO<sub>4</sub> and Li<sub>2</sub>S<sub>2</sub>O<sub>3</sub> species generated by the oxidation of polysulfides by LiNO<sub>3</sub>. Finally, beyond its positive effects on SEI formation and the shuttle effect, LiNO<sub>3</sub>

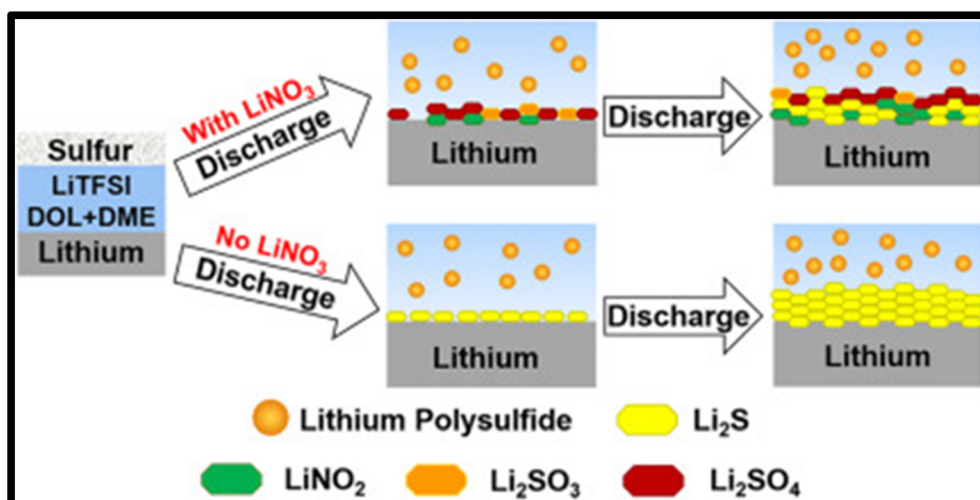


Fig. 2 Comparative mechanisms of SEI formation on lithium anodes with (top) and without (bottom) LiNO<sub>3</sub> additive in electrolytes.<sup>85</sup>





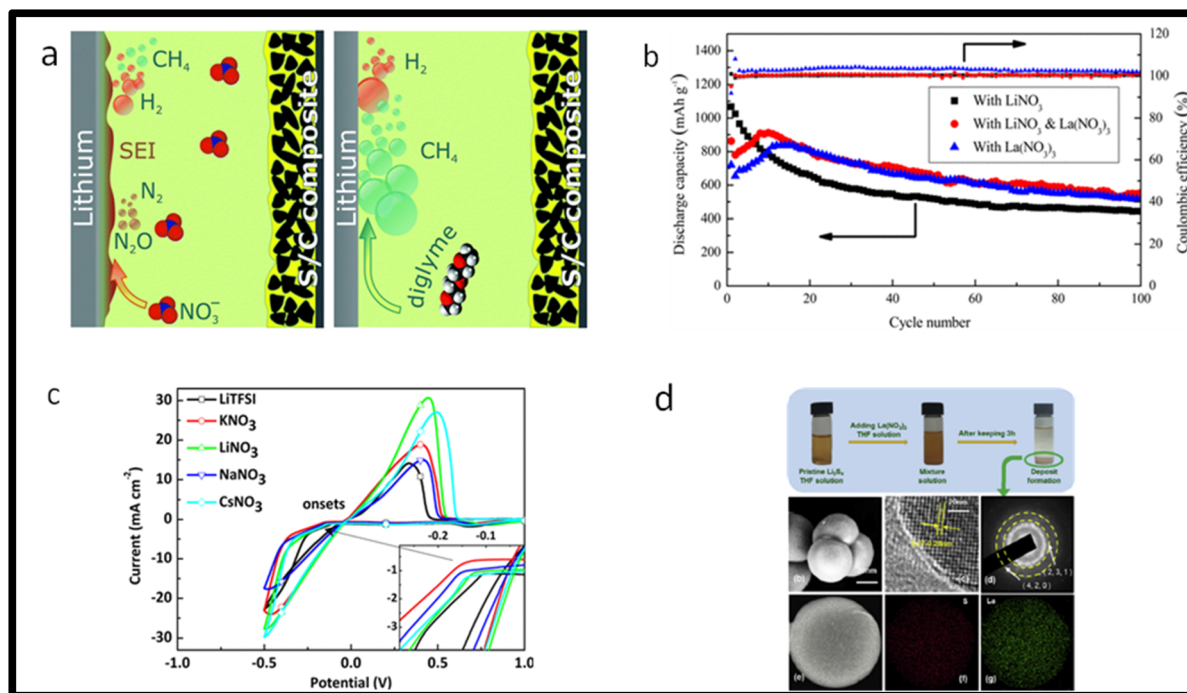


Fig. 3 (a) Overview of the reactions producing gases in Li-S batteries with the diglyme-based electrolyte with (left) and without  $\text{LiNO}_3$  (right),<sup>86</sup> (b) cycle performance of the Li-S cells in common electrolyte with  $\text{LiNO}_3$ , experimental electrolyte with  $\text{LiNO}_3$  and  $\text{La}(\text{NO}_3)_3$ , and electrolyte with only  $\text{La}(\text{NO}_3)_3$  as additive at 0.2C rate,<sup>87</sup> (c) CV curves of Li-Cu cells under different  $\text{RNO}_3$  additives (R = Li, Na, K, and Cs) (inset depicts the amplified part of the reduction onsets),<sup>88</sup> (d) schematic illustration of the reaction between LiPS and  $\text{La}(\text{NO}_3)_3$ ; (b) SEM (c) HRTEM (d) FFT (e–g) mapping of sedimentary product.<sup>89</sup>

can also help to reduce the self-discharge rate of Li-S batteries.<sup>85</sup> However,  $\text{LiNO}_3$ 's role in Li-S batteries is complex. While it offers significant advantages, there are also drawbacks. As  $\text{LiNO}_3$  is consumed in its beneficial reactions, the passivation film on the lithium anode continuously grows. This can potentially hinder lithium-ion transport over time. Additionally,  $\text{LiNO}_3$  itself can undergo irreversible reduction on the carbon surface of the cathode at voltages lower than 1.6 V. These reduction products can negatively impact the capacity and reversibility of Li-S batteries. By increasing the discharge cut-off voltage above 1.6 V, this unwanted reduction on the cathode can be prevented.<sup>90–93</sup> When employing  $\text{LiNO}_3$  as an electrolyte additive—another suggestion made by Rosenman—the lowest discharge potential ought to be more than 1.8 V vs. Li.  $\text{LiNO}_3$  may combine with  $\text{Li}_2\text{S}_n$  to create  $\text{Li}_x\text{SO}_y$  species, which could have detrimental consequences on the sulfur-active material's irreversible oxidation. Another challenge is linked to the choice of binder materials in the cathode. Binders with functional groups containing oxygen can accelerate the breakdown of  $\text{LiNO}_3$ . Therefore, selecting binders without these oxygen-containing groups is crucial to maintain long-term cycling stability when using  $\text{LiNO}_3$ . In addition to the limitations mentioned above,  $\text{LiNO}_3$  also suffers from a lack of control over the passivation layer thickness on the anode. This layer grows with each charging and discharging cycle and can eventually hinder the movement of lithium ions (Li ion diffusion) within the battery. Furthermore,  $\text{LiNO}_3$  is continually consumed during its beneficial reactions, and its effectiveness in

suppressing the shuttle effect diminishes as the number of cycles increases.<sup>94,95</sup>

**2.1.2. Metal halides.** Another approach to improve the SEI layer is the use of halide additives. Halides are compounds containing a halogen element like chlorine (Cl), bromine (Br), or iodine (I), bonded to a metal (M). Examples include various metal halides ( $\text{MX}$ , where M can be lithium (Li) or indium (In)). Liu *et al.* investigated the use of lithium iodide (LiI) as an additive in the electrolyte of Li-S batteries. Their goal was to achieve smoother deposition of lithium metal on the anode during charging. They discovered that LiI promotes the polymerization of ether-based electrolytes, commonly used in Li-S batteries. This polymerization reaction leads to the formation of a more elastic and robust polymer interphase on the lithium anode.<sup>96</sup> One approach to improve the SEI layer is the use of halide additives, as previously discussed with lithium iodide (LiI). Kim *et al.* conducted extensive research on metal iodides as electrolyte additives in Li-S batteries, revealing several key insights. They found that not all metal iodides are equally effective in promoting a stable solid electrolyte interphase (SEI) on the lithium metal anode, underscoring the need for careful selection of metal-iodine combinations. Iodine ions can suppress the polysulfide shuttle effect by increasing the electrolyte's viscosity through ether solvent polymerization, but this also hampers lithium-ion movement, affecting battery performance. Some metal iodides can form alloy phases with lithium, enhancing SEI stability. The type and amount of metal iodide additive significantly impact the battery's electrochemical

performance, with LiI and  $\text{MgI}_2$  showing high ionic conductivity and appropriate viscosity levels. The chemical reactivity of the metal iodide additive is crucial for controlling polysulfide diffusion and stabilizing the lithium metal surface. Further investigation into LiI's specific mechanisms revealed that it facilitates lithium-ion movement within the SEI layer, promoting a more porous and stable interphase on the lithium metal anode. This porous structure improves lithium-ion mobility, reduces transport limitations, and enhances cycling stability by potentially reducing dendrite formation. These positive effects were confirmed through the performance of Li||Li symmetrical cells. When LiI is added to the electrolyte in such a cell, it exhibits exceptional long-term cycling stability, lasting for 2000 hours. Additionally, the cell demonstrates a low hysteresis voltage of 57 mV at a current density of  $0.5 \text{ mA cm}^{-2}$ . These results highlight the effectiveness of LiI in promoting a stable and functional SEI layer for lithium metal anodes. Beyond LiI, other lithium halide salts are being explored as potential SEI additives. These include lithium fluoride (LiF),<sup>97</sup> lithium chloride (LiCl),<sup>98</sup> and lithium bromide (LiBr)<sup>57</sup> (Fig. 4(e)). Research suggests that these lithium halides can also form stable components within the SEI layer through chemical or electrochemical reactions between the lithium metal anode and the electrolyte. This opens up possibilities for further optimization of the SEI for improved battery performance. The positive influence of lithium halide additives is further emphasized by the work of F. Wu *et al.* They reported that adding lithium iodide (LiI) to the electrolyte in Li-S cells led to extended cycle life. This improvement is attributed to the formation of protective layers containing iodine on both the anode and cathode sides of the battery. These layers help to suppress the "polysulfide shuttle effect", a major challenge in Li-S batteries, by limiting the movement of dissolved sulfur compounds.<sup>101</sup>

A promising advancement in Li-S batteries involves using lithium bromide (LiBr) as an additive. This study shows that LiBr can promote the formation of a robust and lithium-ion permeable cathode electrolyte interphase (CEI) on the cathode. This process requires pre-cycling the sulfur cathode at high potentials, which is believed to oxidize bromide ions ( $\text{Br}^-$ ) in the electrolyte, generating DME ( $^{\cdot}\text{H}$ ) radicals. These radicals contribute to the polymerization of the electrolyte components, forming a protective layer on the cathode surface. The resulting CEI is a strong and stable layer, effectively shielding the cathode from detrimental reactions with the electrolyte and polysulfide shuttling, while also being permeable to lithium ions, allowing efficient battery operation.<sup>57</sup>

One promising additive for the anode is indium(III) iodide ( $\text{InI}_3$ ). As reported by Jiang *et al.*,  $\text{InI}_3$  acts as a bifunctional additive, meaning it benefits both the anode and the cathode in Li-S batteries, preferentially depositing on the lithium metal anode during initial charging to create a protective layer that shields it from polysulfide corrosion (refer to Fig. 4(a and b) for a visual representation).<sup>58,99</sup>

While  $\text{InI}_3$  offers advantages for the anode, other additives are being investigated to improve the overall performance of Li-S batteries. One such example is silicon tetrachloride ( $\text{SiCl}_4$ ). Research by Archer *et al.* explores the use of  $\text{SiCl}_4$  as an additive to create a unique type of SEI layer on the electrode surface,<sup>102</sup> this SEI layer is a hybrid, combining organic and inorganic components. Notably, the organic component features silicon-linked oligomer films. Another promising approach for the anode involves the use of thionyl chloride ( $\text{SOCl}_2$ ). Recent research suggests that  $\text{SOCl}_2$ , when added to an electrolyte composed of 1.0 M  $\text{LiPF}_6$  in PC/EC/DEC (1/4/5, volume ratio), can react with lithium metal to form a unique and beneficial SEI layer. This SEI layer is rich in lithium chloride (LiCl). This layer not only suppresses dendrite growth but also acts as a barrier

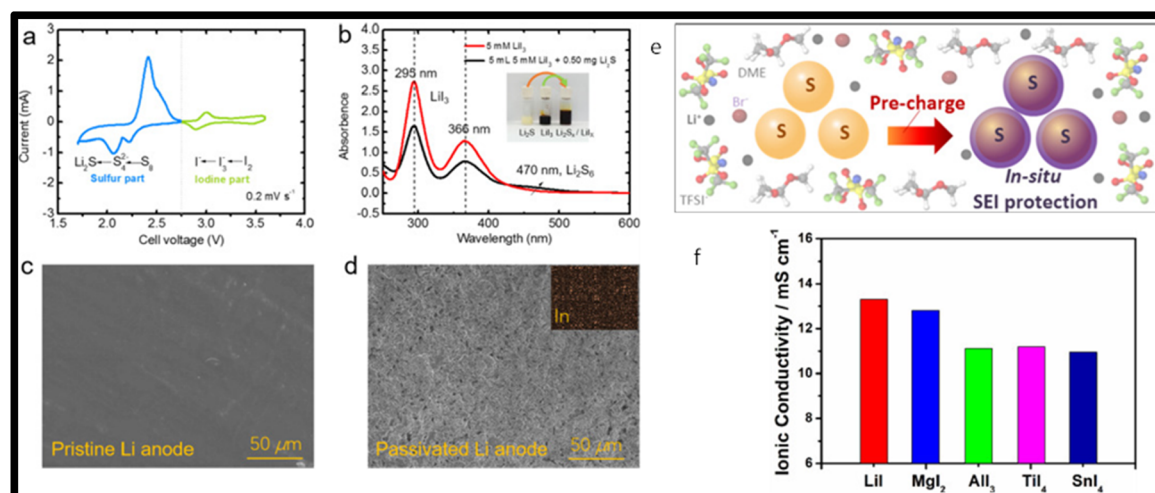


Fig. 4 (a) Cyclic voltammetry (CV) of Li-S battery with the addition of  $\text{InI}_3$ ; (b) UV-Vis spectra of the 5 mM  $\text{LiI}_3$  in DME solution and the mixture of 5 mM  $\text{LiI}_3$  + 0.50 mg  $\text{Li}_2\text{S}$  in DME, the inset shows the photograph of  $\text{Li}_2\text{S}$  suspension ( $0.20 \text{ mg mL}^{-1}$  in DME), 10 mM  $\text{LiI}_3$  in DME solution and their mixture. (c) Pristine Li anode; (d) passivated Li anode with the deposited In layer.<sup>99</sup> (e) The concept showing *in situ* SEI protection on S cathodes induced by LiBr and pre-charge,<sup>57</sup> (f) ionic conductivities of 1 M LiTFSI in DME/DOL with an additive of 3000 ppm LiI,  $\text{MgI}_2$ ,  $\text{AlI}_3$ ,  $\text{TiI}_4$ , or  $\text{SnI}_4$ .<sup>100</sup>



between the electrolyte and the lithium metal, reducing unwanted reactions. By promoting the formation of this functional and protective SEI layer,  $\text{SOCl}_2$  as additive holds promise for improving the safety and stability of the lithium metal anode in Li-S batteries.<sup>103</sup> Beyond promoting a stable SEI layer,  $\text{SOCl}_2$  offers an additional advantage. During its breakdown, excess active sulfur is produced. This excess sulfur can contribute to the battery's overall capacity, potentially offsetting the gradual loss of active sulfur from the cathode during battery operation. The net effect can be a partially self-healing cathode with improved capacity retention.

While  $\text{SOCl}_2$  addresses the anode, other additives target the cathode and overall battery performance. One such example is tetrapotassium heptafluorobismuthate ( $\text{K}_4\text{BiF}_7$ ). Research by Tu *et al.* explored the use of  $\text{K}_4\text{BiF}_7$  as an additive to modify the electrolyte.<sup>104</sup> This additive appears to influence the formation of the SEI layer in a unique way. The  $\text{K}_4\text{BiF}_7$  additive is reported to promote the creation of an SEI layer with a particular "mosaic-like and dendrite-free morphology". This suggests a well-formed and stable SEI structure that can effectively prevent dendrite growth. Furthermore, the  $\text{K}_4\text{BiF}_7$ -modified electrolyte exhibited enhanced performance across different battery types, including Li||Li symmetrical cells (cells with identical electrodes), Li||Cu cells (cells with lithium metal anode and copper cathode), and even Li-S batteries. This indicates that  $\text{K}_4\text{BiF}_7$  may offer broader positive effects on the overall electrochemical performance of various battery systems.

In conclusion, both  $\text{SOCl}_2$  and  $\text{K}_4\text{BiF}_7$  represent valuable advancements in Li-S battery technology.  $\text{SOCl}_2$  promotes a stable and protective SEI layer on the anode, while  $\text{K}_4\text{BiF}_7$

contributes to the formation of a highly  $\text{Li}^+$  conductive SEI layer that benefits overall battery performance. These ongoing research efforts hold promise for the development of safer, more stable, and higher-performing Li-S batteries.

**2.1.3. Lithium polysulfides.** The quest for improved lithium-sulfur (Li-S) batteries involves a multifaceted approach. One key challenge is ensuring compatibility between the lithium metal anode and the electrolyte. Traditionally, researchers have focused on mitigating the negative effects of dissolved lithium polysulfides ( $\text{Li}_2\text{S}_x$ ) on the anode, considered detrimental to the lithium metal anode. However, recent studies suggest a surprising possibility:  $\text{Li}_2\text{S}_x$  themselves can act as additives to enhance the compatibility of the electrolyte with the lithium metal anode.<sup>105,106</sup> The  $\text{Li}_2\text{S}_x$  additive facilitates the formation of a double-layered SEI structure on the lithium anode surface, as illustrated in Fig. 5 by Xiong *et al.*'s study. The outer layer consists of decomposition products originating from the lithium salt ( $\text{LiTFSI}$ ) in the electrolyte due to direct contact with the lithium anode. The inner layer, composed of lithium sulfide ( $\text{Li}_2\text{S}$ ), is generated through the reaction between the  $\text{Li}_2\text{S}_x$  additive and the lithium metal anode. This dual-layer SEI structure offers significant advantages. It effectively hinders the further decomposition of the lithium salt on the lithium anode, enhancing stability and contributing to a longer lifespan and better cycling performance for the battery. The SEI layer also acts as a protective barrier, shielding the lithium metal anode from unwanted reactions with the electrolyte, which reduces degradation and improves the overall stability of the anode.<sup>109</sup> However, while the inner layer effectively prevents continuous anode reaction with  $\text{LiTFSI}$ , the surface film alone does not fully

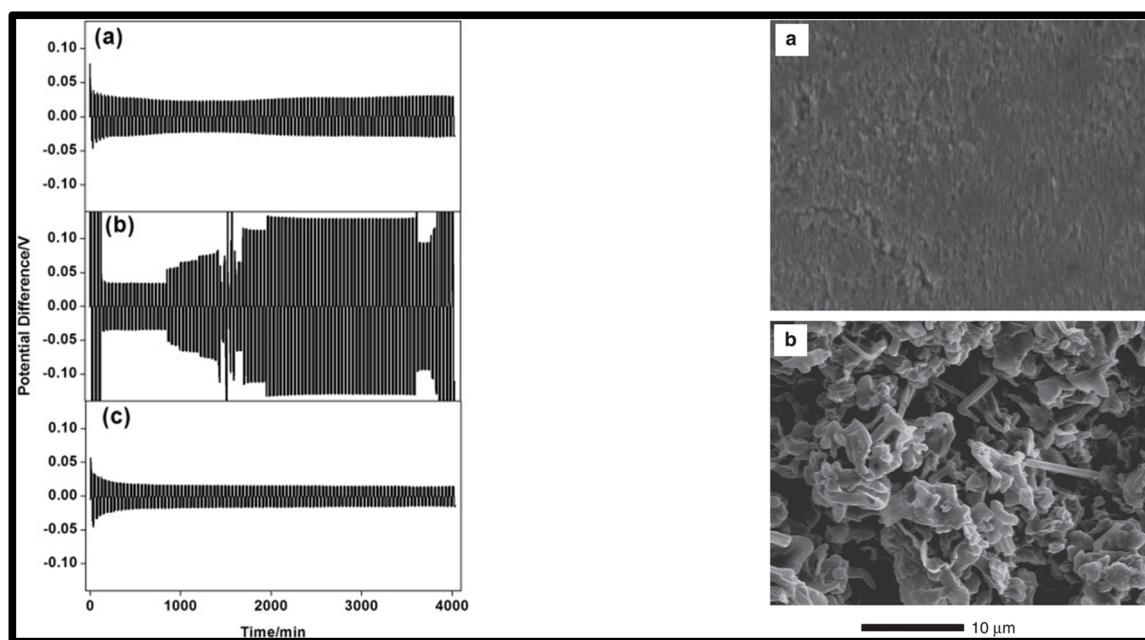


Fig. 5 (Left) Cycling behaviour of a symmetrical cell with the electrolytes (a) 0.2 M  $\text{Li}_2\text{S}_6$ /DIOX/DME (1 : 1, v/v), (b) 0.2 M  $\text{LiNO}_3$ /DIOX/DME (1 : 1, v/v) and (c) 0.1 M  $\text{LiNO}_3$ /0.1 M  $\text{Li}_2\text{S}_6$ /DIOX/DME (1 : 1, v/v).<sup>107</sup> (Right) SEM images of the top surface of the deposited lithium (edge region) after 100 cycles of charge/discharge at  $2 \text{ mA cm}^{-2}$  using electrolyte (a) with the addition of both  $\text{Li}_2\text{S}_8$  (0.18 M) and  $\text{LiNO}_3$  (5 wt%), and (b) with the addition of only  $\text{LiNO}_3$  (5 wt%) at a deposition capacity of  $2 \text{ mA h cm}^{-2}$ .<sup>108</sup>



prevent the  $\text{Li}_2\text{S}_x$  shuttle. Consequently, the introduction of  $\text{Li}_2\text{S}_x$  as a co-additive, in conjunction with lithium nitrate ( $\text{LiNO}_3$ ), becomes essential for comprehensive lithium anode protection. A synergistic effect is observed between these co-additives, resulting in the formation of a stable and uniform SEI layer on the lithium surface. This significantly reduces electrolyte decomposition and also inhibits the growth of lithium dendrites.<sup>110</sup> Zhang *et al.* also demonstrated that the combination of  $\text{LiTFSI-LiNO}_3\text{-Li}_2\text{S}_5$  facilitates the formation of a dense SEI layer. This compact SEI layer plays a crucial role in achieving a dendrite-free anode and enhancing coulombic efficiencies.<sup>59</sup> Lithium polysulfides (LiPS) have also found extensive use as an electrolyte additive in Li-S batteries when present in a LiPS- $\text{LiNO}_3$ -containing ether-based electrolyte. An electrolyte comprising 0.020 M  $\text{Li}_2\text{S}_5$  (equivalent to 0.10 M sulfur) and 5.0 wt%  $\text{LiNO}_3$  has the capability to spontaneously generate a stable inorganic layer *in situ*, providing protection for the lithium metal anode. However, when the concentration of polysulfides exceeds 0.50 M sulfur in the organic electrolyte, the *in situ* formed SEI struggles to maintain stability, leading to gradual etching of the lithium metal.<sup>111</sup> Cui *et al.* utilized a combination of lithium polysulfide ( $\text{Li}_2\text{S}_8$ ) and  $\text{LiNO}_3$  as additives in an ether-based electrolyte. This combination was employed to create a stable and uniform SEI layer. The resulting SEI layer effectively prevents dendrite growth and minimizes electrolyte decomposition.<sup>112</sup>

The discovery of  $\text{Li}_2\text{S}_x$  as a beneficial additive represents a fascinating twist in Li-S battery research. By leveraging these additives and the resulting SEI layer formation, researchers are making significant strides towards creating more stable and durable Li-S batteries.

Lithium polysulfides (LiPSs) exhibit limited solubility in carbonate esters, but their high reactivity can lead to nucleophilic addition or substitution reactions with these esters, resulting in the loss of active sulfur species, which degrades battery capacity and performance.<sup>113</sup> Consequently, ether-based electrolytes are preferred in lithium-sulfur (Li-S) batteries, where lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) serves as the source of  $\text{Li}^+$  ions, and a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) is used as the solvent for LiTFSI. To minimize the dissolution of polysulfides into the electrolyte and thereby enhance battery stability, several approaches have been explored, including strategies to prevent LiPS dissolution, alteration of the reaction pathway of LiPSs, and regulate electrolyte concentration to control polysulfide behavior effectively.

Fluorination significantly reduces polysulfide solubility, primarily because the fluorine atoms hinder oxygen's electron-donating capability within the electrolyte. This reduced donor-ability limits interactions with polysulfides, thereby decreasing their solubility.<sup>114</sup> Wang *et al.* effectively minimized the solubility of lithium polysulfides (LiPSs) by incorporating an inert fluoroalkyl ether, specifically 1*H*,1*H*,5*H*-octafluoropentyl-1,1,2,2-tetrafluoroethyl ether (OFE), into a LiFSI/DME electrolyte system. This addition of OFE reduced LiPS dissolution, enhancing the electrolyte's stability.<sup>115</sup> Batteries assembled with the addition of OFE in the LiFSI/DME electrolyte show enhanced

performance. Additionally, the fluorinated ether solvents help mitigate the polysulfide shuttle effect by forming a lithium fluoride (LiF)-rich solid electrolyte interphase (SEI) layer on the lithium metal surface, which stabilizes the anode and minimizes active material loss.<sup>116</sup> An alternative strategy to mitigate this issue is to alter the sulfur reaction pathway, thereby preventing the formation of long-chain LiPSs responsible for the shuttle phenomenon. For instance, Wang *et al.* added dimethyl disulfide (DMDS) to a 1 M LiTFSI solution in DOL/DME, effectively modifying the sulfur reaction pathway and minimizing LiPS formation. This approach offers a promising route to stabilize sulfur reactions and enhance the performance of lithium-sulfur batteries.<sup>117</sup> As the content of DMDS in the electrolyte increases, the high-voltage discharge plateau at 2.4–2.3 V, typically associated with the reduction of solid  $\text{S}_8$  to soluble polysulfides, disappears. This absence is accompanied by a change in the electrolyte colour, indicating that no soluble polysulfides are formed during discharge. *Operando* proton nuclear magnetic resonance (NMR) analysis further confirms that the reduction of solid sulfur results in the formation of soluble dimethyl polysulfide species, which subsequently react to form lithium organosulfides and  $\text{Li}_2\text{S}$ . In a different approach, Goodenough *et al.* demonstrated that the use of bis(4-nitrophenyl)carbonate (BNC), a highly polar additive, effectively mitigates the shuttle effect. In their study, BNC reacts with soluble polysulfides to produce an insoluble sulfide complex and lithium 4-nitrophenolate, thus limiting the migration of polysulfides within the cell.<sup>71</sup> Leveraging the shuttle-free characteristic, the sulfur cathode with the BNC-added electrolyte demonstrates an exceptionally high coulombic efficiency ( $\approx 100\%$ ) at a sulfur loading of  $1.4 \text{ mg cm}^{-2}$ .

**2.1.4. Organic functional group additives (polymers, oligomers, sulfides).** In a recent publication, Wu *et al.* investigated the application of biphenyl-4,4'-dithiol (BPD) as an electrolyte additive in Li-S batteries to improve their cycling stability. Their findings revealed the formation of BPD-short chain lithium polysulfide complexes ( $\text{BPD-S}_x^{2-}$ ; where  $x$  ranges from 1 to 4) during charge-discharge processes. As shown in Fig. 5, these complexes not only modulated the reaction rates of short-chain polysulfide formation but also suppressed their dissolution, leading to enhanced battery performance.<sup>60</sup>

Ming *et al.* investigated the use of redox-active species, such as  $\text{Li}_2\text{S}_8$  polysulfides, within the electrolyte, which demonstrated significantly reduced polarization and enhanced stability. The dissociated  $\text{Li}^+/\text{S}_x^{2-}$  ions notably accelerated lithium-ion diffusion.<sup>118</sup> Additionally, the group employed a polysulfide-modified electrolyte in combination with a polyethersulfone (PES) polymeric binder, which further improved ion transport and effectively mitigated the polysulfide shuttle effect.<sup>119</sup> Huang *et al.* employed 3,5-bis(trifluoromethyl)thiophenol (BTB) as an electrolyte additive to promote lithium anode stabilization, as demonstrated in Fig. 6. The active sulfhydryl group in BTB reacts with lithium metal, leading to the formation of organic Ph-S-moieties within the solid electrolyte interphase (SEI). This organosulfur-rich SEI serves as a protective layer for the lithium anode by suppressing undesirable side reactions with lithium polysulfides. Consequently, this mitigates the consumption of both fresh lithium and electrolyte.<sup>61</sup>





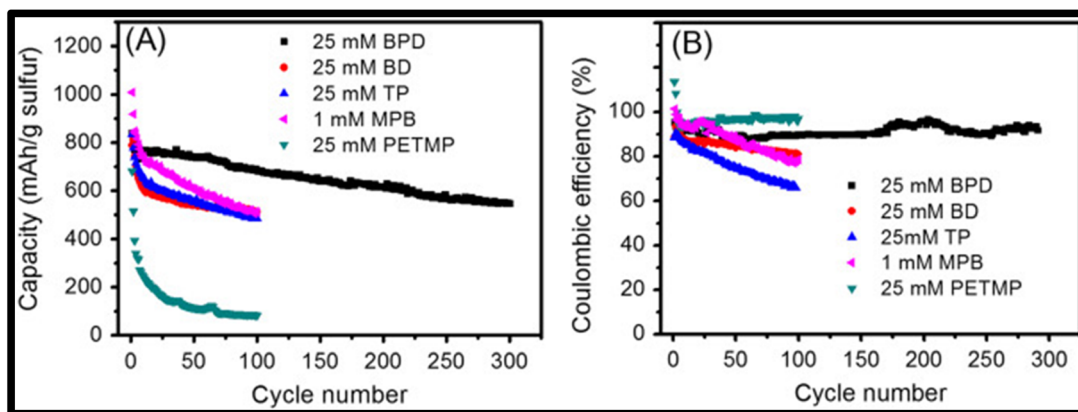


Fig. 6 The evaluated cycling performance including the (A) discharge capacity and (B) coulombic efficiency of the sulfur-carbon cathode with different thiol-based additives at the rate of 0.1C (based on the weight of sulfur-carbon cathode). The additives tested were biphenyl-4,4'-dithiol (BPD), benzene-1,4-dithiol (BD), thiophenol (TP), 1,4-bis(4-mercaptophenyl)benzene (MPB), and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP).<sup>60</sup>

In 2017, Kim *et al.* described a composite solid electrolyte interphase (SEI) fabricated *via* the concurrent deposition of organic molecules (organosulfides and organopolysulfides) and inorganic components ( $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ ) using poly(sulfur-random-triallylamine) (PST). The incorporation of organic components functions as a mobility enhancer, augmenting the combined elastic and viscous behavior (viscoelasticity) of the SEI, thereby promoting its flexibility and stability. Concomitantly, the inorganic components offer a pathway for Li-ion conduction and impart the requisite mechanical strength to the SEI layer.<sup>103</sup> Zhang *et al.* introduced the concept of a “sulfur container” for direct manipulation of lithium polysulfides within the cathode, employing di(tri)sulfide polyethylene glycol ( $\text{PES}_n$ ).<sup>70</sup>  $\text{PES}_n$  features grafted (di/tri)sulfide groups on both ends of its polyether chains, enabling reversible capture and release of sulfur species *via* chain extension and shortening, respectively. This approach transforms soluble polysulfides in the electrolyte into bulkier organosulfur species confined by the sulfur container (S container). This confinement effectively suppresses polysulfide dissolution and migration, leading to improved battery performance. As a result, the authors observed an increase in the initial capacity of Li-S cells from  $833 \text{ mA h g}^{-1}$  to  $1009 \text{ mA h g}^{-1}$  at 0.5C with  $\text{PES}_n$ , and a high capacity of  $748 \text{ mA h g}^{-1}$  was maintained after 100 cycles.

Building upon the concept of SEI (solid electrolyte interphase) modification, a recent study by Guo *et al.*, described 1,3,5-benzenetrithiol (BTT) as an electrolyte additive that facilitates the formation of a dual stable SEI on both the cathode and anode surfaces. This unique SEI is generated through *in situ* interfacial electrochemical/chemical reactions, promoting exceptional cycling stability. The BTT-derived SEI on the anode surface facilitates reversible lithium stripping/deposition processes. Notably, BTT also interacts with sulfur on the cathode, leading to the formation of an oligomeric/polymeric SEI layer. This modification alters the sulfur redox pathway and effectively hinders the detrimental “sulfur shuttle effect” (Fig. 7).<sup>62</sup>

**2.1.5. Other additives.** In their exploration of functional electrolyte additives for Li-S batteries, Liang *et al.* investigated the application of phosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ). Their research highlighted the dual function of  $\text{P}_2\text{S}_5$ : enhancing  $\text{Li}_2\text{S}$  dissolution and mitigating lithium metal corrosion.<sup>63</sup>  $\text{P}_2\text{S}_5$  promotes the dissolution of lithium sulfide ( $\text{Li}_2\text{S}$ ), a crucial intermediate product in Li-S batteries, thereby alleviating capacity loss associated with  $\text{Li}_2\text{S}$  precipitation. Furthermore,  $\text{P}_2\text{S}_5$  reacts with the lithium metal surface to form lithium tetrathiosulfide ( $\text{Li}_3\text{PS}_4$ ) as a primary component. This passivation layer effectively suppresses the polysulfide shuttle phenomenon, contributing to a high coulombic efficiency exceeding 98% during the initial 20 cycles.<sup>63</sup> Despite their high ionic conductivity and favorable electrode contact, ether-based electrolytes in Li-S batteries suffer from the dissolution of intermediate polysulfides. To address this challenge and prevent lithium metal anode degradation, the incorporation of suitable additives is essential.<sup>121</sup> Gewirth *et al.* investigated the influence of water ( $\text{H}_2\text{O}$ ) on the Li-S battery SEI (solid electrolyte interphase).<sup>64</sup> Their findings revealed that incorporating 250 ppm  $\text{H}_2\text{O}$  into the electrolyte promoted the formation of  $\text{LiOH}$  within the SEI, which shielded the lithium metal anode from degradation caused by polysulfides. This approach facilitated stable charge-discharge behavior. However, the researchers also noted that  $\text{H}_2\text{O}$  consumption during cycling has detrimental effects on the long-term stability of Li-S batteries.<sup>64</sup> An alternative strategy for Li-S battery anode protection involves the development of a LiF (lithium fluoride)-rich SEI film, as demonstrated by Ni *et al.* This passivation layer effectively hinders polysulfide shuttling, thereby preventing the formation of an insulating layer composed of  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  on the lithium anode surface. Consequently, this LiF-rich SEI film contributes to superior lithium anode stability.<sup>122</sup> Complementing the findings of Ni *et al.*, Wu *et al.* explored the application of lithium difluoro(oxalato)borate ( $\text{LiODFB}$ ) as an additive in the conventional 1.0 M LiTFSI DOL/DME electrolyte for Li-S batteries.<sup>65</sup> Their research revealed that incorporating



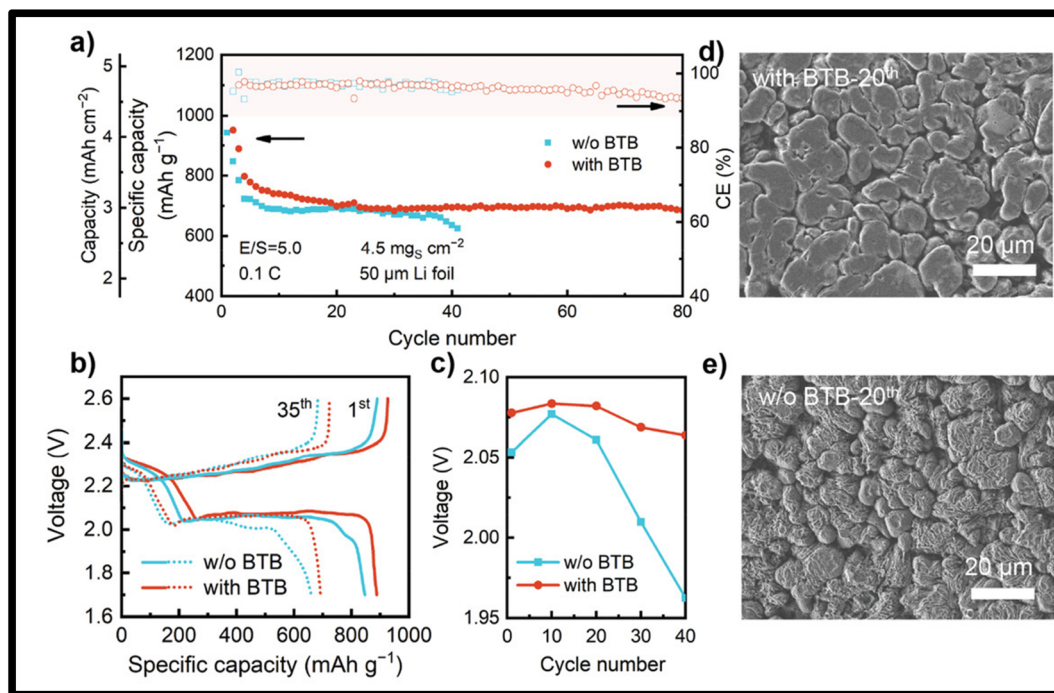


Fig. 7 The electrochemical performance of Li-S batteries and the corresponding Li deposition morphology. (a) The cycling performance of Li-S batteries at 0.1C under practical conditions with a high loading S cathode (4.5 mg S cm<sup>-2</sup>), a low E/S ratio (5.0 μL mg S<sup>-1</sup>), and an ultrathin Li anode (50 μm). 2% LiNO<sub>3</sub> additive was used in both electrolytes. (b) The galvanostatic discharge-charge profiles at the 1st and the 35th cycle. (c) The discharge voltage at the 80% of discharge capacity at different cycles. The SEM images of the cycled Li anode with (d) and without (e) BTB additive in Li-S batteries after the 20th cycle.<sup>120</sup>

an optimal concentration of LiODFB facilitates the formation of a LiF-rich passivation layer on the lithium metal anode surface. This LiF-rich SEI film significantly enhances battery performance by promoting exceptionally high coulombic efficiency and improved cycle life.<sup>65</sup> A recent innovation in Li-S battery technology involves the utilization of boron nitride nanosheets (BNNs) as an electrolyte additive [ref. for recent development]. This novel strategy offers the advantage of autonomous and continuous flattening of lithium (Li) deposits during plating and stripping processes. This self-regulating characteristic effectively accommodates volume changes associated with Li cycling, leading to improved battery stability. The boron atoms within BNNs act as Lewis acid sites, facilitating interactions with Lewis basic anions present in the electrolyte. This interaction helps to regulate the Li<sup>+</sup> ion concentration gradient, promoting more uniform and controlled lithium deposition. Li-S batteries incorporating BNNs in the electrolyte demonstrated exceptional electrochemical performance, achieving reversible capacities of 574 mA h g<sup>-1</sup> at a high current rate (2C). Notably, even under harsh conditions, such as sub-zero temperatures (-20 °C) and a low current rate (0.1C), these batteries retained a significant portion (43.3%) of their room-temperature capacity, highlighting their potential for wider operational ranges.<sup>66</sup> Another electrolyte additive researchers have explored, is the application of fluorinated ether 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) as an electrolyte additive.<sup>67</sup> TTE is believed to promote the formation of a compact, smooth, and homogeneous surface layer on the

lithium anode surface.<sup>67</sup> This favorable morphology is expected to enhance the stability of the electrode-electrolyte interface and mitigate detrimental side reactions during battery operation.<sup>67</sup> Fluorinated ether-based electrolytes have emerged as a promising strategy to address the limitations of conventional electrolytes in lithium-sulfur (Li-S) batteries. Compared to traditional electrolytes, these novel electrolytes demonstrably enhance both cell capacity and cycling stability.<sup>123</sup> This improvement stems from their influence on the reaction mechanism within the battery. Fluorinated ether-based electrolytes effectively reduce the solubility and diffusion of lithium polysulfides, a key challenge in Li-S batteries. Consequently, the problematic "shuttle effect" of polysulfides is suppressed, leading to significantly improved overall electrochemical performance.<sup>123</sup> Building upon the promise of fluorinated ether electrolytes like TTE, researchers have explored the synergistic effects of co-additives. One such example involves tetrabutylammonium iodide (TBAI, [Bu<sub>4</sub>N]<sup>+</sup>I<sup>-</sup>). The lipophilic nature of the TBA<sup>+</sup> cation allows it to effectively transport iodide anions (I<sup>-</sup>) within the concentrated electrolyte. This *in situ* generation of iodine (I<sub>2</sub>) facilitates the removal of sulfur deposits on the lithium surface, thereby promoting anode stability and improved battery performance.<sup>124</sup> Armand *et al.* investigated the application of lithium azide (LiN<sub>3</sub>) as an electrolyte additive in Li-S batteries.<sup>68</sup> Their research revealed that LiN<sub>3</sub> promotes the formation of thin and compact lithium nitride (Li<sub>3</sub>N) layers on the lithium anode surface. This process is believed to involve the oxidation of LiN<sub>3</sub> at the cathode, leading to the generation of



nitrogen gas ( $N_2$ ).<sup>68</sup> The  $N_2$  gas then migrates to the anode and reacts with lithium metal to form the beneficial  $Li_3N$  layer. The study reports that incorporating 2 wt%  $LiN_3$  in the electrolyte significantly improves cycling stability and enhances the utilization of active sulfur within the battery.<sup>68</sup> These findings are further supported by the effectiveness of pre-formed artificial  $Li_3N$  passivation layers applied directly to anodes, demonstrating their ability to protect lithium and suppress polysulfide shuttling.<sup>125</sup> The effectiveness of  $LiN_3$  as an additive can be partially attributed to the properties of lithium nitride ( $Li_3N$ ) itself.  $Li_3N$  possesses high lithium-ion conductivity (approximately  $10^{-3} \text{ S cm}^{-1}$ ).<sup>126</sup> This property could potentially facilitate lithium-ion transport within the SEI layer formed by the  $Li_3N$ . Additionally, independent research by Zu *et al.*,<sup>69</sup> has explored the application of copper acetate ( $Cu(CH_3COO)_2$ ) as an electrolyte additive for Li-S batteries. Their work highlights the formation of a protective SEI film containing copper sulfides ( $CuS/Cu_2S$ ) on the lithium anode surface *via in situ* chemical reactions between the electrolyte and  $Cu(CH_3COO)_2$ . This SEI layer serves to safeguard the lithium metal from detrimental interactions with polysulfides and organic electrolyte components.<sup>69</sup> While the mechanism of action for  $LiN_3$  differs from  $Cu(CH_3COO)_2$ , both additives demonstrate the potential for engineered SEI layers to improve stability in Li-S batteries.

## 2.2. Dendrite suppression

The emergence of lithium-sulfur (Li-S) batteries as high-capacity energy storage devices is hindered by the detrimental phenomenon of lithium metal dendrite growth during cycling. These lithium protrusions can penetrate the separator, leading to catastrophic battery failure through internal short circuits and posing significant safety hazards. Additionally, dendrite formation consumes active lithium metal and disrupts uniform lithium plating/stripping processes, ultimately degrading battery performance and lifespan. To address this challenge, researchers have actively explored the incorporation of various electrolyte additives to suppress dendrite growth in Li-S batteries. The synergistic effect of combining  $CsNO_3$  and  $KNO_3$  in Li-S battery electrolytes has been investigated to address lithium dendrite growth.<sup>127</sup> This approach leverages the unique properties of both  $NO_3^-$  anions and non-lithium alkali cations ( $Cs^+$  and  $K^+$ ). The  $NO_3^-$  anions are believed to facilitate the formation of protective layers containing  $LiNO_x$  compounds on the lithium anode surface.<sup>127</sup> These layers can shield the anode and suppress dendrite growth. Furthermore, the study suggests that low concentrations of  $Cs^+$  and  $K^+$  cations play a role in hindering the self-healing electrostatic shield mechanism, which can contribute to dendrite formation.<sup>127</sup> It is important to note that this strategy of manipulating lithium deposition behavior and utilizing cations for electrostatic shielding is not unique to  $CsNO_3$ - $KNO_3$  mixtures. Similar effects have been observed with other nitrate additives, such as  $CsNO_3$  alone<sup>128</sup> and  $NaNO_3$ ,<sup>129</sup> suggesting a broader applicability of nitrate-based additives for dendrite suppression in Li-S batteries. Studies by Liu<sup>55</sup> and Jin *et al.*<sup>130</sup> explored the application of  $La(NO_3)_3$  as an electrolyte additive in Li-S batteries. This

additive is believed to transform into lanthanum sulfides *in situ*, generating a protective coating on both the lithium anode and sulfur cathode surfaces. This coating is hypothesized to facilitate smoother lithium deposition and enhance the chemical adsorption of lithium polysulfides, potentially improving battery performance. Building upon this concept, Jia *et al.*<sup>54</sup> investigated the effectiveness of various nitrate salts ( $KNO_3$ ,  $LiNO_3$ ,  $NaNO_3$ , and  $CsNO_3$ ) as electrolyte additives in Li-S batteries. Their research suggests that  $KNO_3$  and  $LiNO_3$  exhibit superior performance compared to  $NaNO_3$  and  $CsNO_3$  in terms of achieving higher coulombic efficiencies. While the specific mechanism of action for these nitrates is not mentioned in the provided text, their findings highlight the potential of nitrate additives for enhancing Li-S battery performance, possibly through a combination of effects on lithium deposition and polysulfide interactions. Jia *et al.*'s study<sup>54</sup> attributed the lower coulombic efficiencies observed with  $NaNO_3$  and  $CsNO_3$  compared to  $KNO_3$  and  $LiNO_3$  to their higher impedance. This suggests that  $NaNO_3$  and  $CsNO_3$  may hinder efficient charge transfer within the battery, potentially limiting performance. The research also suggests that KI (0.1 M) is not as effective as  $KNO_3$  (0.1 M) in reinforcing the SEI layer.<sup>54</sup> Furthermore, the text raises a critical concern regarding the use of  $MnO_3$  (metal nitrate) additives. While the specific metal (M) is not mentioned, the text highlights that  $MnO_3$  is slowly consumed on lithium metal anodes during cycling, potentially compromising its protective effect over time. More importantly, the strong oxidizing properties of  $MnO_3$  pose safety risks, including Li-S pouch cell swelling at high temperatures. These drawbacks necessitate careful consideration when evaluating  $MnO_3$  additives for Li-S batteries. The text concludes by mentioning fluoroethylene carbonate (FEC) as a commonly used and effective electrolyte additive. FEC is known for its ability to create a stable SEI layer on lithium metal anodes, promoting uniform lithium deposition and enhancing battery performance.<sup>131</sup> The solid electrolyte interphase (SEI) layer plays a crucial role in reducing dendrite formation and enhancing the cycling stability of Li-S batteries. Building upon the success of carbonate-based additives like FEC, researchers have explored other promising candidates. Vinylene carbonate (VC) is another carbonate-based additive that has been demonstrated to enhance the stability of the solid electrolyte interphase (SEI) layer formed on lithium metal anodes.<sup>132</sup> This robust SEI layer plays a crucial role in suppressing the growth of lithium dendrites, ultimately contributing to improved safety and performance characteristics of Li-S batteries. Trimethyl phosphate (TMP) represents a distinct approach to dendrite suppression. Unlike additives that influence the SEI layer, TMP exhibits a direct effect on dendrite formation. Studies suggest that TMP facilitates the formation of a protective layer on the lithium surface, physically hindering the growth of dendrites.<sup>133</sup> This translates to enhanced safety and extended battery lifespan due to reduced dendrite formation. Lithium bis(oxalato)borate (LiBOB) offers yet another strategy for dendrite mitigation in Li-S batteries. This boron-based additive functions by improving the stability of the existing SEI layer, consequently mitigating the formation of lithium dendrites on the lithium anode.<sup>134</sup> This enhanced



stability contributes to improved safety and performance in Li-S batteries.

### 2.3. Strategies to suppress polysulfide dissolution and shuttling in Li-S batteries

The long-term cyclability of Li-S batteries is plagued by a critical phenomenon known as the “shuttle effect.” This process wreaks havoc on the battery’s performance over repeated cycles. During discharge and charge, the “shuttle effect” leads to a depletion of active materials. Soluble lithium polysulfides, formed during discharge, dissolve into the electrolyte. These polysulfides may not readily participate in the subsequent charge cycle, effectively reducing the amount of active sulfur available for storing energy. Additionally, the “shuttle effect” contributes to the irreversible corrosion of the lithium anode. Dissolved polysulfides can migrate towards the anode and undergo unwanted reduction reactions. This not only consumes lithium metal but also forms insoluble lithium sulfide products that accumulate on the anode surface. Over time, this process degrades the anode and hinders battery performance.

To effectively overcome the “shuttle effect” and unlock the full potential of Li-S batteries, researchers require a multifaceted approach. A comprehensive understanding of several key aspects is crucial. First, elucidating the detailed mechanism by which sulfur undergoes reduction and oxidation during discharge and charge cycles (sulfur redox mechanism) is essential for optimizing electrode design and promoting efficient utilization of active materials. Second, understanding the factors governing the breakdown of higher-order polysulfides into lower-order forms (disproportionation reactions of lithium polysulfides) is critical. Ideally, these reactions should be controlled to favor the formation of less soluble polysulfides, thereby minimizing their migration within the battery. Finally, a thorough grasp of how lithium polysulfides dissolve and migrate through the electrolyte (lithium polysulfide transport in the electrolyte) is necessary for developing strategies to confine them within the cathode region and prevent their detrimental interaction with the anode. By gaining in-depth knowledge of these fundamental processes, researchers can develop strategies to mitigate the “shuttle effect” and unlock the full potential of Li-S batteries for long-lasting and high-performance energy storage applications. The presence of highly reactive lithium polysulfides in Li-S batteries poses a significant challenge. These intermediate species can dissolve into the electrolyte and migrate throughout the cell, leading to a phenomenon known as the “shuttle effect”. This process contributes to capacity fade, hinders cycle life, and can even compromise battery safety.<sup>135–139</sup> Therefore, effective management of polysulfide dissolution and diffusion within the electrolyte is critical for achieving optimal Li-S battery performance.

Researchers have explored various strategies to address this challenge. One promising approach involves the use of thiol-based electrolyte additives. Biphenyl-4,4'-dithiol (BPD) is an example of such an additive, and studies suggest it improves capacity retention in Li-S batteries by effectively regulating polysulfide dissolution.<sup>140,141</sup> This improvement is believed to be

primarily due to the formation of stable complexes between BPD and lithium polysulfides. These complexes can help to reduce the free diffusion of polysulfides within the electrolyte, thereby mitigating the detrimental effects of the “shuttle effect”. Another approach utilizes additives like bis(4-nitrophenyl) carbonate (BNC). BNC interacts with soluble  $\text{Li}_2\text{S}_x$  polysulfides, promoting their conversion into insoluble forms.<sup>71</sup> This transformation effectively traps the polysulfides within the cathode region, minimizing their interaction with the lithium anode. Furthermore, the byproduct generated during this reaction can contribute to the formation of a protective layer on the lithium anode surface. This layer can act as a proficient lithium-ion conductor, facilitating efficient lithium plating and stripping processes while maintaining low interfacial impedance. Researchers are continuously exploring novel strategies to address the polysulfide issue in Li-S batteries. Beyond thiol-based additives, alternative approaches are emerging that target both polysulfide capture and improved cell performance. One such approach utilizes aluminium phosphate ( $\text{AlPO}_4$ ) as a bifunctional additive.<sup>72</sup> won Lee *et al.* reported that  $\text{AlPO}_4$  can capture lithium polysulfides through Lewis acid-base interactions between the  $\text{P}=\text{O}$  groups in the  $(\text{PO}_4)^{3-}$  units and the polysulfides.<sup>72</sup> This adsorption process facilitates the conversion of captured polysulfides to less harmful thiosulfates/polythionates. By promoting this conversion and subsequent immobilization,  $\text{AlPO}_4$  helps to prevent the dissolution and migration of detrimental polysulfides within the electrolyte, thereby mitigating the “shuttle effect”. Studies have demonstrated the effectiveness of this approach, with Li-S cells containing 1.0 wt%  $\text{AlPO}_4$  exhibiting good capacity retention (76% after 100 cycles) and high discharge capacity ( $453 \text{ mA h g}^{-1}$ ) even at elevated current rates.

Another promising approach involves the use of organosulfide additives. Yang *et al.* investigated trithiocyanuric acid trithium salt (TTCA-Li) as an electrolyte additive.<sup>142</sup> This organosulfide additive is particularly interesting because it can react *in situ* during the initial charge cycle of a Li-S battery to form a protective coating on the cathode surface. This coating offers several benefits: it reduces the energy required to oxidize  $\text{Li}_2\text{S}$  (lowering the oxidation overpotential) and helps to suppress the undesirable redistribution of sulfur and  $\text{Li}_2\text{S}$  species throughout cycling. These combined effects contribute to improved battery performance and stability. The development of bifunctional additives like  $\text{AlPO}_4$  and *in situ* formed protective coatings from organosulfides like TTCA-Li represent significant advancements in Li-S battery technology. These strategies offer promising avenues for overcoming the challenges associated with polysulfides and unlocking the full potential of Li-S batteries for next-generation energy storage applications (Fig. 8).

Researchers are exploring unconventional approaches to address challenges in Li-S battery development. A unique study by Yu *et al.* investigated the use of dithiothreitol (DTT), a biological reagent, as an electrolyte additive.<sup>73</sup> When incorporated into a traditional Li-S battery electrolyte, DTT significantly improved the performance of the battery. This improvement is attributed to DTT's ability to enhance the efficiency of





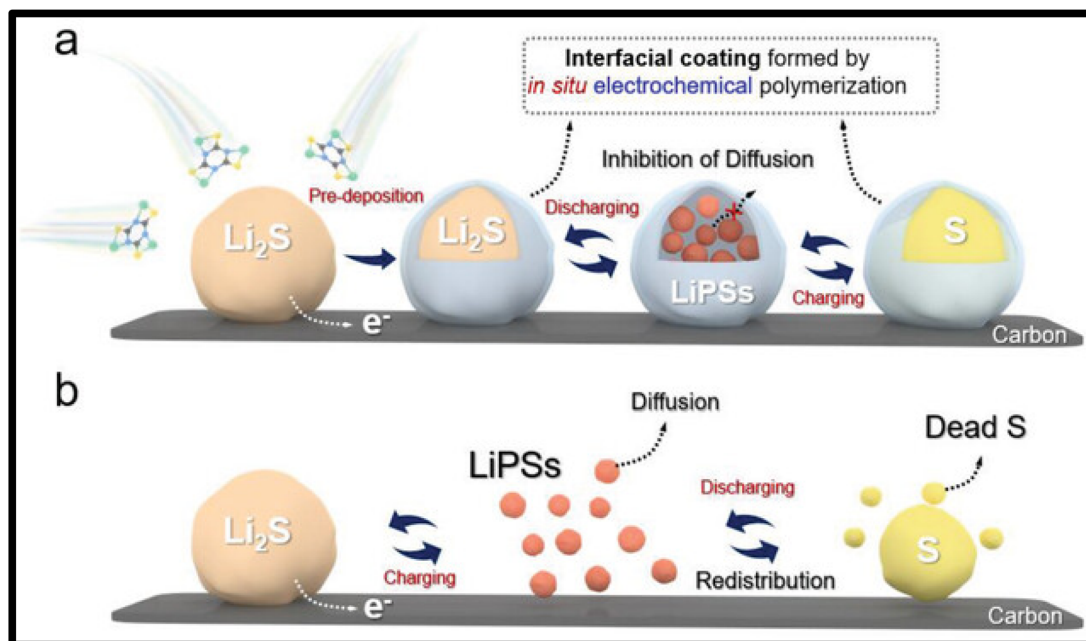


Fig. 8 Schematic of *in situ* coating  $\text{Li}_2\text{S}$  with polymerizable electrolyte additive. (a) The soluble TTCA-Li electrochemically polymerizes on the  $\text{Li}_2\text{S}$  surface to form a POS coating during the initial charging, which inhibits the out-diffusion of  $\text{LiPSs}$  during subsequent cycling. (b)  $\text{Li}_2\text{S}$  cathodes without TTCA-Li additive generate soluble  $\text{LiPSs}$  and undergo uncontrollable sulfur redistribution during cycling.<sup>142</sup>

electrochemical reactions during cycling, leading to a reduction in the detrimental “shuttle effect” caused by lithium polysulfides. In their experiment, Yu *et al.* employed a hierarchical porous carbon/sulfur cathode paired with an electrolyte containing 10 g per L DTT. This combination yielded impressive results. The battery exhibited enhanced rate capability, delivering a higher discharge capacity at a faster discharge rate compared to the control electrolyte. Additionally, the cell achieved a higher initial discharge capacity. Notably, the battery demonstrated remarkable stability with a very low-capacity fade rate over extended cycling. These findings suggest that DTT is a promising candidate as a novel electrolyte additive for Li-S batteries. Further research is necessary to fully understand the mechanisms by which DTT enhances cell performance. However, this study highlights the potential of exploring unconventional additives to overcome longstanding challenges in Li-S battery development. Researchers are continuously developing strategies to address the “shuttle effect” in Li-S batteries. A recent study by Wang *et al.* explored the use of 1,3,5-triformylphloroglucinol (TFP) as a novel electrolyte additive.<sup>143</sup> Furthermore, the aggregated organopolysulfides possess the ability to adsorb unreacted polysulfides and act as active redox mediators, thereby promoting the rapid conversion of sulfur species. As a result, the Li-S battery incorporating the 1,3,5-triformylphloroglucinol (TFP) additive exhibits an initial capacity of 1219 mA h g<sup>-1</sup> and retains 69.7% of its capacity after 280 cycles at 0.2C.

#### 2.4. Enhancing conductivity

The performance of Li-S batteries relies significantly on the ionic conductivity of the electrolyte, as both ionic and electronic

conductivities play distinct roles in battery function. Ionic conductivity indicates how efficiently ions, such as lithium ions, move through the electrolyte, impacting the rate at which the battery can charge and discharge. To measure ionic conductivity, Electrochemical Impedance Spectroscopy (EIS) is frequently used. In EIS, a small AC voltage is applied, and the electrolyte's resistance to ion movement is assessed across various frequencies. High ionic conductivity enables rapid lithium-ion transport between the anode and cathode, which is crucial for sustaining battery capacity and efficiency. EIS data can provide critical insights, or at least guide informed estimations, on how an additive may alter key properties of the electrolyte, such as overall conductivity, dielectric constant, Li-ion transference number, and diffusion constant. By analysing the impedance response across different frequencies, EIS allows us to infer the additive's impact on ion mobility and interaction within the electrolyte matrix. For instance, changes in conductivity and dielectric constant can indicate shifts in the electrolyte's ability to facilitate ion transport, while variations in Li-ion transference number and diffusion constant provide clues about ion diffusion rates and the preferential movement of lithium ions relative to other ionic species.

While the electrolyte's primary role is to support ionic transport, some additives may also contribute slightly to electronic conductivity. This can be evaluated through Cyclic Voltammetry (CV) or four-point probe measurements, which help determine if additives contribute to parasitic reactions (unwanted side reactions) or enhance electron transport in the sulfur cathode. In Li-S batteries, however, balancing high ionic conductivity with minimal electronic conductivity is essential to avoid short circuits and reduce self-discharge. Thus, achieving

high ionic conductivity while maintaining low electronic conductivity is key for optimal performance and battery safety. These key parameters dictate the efficiency of lithium-ion transport between the cathode and anode during charge and discharge cycles. To address this critical factor, researchers have explored various strategies aimed at improving the electrolyte's ionic conductivity. One approach involves the incorporation of electrolyte additives. These additives are specifically designed to enhance the mobility of lithium ions within the electrolyte solution. By promoting efficient lithium-ion transport, these additives contribute to improved cell kinetics, higher discharge capacity, and better overall electrochemical performance of Li-S batteries.

**2.4.1. Ionic liquids.** ILs offer a multifaceted approach, addressing several critical challenges in Li-S batteries. One key benefit of IL additives lies in their ability to mitigate the detrimental “shuttle effect” caused by lithium polysulfides. During charge and discharge cycles, these intermediate polysulfide species can dissolve within the electrolyte and migrate throughout the battery. This migration can lead to a loss of active material and unwanted side reactions at the lithium anode, ultimately hindering battery performance and stability. Studies suggest that ILs can interact with polysulfides through various mechanisms, such as complexation or adsorption.<sup>144</sup> These interactions effectively reduce the free movement of polysulfides within the electrolyte, thereby suppressing the “shuttle effect.” Consequently, IL additives can contribute to improved coulombic efficiency, where a higher percentage of lithium ions return to the cathode during charging, leading to enhanced overall battery performance.

Safety is another crucial aspect for Li-S batteries. Conventional electrolytes often have limitations in terms of thermal stability, raising concerns about potential flammability hazards. IL additives offer a significant improvement in this area. Due to their unique chemical structure, ILs typically exhibit higher flash points and lower flammability compared to traditional electrolytes.<sup>145</sup> By incorporating IL additives, researchers can contribute to a safer battery design with reduced fire risk.

Beyond these benefits, IL additives can also influence the formation of the solid electrolyte interface (SEI) layer on the lithium anode. This layer plays a critical role in regulating the flow of lithium ions and protecting the anode from unwanted side reactions. Traditionally, the SEI layer is formed from inorganic components of the electrolyte. However, IL additives can promote the formation of a more stable, organic-based polymerized layer on the SEI.<sup>145</sup> This modified SEI can offer several advantages. It can help to mitigate the unwanted deposition of sulfur on the anode during cycling, a process that can contribute to capacity fade and hinder battery performance. Additionally, a more stable SEI formed with the influence of IL additives can improve the overall lifespan of Li-S batteries.

Matic *et al.* investigated *N*-methyl-(*n*-butyl)pyrrolidinium bis(trifluoromethylsulfonyl)imide (Py1,4TFSI) as an IL additive in Li-S cells.<sup>146</sup> Their study aimed to achieve multiple improvements: stabilizing the solid electrolyte interface (SEI) layer, reducing electrolyte flammability, and extending the cycle

life of Li-S cells, particularly when using high-sulfur content cathodes. The introduction of Py1,4TFSI appears to offer several benefits. First, it suppresses the reactivity between the electrolyte and lithium metal anode. Second, it reduces the flammability of the solvent, leading to enhanced safety characteristics. Compared to LiNO<sub>3</sub>, a traditional additive, Py1,4TFSI demonstrates superior performance. Cells with the IL additive exhibited excellent cycling stability (over 99% coulombic efficiency) even after extended cycling (300 cycles). In contrast, cells with LiNO<sub>3</sub> showed a significant drop in performance after 150 cycles, likely due to the continuous consumption of the additive. Additionally, the study suggests that Py1,4TFSI mitigates sulfur deposition on the lithium anode by hindering the migration of lithium polysulfides.

Another promising IL additive, tris(dioxa-3,6-heptyl) amine (TDA) + TFSI, was recently introduced by Du *et al.*<sup>147</sup> Their study demonstrates that incorporating 5% TDA + TFSI into the electrolyte significantly enhances the cycling performance of Li-S cells. Compared to cells without the additive, those with TDA + TFSI exhibited a higher initial discharge capacity (1167 mA h g<sup>-1</sup>) and improved capacity retention (579 mA h g<sup>-1</sup> and 523 mA h g<sup>-1</sup> after 100 and 300 cycles, respectively, at 0.5C). Notably, the average capacity decay rate per cycle was only 0.18% over 300 cycles, significantly lower than cells without the TDA + TFSI additive. The effectiveness of TDA + TFSI is attributed to its ability to promote the formation of denser and more uniform SEI films during cycling. This enhanced SEI film contributes to improved stability in the electrochemical reactions, ultimately leading to better overall battery performance and longevity.

Despite the promising results, it is important to acknowledge the ongoing challenges associated with IL additives. These include inherent trade-offs between desired properties, such as high viscosity impacting ionic conductivity and low specific capacity. Additionally, some ILs can exhibit high solubility for lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>), potentially exacerbating the “shuttle effect”, and may lead to reduced coulombic efficiency. Overcoming these hurdles remains an active area of research for achieving high-performance Li-S batteries.

**2.4.2. Metal-organic frameworks (MOFs).** Metal-Organic Frameworks (MOFs) are a versatile class of crystalline materials with high porosity, constructed from metal ions or clusters linked by organic linker molecules. Some MOFs exhibit intrinsic electrical conductivity due to specific properties of their building blocks. This conductivity can arise from pi-conjugated organic linkers containing alternating single and double carbon bonds, or from metal ions with delocalized electrons in their orbitals. Additionally, MOFs can be strategically designed or modified to introduce conductive pathways within their structure, further enhancing their electrical conductivity. This unique property of conductive MOFs makes them promising candidates as electrolyte additives for Li-S batteries. When incorporated into the electrolyte solution, these MOFs can improve its overall conductivity. Their conductive nature facilitates the transport of electrons within the electrolyte, leading to a reduction in internal resistance and improved battery performance during charge and discharge cycles (kinetics).



Several studies have explored the potential of MOFs for this application. Wang *et al.* investigated the use of HKUST-1  $\supset$  S, a MOF containing copper (Cu) that can encapsulate sulfur species.<sup>148</sup> Their findings suggest that this MOF can contribute to improved battery performance. Building upon this work, Bai *et al.* employed the conventional Cu-based MOF, HKUST-1, as a potential host material for the TFSI<sup>−</sup> anion within the electrolyte.<sup>149</sup>

Beyond MOFs, other novel additives are being explored. Shen *et al.* investigated the use of MIL-100(Al) as a particulate anion sorbent in ether-based electrolytes for lithium metal batteries.<sup>150</sup> This approach demonstrates the potential for targeted modifications to improve stability within different battery chemistries. Another interesting avenue involves the use of organometallic salt additives. Wang *et al.* reported that incorporating a small amount (0.5 wt%) of the organometallic salt NiDME into the electrolyte can significantly enhance Li-S battery performance.<sup>145</sup> This additive functions by capturing lithium polysulfides within the electrolyte, promoting their conversion at uniform interfaces, and facilitating the deposition of Li<sub>2</sub>S. Consequently, batteries incorporating NiDME exhibit stable cycling performance with high-capacity retention (784 mA h g<sup>−1</sup> after 500 cycles at 1.0C) and can even operate with a lean electrolyte ratio (5  $\mu$ L electrolyte per mg sulfur), highlighting its efficiency.

These studies showcase the ongoing advancements in electrolyte design for Li-S batteries. The exploration of conductive MOFs, targeted anion sorbents, and functional organometallic salt additives holds significant promise for overcoming longstanding challenges and unlocking the full potential of Li-S battery technology.

## 2.5. Redox mediators

Redox mediators are a class of compounds strategically incorporated into battery electrolytes to enhance their performance. These mediators' function by shuttling electrons between the cathode and anode, facilitating the crucial redox reactions that power the battery. In the context of Li-S batteries, redox mediators offer a promising approach for addressing key challenges and improving overall battery performance.<sup>151</sup> One strategy involves the use of organic polysulfides as redox mediators within the electrolyte. When incorporated, these mediators can initiate reactions with sulfur in the cathode, generating soluble polysulfide intermediates. This process can enhance the electrochemical reversibility of the sulfur cathode, potentially leading to increased capacity and improved cell stability. Studies by various research groups have explored the effectiveness of organodisulfides and organodiselenides as mediators for Li-S batteries. Wang *et al.* pioneered the use of organosulfides as redox mediators to regulate the electrochemical behavior of lithium polysulfides.<sup>152</sup> Their work highlighted the potential for this approach in Li-S battery development. Building upon this foundation, Anouti *et al.* investigated aromatic organic disulfides, demonstrating their ability to positively influence the transformation of sulfur species during charge and discharge cycles.<sup>78</sup> Similar to dimethyl disulfide (DMDS), these aromatic disulfides (like diphenyl disulfide,

PhS<sub>2</sub>Ph) can undergo an electrochemical process that promotes the conversion between sulfur, higher-order lithium polysulfides (Li<sub>2</sub>Sn), and lower-order lithium polysulfides (Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S) through alternative reaction pathways. Further research by Huang *et al.* explored the use of diphenyl diselenide (DPDSe) as a redox mediator to modify the behavior of polysulfides and enhance their reaction kinetics.<sup>153</sup> These findings, along with studies on other redox mediators like tetrathiafulvalene (TTF),<sup>154</sup> ferrocene derivatives,<sup>155</sup> and quinones,<sup>156</sup> showcase the diverse potential of this approach.

However, it is important to acknowledge that the design and optimization of redox mediators for Li-S batteries remain an active area of research. Effective implementation requires careful consideration of several factors, including the mediator's redox potential, solubility, stability, and compatibility with other battery components. By tailoring redox mediators for specific Li-S battery chemistries and operating conditions, researchers are paving the way for significant advancements in battery performance and addressing longstanding challenges in this promising battery technology.

## 2.6. Versatile additives

Zhuo *et al.* explored the use of carbon disulfide (CS<sub>2</sub>) as an additive in Li-S batteries, revealing its diverse impacts on battery performance.<sup>74</sup> Their study identified two primary advantages associated with CS<sub>2</sub>: one of the critical challenges in Li-S batteries is the "shuttle effect," where long-chain lithium polysulfides dissolve and migrate. Zhuo *et al.* found that CS<sub>2</sub> effectively mitigates this issue through complexation with polysulfides, restricting their movement within the electrolyte. Additionally, CS<sub>2</sub> facilitates the passivation of both the lithium anode and sulfur cathode, forming protective layers such as thiosulfates on the anode and a polymerized layer within the cathode electrolyte interphase (CEI) under operating conditions. These combined effects suppress the polysulfide shuttle effect, enhancing battery stability and performance. CS<sub>2</sub> also demonstrates potential in activating inactive sulfur within the cathode, which otherwise reduces battery capacity. Its strong solvating power for elemental sulfur contributes to this activation, while the polymerized protective layer within the CEI further prevents polysulfide dissolution during battery operation. By improving sulfur utilization, CS<sub>2</sub> offers a pathway to enhance battery capacity and overall performance. These insights by Zhuo *et al.* provide a foundation for further investigation into the mechanisms underlying CS<sub>2</sub>'s role as a Li-S battery additive. While optimizing its application requires additional research, these initial findings underscore CS<sub>2</sub>'s potential as a versatile solution to address key challenges in Li-S battery technology (Fig. 9).<sup>74</sup>

Yang *et al.* proposed a groundbreaking approach to improve cathode performance in lithium-sulfur (Li-S) batteries by introducing pyrrole (Py) as an electrolyte additive.<sup>75</sup> Their strategy revolves around the formation of a functional protective layer directly on the sulfur cathode during battery operation. This layer is created through a fascinating process called electrochemical oxidative polymerization. Py undergoes a reaction triggered by



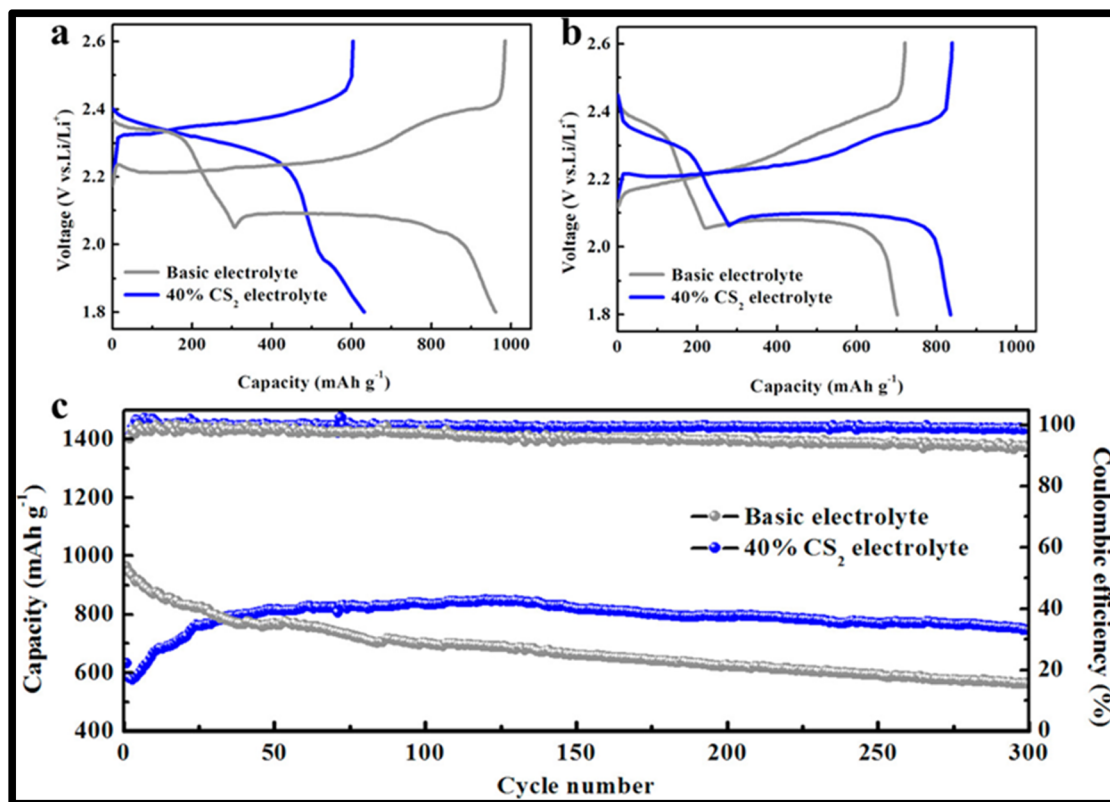


Fig. 9 Electrochemical performance of Li-S cells with basic and 40 wt% CS<sub>2</sub> electrolytes. (a) The initial charge-discharge voltage profiles at 0.5C rate. (b) The 100th charge-discharge profiles at 0.5C rate. (c) Cycle performance of Li-S cells with different electrolytes at 0.5C.<sup>74</sup>

the battery's cycling process, essentially growing into a polypyrrole layer. This polypyrrole layer boasts unique functionalities that can significantly enhance battery performance: firstly, the polypyrrole layer acts as a highly effective conductive agent. By facilitating the transport of electrons within the cathode, this improved conductivity can lead to faster rates of charge and discharge, ultimately contributing to higher overall battery efficiency. Secondly, the polypyrrole layer goes beyond just conductivity. It functions as a double-edged sword against lithium polysulfides, a major challenge in Li-S batteries. The layer acts as an adsorbent, capturing these polysulfides and preventing them from causing problems. Additionally, it functions as a physical barrier, hindering their migration within the battery. This combined effect of adsorption and physical blockage significantly improves battery stability and performance by reducing capacity fade and enhancing cycle life by suppressing the polysulfide shuttle effect.<sup>75</sup> Liu *et al.* investigated the use of trifluoromethane sulfonamide (TFMSA) as an electrolyte additive to improve Li-S battery performance.<sup>76</sup> They addressed a significant issue: the formation of insulating products on the sulfur cathode surface during battery operation, which impedes sulfur utilization and slows reaction kinetics. Their research revealed that TFMSA can enhance battery performance by promoting the dissolution of these insulating species. TFMSA forms intermolecular hydrogen bonds with Li<sub>2</sub>S species, breaking them down and facilitating their dissolution into the electrolyte. This process improves the utilization of

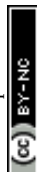
active sulfur material and enhances reaction kinetics, ultimately boosting overall battery performance (Fig. 10).<sup>76</sup>

In a separate study, Wang *et al.* explored hexadecyl-trioctylammonium iodide (HTOA<sup>+</sup>I<sup>-</sup>) as a dual-acting electrolyte additive to tackle two critical challenges in Li-S batteries.<sup>77</sup> First, HTOA<sup>+</sup>I<sup>-</sup> helps form a protective solid electrolyte interphase (SEI) on the lithium anode, reducing harmful interactions between lithium and lithium polysulfides, thereby enhancing anode stability. Second, HTOA<sup>+</sup> suppresses the polysulfide shuttle effect. The HTOA<sup>+</sup> cation binds strongly to polysulfide anions, preventing their migration towards the lithium anode. Additionally, the larger size of HTOA<sup>+</sup> compared to lithium ions creates an electrostatic shielding effect, promoting uniform lithium deposition during cycling and extending the anode's lifespan. These functionalities collectively enhance the cycling stability of Li-S batteries incorporating HTOA<sup>+</sup>I<sup>-</sup>.

These studies underscore the multifaceted strategies being explored to address challenges in Li-S battery technology. TFMSA offers a solution for dissolving harmful byproducts on the cathode, while HTOA<sup>+</sup>I<sup>-</sup> functions as a dual-acting additive that protects the lithium anode and suppresses the polysulfide shuttle effect. Further research on these and other innovative additives is essential for realizing the full potential of Li-S batteries.

## 2.7. Enhancing safety and environmental concerns

The practical deployment of lithium-sulfur (Li-S) batteries faces significant safety challenges due to the presence of several





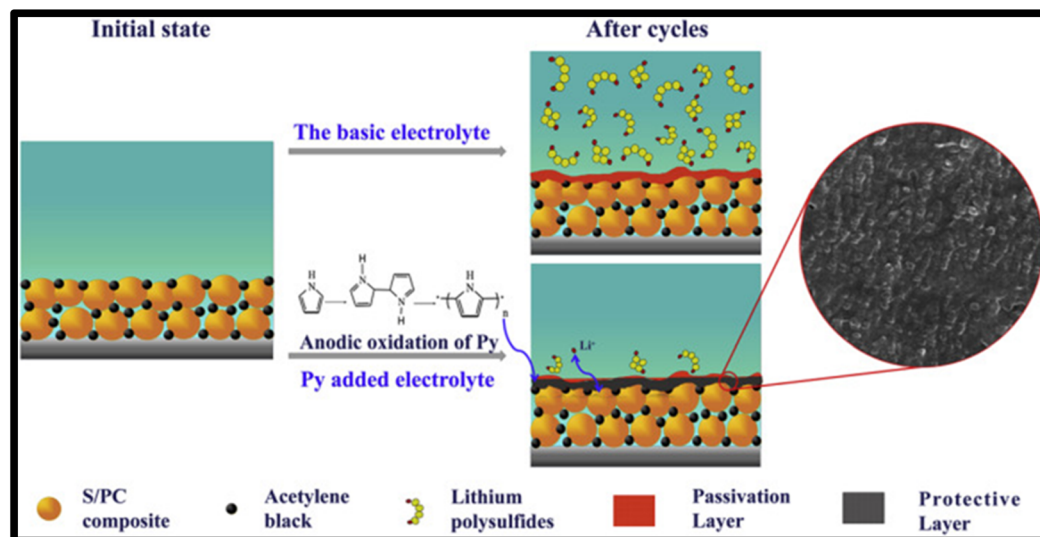


Fig. 10 Schematic illustration of the formed protective layer on the surface of sulfur cathode by adding pyrrole into the electrolyte.<sup>75</sup>

flammable materials within the cell. The highly reactive lithium metal anode can easily ignite upon contact with the electrolyte. Lithium nitrate, an electrolyte additive, increases the flammability of the electrolyte. Carbon materials with high specific surface areas in the cathode foster unwanted side reactions and heat generation. Elemental sulfur in the cathode is also flammable. Ether-based electrolytes, chosen for their sulfur-dissolving capabilities, have low boiling points that heighten the risk of leakage and flammability.<sup>157,158</sup> Various classes of compounds have been investigated as electrolyte additives for lithium-ion batteries (LIBs) and, by extension, lithium-sulfur (Li-S) batteries, with the goal of improving safety through flame retardancy. These include alkyl phosphates, fluorinated alkyl phosphates, ionic liquids, and phosphazenes. These additives have been extensively documented in the literature for their ability to inhibit flammability and enhance the overall safety of the electrolyte system, which is a critical consideration for the widespread adoption of LIBs and Li-S batteries.<sup>159,160</sup> According to the work reported by Mandal *et al.*, the addition of two novel compounds, diethyl(2,6-di-*tert*-butyl-4-methylphenyl)phosphate (referred to as TRI-001) and diethylphosphorodiphenylamidate (referred to as TRI-013), was found to inhibit the occurrence of thermal runaway in lithium battery electrolytes. These two compounds, which have not been extensively explored in the context of lithium-sulfur battery electrolytes, were demonstrated to exhibit flame-retardant properties and the ability to enhance the thermal stability of the electrolyte system.<sup>161</sup> According to the literature, the addition of triphenyl phosphite (TPPi) as an electrolyte additive has been shown to function as a flame retardant, contributing to the improved safety of lithium-sulfur (Li-S) batteries. When incorporated into the conventional 1.0 M LiPF<sub>6</sub> in EC/DEC = 50/50 (v/v) electrolyte at a concentration of 5 wt%, TPPi has been reported to simultaneously enhance the thermal stability of the electrolyte and improve the overall electrochemical performance of the Li-S battery system. The flame-retardant mechanism of TPPi is

attributed to its ability to generate free radicals, such as PO<sup>•</sup>, which can actively capture other reactive free radicals, such as H<sup>•</sup> and OH<sup>•</sup>, that are typically emitted during the combustion of the electrolyte. This radical scavenging process helps to retard the propagation of the thermal runaway reaction, thereby enhancing the overall safety of the Li-S battery. The presence of TPPi in the electrolyte can also contribute to the formation of a more stable and conductive solid electrolyte interphase (SEI) on the electrode surfaces, which can help mitigate issues related to polysulfide dissolution and improve the cycling performance of the Li-S battery.<sup>78</sup> Studies have shown that when incorporated into carbonate electrolytes at an optimized concentration range of 7–11 wt%, dimethyl methylphosphonate (DMMP) can significantly suppress the flammability of the electrolyte and enhance the overall thermal stability of Li-S batteries.<sup>79</sup> The specific mechanism by which DMMP functions as a flame retardant is still under investigation. However, it is believed to play a role in interfering with the combustion process, potentially by quenching free radicals or decomposing into non-flammable products during thermal runaway events. Interestingly, beyond its flame-retardant properties, DMMP appears to offer additional benefits for Li-S batteries. Research suggests that this additive can modify the interfacial film that forms between the electrode and the electrolyte. This modification can lead to improved Li-ion diffusion coefficients, essentially allowing lithium ions to move more freely within the battery. As a result, the battery may experience accelerated electrochemical reactions, potentially translating to improved performance.<sup>162</sup>

According to the work reported by Huang *et al.*, a novel flame-retardant electrolyte system for lithium-sulfur (Li-S) batteries has been developed by incorporating a tris(pentafluorophenyl) borane (TB) additive into a polymerized 1,3-dioxolane (DOL) electrolyte.<sup>80</sup> In this design, the TB additive serves a dual purpose – it acts as an initiator for the *in situ* polymerization of the DOL solvent, and it also functions as



a multifunctional additive with flame-retardant properties. The presence of a small quantity of TB molecules in the electrolyte enables the generation of highly reactive fluorine radicals, which contribute to the flame-retardant characteristics of the resulting polymer electrolyte. Furthermore, the fluorinated nature of the TB additive, with its high fluorine content, facilitates the formation of a highly stable solid electrolyte interphase (SEI) that is rich in lithium fluoride (LiF).

The solid Li-S battery assembled with this polymer electrolyte, without the inclusion of  $\text{LiNO}_3$ , exhibits improved performance. It showcases an initial capacity of  $1060 \text{ mA h g}^{-1}$  at a 0.2C rate and maintains a reversible capacity of  $660 \text{ mA h g}^{-1}$  after 500 cycles. Additionally, the Li-S battery utilizing this polymer electrolyte achieves a notable reversible capacity of  $700 \text{ mA h g}^{-1}$  at  $20^\circ\text{C}$ .

The dual functionality of the TB additive, as both a polymerization initiator and a flame-retardant agent, has enabled the development of a safe and high-performance polymer electrolyte for Li-S battery systems, addressing the challenges associated with the flammability of conventional electrolytes and contributing to the overall improvement in the cycling performance of the battery.

The findings from the excellent research papers provide robust evidence that incorporating flame-retardant additives into electrolytes is a straightforward and highly effective strategy for improving the safety of lithium-sulfur (Li-S) batteries. This approach offers a promising solution to mitigate safety concerns associated with thermal runaway and fire hazards, thereby enhancing the overall reliability and usability of Li-S battery systems.

Choosing environmentally friendly electrolyte additives for Li-S batteries is crucial to minimize environmental impact and ensure sustainable energy storage solutions. Some of the environmentally friendly electrolyte additives that have been explored for use in Li-S batteries include biodegradable compounds such as succinic acid, citric acid, and derivatives of natural products. Another group of compounds that have gained attention very recently are bio-based additives, more specifically those derived from biomass or agricultural waste. Although this area is still in its infancy, the implementation of environmentally friendly additives offers alternatives that can improve the performance of Li-S batteries while contributing to sustainability and reducing dependence on fossil fuels.

The incorporation of these flame-retardant and environmentally friendly additives into the electrolyte composition used in Li-S batteries represents a promising approach to address both safety and sustainability concerns, ultimately enhancing the overall viability and acceptance of these high-energy density energy storage systems.

### 3. Challenges

#### 3.1. Regulating electrolyte concentration

Typically, lithium-sulfur battery electrolytes have concentrations around  $1\text{--}1.5 \text{ mol L}^{-1}$ , providing ample free solvent to dissolve lithium polysulfides (LiPSs). However, as concentration increases, the quantity of free solvent gradually declines due to the formation

of contact ion pairs and cation-anion solvated aggregates. In a notable study, Suo *et al.* introduced a "Solvent-in-Salt" electrolyte with an ultra-high salt concentration of  $7 \text{ mol L}^{-1}$ . In this highly concentrated electrolyte, soluble intermediates become much less soluble, as demonstrated by LiPS dissolution experiments, likely due to a saturation effect in the limited solvent.<sup>163</sup> In this context, nearly 100% coulombic efficiency and long-term cycling stability were attained. Nevertheless, sulfur cathodes in high-concentration electrolytes continue to follow a solid-liquid-solid lithiation pathway, and the precise formation mechanism of lithium polysulfides (LiPSs) under these conditions remains unclear. Additionally, the source of free solvent in such concentrated electrolytes is still in question. Amine *et al.* revealed that differences in solvating power among various cations and anions with the solvent can trigger a solvation-ion-exchange process, leading to solvation and reformation of soluble LiPSs. To address this, they developed a concentrated siloxane-based (DMTS) electrolyte for lithium-sulfur batteries, effectively eliminating the hidden solvation-ion-exchange mechanism. This approach significantly reduces LiPS dissolution, thereby minimizing the shuttle effect.<sup>164</sup> On the other hand, reducing electrolyte volume to enhance energy density introduces unique challenges under lean electrolyte conditions. Lean electrolyte conditions refer to environments where the electrolyte volume is minimized relative to the electrode surface area, which can be common in high-energy-density batteries where space is constrained. In such cases, the electrolyte's limited availability can lead to faster depletion of active lithium ions and more severe degradation of battery components, as there is less of a buffer for side reactions. Under these conditions, the role of electrolyte additives becomes critical in stabilizing battery performance and mitigating the polysulfide shuttle effect.<sup>165,166</sup> One of the primary functions of electrolyte additives in lean electrolyte environments is the formation of a stable solid electrolyte interphase (SEI) on the anode surface. Under lean electrolyte conditions, additives such as vinylene carbonate (VC)<sup>167,168</sup> and fluoroethylene carbonate (FEC)<sup>169–171</sup> help generate a thin yet robust SEI layer, which is critical in preventing further reaction of the electrolyte with the electrode material. This SEI acts as a protective barrier, reducing continuous electrolyte consumption and helping maintain battery capacity over time. In conventional conditions with sufficient electrolytes, SEI formation is generally stable due to the availability of lithium salts and solvent, which can easily replenish any degradation at the electrode interface. However, with lean electrolytes, any degradation in SEI integrity can rapidly lead to battery failure since there is insufficient electrolyte to compensate for loss, making the role of additives crucial for sustainable SEI formation.<sup>172–175</sup> Another key role of additives in lean electrolyte conditions is the enhancement of ionic conductivity. Under conventional electrolyte concentrations, ionic transport is usually sufficient, enabling lithium ions to move effectively between electrodes. However, in lean electrolyte conditions, the reduced ion concentration leads to poor conductivity, affecting battery power and efficiency. Additives like lithium bis-(fluorosulfonyl)imide (LiFSI) can increase ionic conductivity even in lower concentrations, enabling efficient ion movement and reducing internal resistance in the battery. This differs from conditions with sufficient electrolyte, where conductivity is less of



an issue due to a higher lithium salt concentration. Moreover, lean electrolytes are more susceptible to thermal and chemical instability due to the reduced volume and higher concentration of reactive components in a confined space. Additives can act as stabilizers to prevent side reactions that might otherwise result in thermal runaway or degradation of battery materials. For example, phosphorous-containing additives such as triethyl phosphate (TEP)<sup>176–178</sup> are used to inhibit flammability and stabilize the electrolyte, reducing the risks associated with overheating. In contrast, under conventional conditions, the larger volume of electrolyte provides more thermal buffer and dilution, reducing the likelihood of such instabilities.

### 3.2. Trade offs

Improving electrolyte additives for lithium–sulfur (Li–S) batteries involves navigating a series of trade-offs, including balancing polysulfide solubility with stability, enhancing ionic conductivity without compromising electrolyte integrity, and optimizing transport properties while managing viscosity. Each modification has the potential to enhance battery performance but may introduce new challenges, underscoring the need for multifunctional additives or mixed-solvent systems.

One of the primary goals in electrolyte modification is to increase the solubility of polysulfides, which can boost sulfur conversion and allow a higher proportion of active sulfur to participate in redox reactions, ultimately increasing battery capacity. However, soluble lithium polysulfides formed during discharge can migrate toward the lithium anode, leading to polysulfide shuttling. This migration results in self-discharge, sulfur loss, and capacity degradation as polysulfides are gradually leached from the cathode. The challenge, therefore, is finding additives that allow for moderate polysulfide solubility to optimize sulfur utilization while minimizing the undesirable effects of polysulfide shuttling. Strategies to address this include using additives that anchor polysulfides to the cathode or modifying the electrolyte composition to stabilize the polysulfide interface and prevent diffusion.

Another key function of electrolyte additives is enhancing ionic conductivity, which is critical for improving lithium-ion mobility between the electrodes and enabling faster charging and discharging. However, boosting ionic conductivity may introduce chemical instability, as some additives or solvents that enhance ion transport can react with lithium, leading to the formation of byproducts that degrade battery performance over time. Therefore, the ideal additive must improve conductivity while minimizing the risk of side reactions, ensuring both enhanced performance and long-term electrochemical stability. Viscosity plays a significant role in the electrolyte's ability to facilitate ion transport. Low-viscosity solvents generally enhance lithium-ion movement, improving the battery's power density and cycling efficiency. However, such solvents may struggle to dissolve larger or more complex additives that can help stabilize polysulfides or prevent shuttling. On the other hand, high-viscosity solvents may better support the dissolution of such additives but can hinder ion transport, reducing the battery's performance, especially at high power densities. To

address this, researchers often use mixed-solvent systems that combine low- and high-viscosity solvents to strike a balance between effective ion transport and optimal additive solubility.

The performance of Li–S batteries must remain stable across a wide temperature range, especially in applications such as electric vehicles. Additives that stabilize polysulfides at room temperature may lose their effectiveness at higher or lower temperatures. For example, some additives that improve sulfur utilization under moderate conditions may degrade or become less soluble at extreme temperatures, leading to polysulfide precipitation or increased shuttling. This temperature-sensitive behaviour presents a challenge in designing additives that maintain consistent performance across various operating conditions, an area still under active research. The development of highly effective additives that balance solubility, stability, and conductivity often comes with increased production costs. High-performance additives or custom mixed-solvent systems can be expensive to manufacture, which limits the scalability of these solutions for commercial applications. Thus, creating cost-effective electrolyte formulations remains a priority, as this is essential for the widespread adoption of Li–S batteries. Researchers are focused on achieving performance gains without significantly raising production costs, ensuring that improvements in battery efficiency, lifespan, and commercial viability align with the need for economically sustainable energy storage solutions.

By addressing these challenges and optimizing electrolyte formulations, researchers aim to enhance the efficiency and sustainability of Li–S batteries, driving advancements in energy storage technologies for a wide range of applications.

### 3.3. Solvent choice

The effectiveness of electrolyte additives in Li–S batteries largely depends on their solubility and stability, which are strongly influenced by the electrolyte solvent choice. Solvent polarity, for instance, is crucial in determining an additive's dissolution and efficacy within the battery system. Polar solvents like dimethyl sulfoxide (DMSO) and ethylene carbonate (EC) generally dissolve polar additives well. Lithium nitrate (LiNO<sub>3</sub>), a commonly used additive, exhibits high solubility in polar solvents, enhancing its ability to form a protective layer on the lithium anode. This layer minimizes lithium dendrite growth and reduces polysulfide migration. In contrast, non-polar solvents, such as 1,2-dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME), are often preferred in Li–S batteries for their low reactivity with lithium metal. Non-polar solvents aid in dissolving non-polar additives that inhibit polysulfide dissolution, enhancing cycling stability without significantly compromising lithium metal stability. For example, DME effectively dissolves lithium polysulfides, thereby reducing polysulfide deposition and improving cycle life. However, non-polar solvents may limit additive options by not supporting certain polar additives crucial for battery performance.

The viscosity of the solvent directly impacts ion and additive transport properties within the electrolyte. Low-viscosity solvents like DME promote rapid ion transport, which can



increase charge/discharge rates and improve overall performance. However, lower viscosity can reduce the solubility of additives with larger or more complex structures, such as polymer-based additives, which can stabilize batteries by forming protective films on the anode. Higher-viscosity solvents, such as TEGDME or DMSO, tend to improve the solubility of these additives, thereby expanding the range of functional additives. This can boost stability and capacity retention, albeit potentially at the expense of reduced charging speed due to slower ion transport. Consequently, researchers often optimize solvent viscosity to balance additive solubility with performance and stability. Solvent chemical stability also influences the durability and effectiveness of additives in Li-S batteries. Highly reactive solvents, particularly with lithium metal, can decompose over time, shortening electrolyte and battery lifespan. For example, although DMSO provides high solubility for certain additives, it may react with lithium, generating decomposition products that degrade battery performance. Ethers like DME and TEGDME, on the other hand, offer superior chemical stability, extending additive longevity and reducing unwanted side reactions that decrease battery capacity. Some studies explore mixed-solvent systems to leverage the advantages of both polar and non-polar solvents. Blending DME with DMSO, for instance, balances solubility and stability, allowing the dissolution of polar additives like lithium nitrate while reducing degradation issues associated with pure polar solvents. This combination optimizes additive functionality and minimizes issues related to solvent reactivity with lithium.

## 4. Conclusion and prospectives

The electrolyte plays a crucial role in the performance and safety of lithium-sulfur (Li-S) batteries, acting as a critical medium for transporting lithium ions between the cathode and anode. The electrochemical properties of the electrolyte significantly influence various aspects of battery operation, including cycling stability, charge/discharge capacity, operating voltage, temperature range, and overall safety of the cells. Therefore, optimizing the electrochemical characteristics of the electrolyte is essential for enhancing the overall performance and reliability of Li-S batteries. Extensive research on electrolyte additives is urgently needed to address the challenges associated with Li-S batteries, such as the highly active lithium metal anode leading to safety concerns, low coulombic efficiency and shortened cycling lifespan due to lithium dendrite growth, solubility issues of active species, and the lithium polysulfide shuttle phenomenon. The efficacy of additives primarily relies on their functional groups, and guiding the design of molecular structures and functional groups through theoretical calculations is essential. Functional additives can serve various purposes, including establishing a stable solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI), stabilizing polysulfides through mechanisms such as absorption, oxidation, complexation, and anchoring, promoting the oxidation of  $\text{Li}_2\text{S}$ , and enhancing kinetics. Advanced *in situ* characterization technologies are crucial for analyzing the working mechanisms

and interaction principles of additives. Additionally, considerations such as environmental friendliness, compatibility, cost-effectiveness, and feasibility for mass production are important factors to be carefully evaluated during the development of additives for Li-S batteries. According to the findings of this review, the ideal electrolyte should possess high stability and ion conductivity, exhibit excellent compatibility with both the cathode and anode materials, effectively inhibit the shuttle effect of lithium polysulfides, and ensure high safety standards. The ongoing improvement of electrolyte additives holds promise, indicating a crucial role in the development of high-performance and safe Li-S batteries. Incorporating organodisulfides (or organodiselenides) presents the most viable approach for directly modulating the electrochemical behavior of lithium polysulfides through covalent sulfur binding, while organosulfur compounds featuring thiol groups, known as organothiols, show promise in enhancing the performance of sulfur cathodes. The effectiveness of electrolyte additives in Li-S batteries depends on their interactions with the chosen solvent, as these interactions affect both the solubility and stability of the additives, hence polarity matching, stabilization effects, and the possibility of utilizing mixed-solvent systems should all be considered when designing an ideal additive. Similarly, the use of digital screening for additive optimization, as demonstrated by Sauer *et al.*, who employed a Bayesian optimization algorithm to effectively determine the optimal combinations of FEC and VC additives for enhancing the cycle life of NMC622||graphite batteries, could be adapted for lithium-sulfur batteries. This method offers the advantage of significantly reducing the number of experimental iterations needed to identify appropriate electrolyte additives.<sup>179,180</sup>

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Author contributions

Derek Okene: conceptualization, investigation, writing – original draft, writing – review & editing. Lakshmi Shiva Shankar: writing – review & editing. Alen Vizintin: writing – review & editing. Robert Kun: conceptualization, funding acquisition, review, editing and supervision.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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