The ever-increasing requirement for efficient and economic energy storage technologies has triggered the continued research into advanced battery systems. Lithium-ion batteries, based on the lithium intercalation chemistry, have dominated the battery market since their commercial application in the 1990s. However, conventional lithium-ion batteries are very expensive and their energy densities (theoretically, 350–500 Wh kg$^{-1}$) are insufficient for long-range electrical vehicles and high-end portable electronics. These emerging demands have energized the evolution of other alternative rechargeable batteries with higher energy density and longer lifespan. Lithium–sulfur (Li–S) battery, a ‘beyond Li-ion’ technology, has drawn extensive attentions due to its high theoretical energy density of 2600 Wh kg$^{-1}$ and energy density (2600 Wh kg$^{-1}$) 4–6. The greater energy storage ability of Li–S batteries is realized through the phase-transformation electrochemistry based on elemental sulfur cathode and metallic lithium anode $[S_8 \leftrightarrow 8LiS]$ which is fundamentally different from current transition metal-based cathodes and graphite-based anodes in Li-ion batteries.

The conversion chemistry in a Li–S cell offers not only significant advantages as mentioned above, but also some critical challenges, such as the low conductivity of sulfur and lithium sulfide, the huge volumetric change from sulfur (71 mol L$^{-1}$) to lithium sulfide (36 mol L$^{-1}$), and the shuttle of long-chain polysulfide intermediates during discharge/charge cycling. Therefore, a composite cathode with sulfur in a suitable conductive agent to handle these issues has presented quite a compelling scientific and engineering focus. 15–15 More than 30 years ago, Rauh and Peled firstly introduced the idea of load–discharge sulfur into the porous structure of carbon materials. Since the pioneering work by Nazar and colleagues creating a highly ordered nanostructured carbon—sulfur cathode using CMK-3 in 2009, various strategies have been proposed to address the issues in the cathode of Li–S cells, such as nanostructured hosts, adsorbing/catalytic agents, bifunctional separators, and electrolyte additives. Up to now, high discharging capacity (>1500 mAh g$^{-1}$), high weight percentage of sulfur (>90%), high areal sulfur loading and capacity (>10 mg cm$^{-2}$) and >10 mAh cm$^{-2}$), superior performance at extraordinary high rates (>10 C, 1.0 C = 1672 mA g$^{-1}$), and long lifespan (>1000 cycles) have been achieved with the remarkable progress in material science and electrochemistry. However, most of the publications are conducted in coin cells with at least 1500% lithium and 200% electrolyte excess. Few pouch cells have been declared in scientific publications. Coin-cell format is a very good stage to characterize the potential of materials applied to electrochemical cells, which constructs the best environment for material characterization. However, toward a cell for the practical applications, several applicable indicators are required, such as material cost, discharging capacity and energy density based on the whole cell, and safety performance etc. In the engineering field of Li–S batteries, it is a difficult tradeoff between the energy density (>350 Wh kg$^{-1}$) and lifespan (>100 cycles), even with the neglect of the power density. There is still a long way for Li–S batteries to enter practical applications.

Relative to the extensive research on sulfur cathode in Li–S batteries, the anode investigation is less involved (Figure 1). By June 2014, 69% of the literatures on Li–S batteries focus on the sulfur cathode, while only 3% on the Li anode. However, Li metal anode is an equally major limiting factor for a Li–S battery as a practical energy storage device. For the present Li–S battery in a pouch-cell, the initial energy density is decided by the mass of sulfur in the whole cell, while the capacity retention and service life tightly depend on the Li metal anode. A large proportion of Li–S pouch cells fail by the Li metal powdering and electrolyte depletion, which is usually induced by the uncontrolled Li dendrite growth. In a Li–S battery, the lithium polysulfide (LiPS) intermediates generated in the cathode side can dissolve into the non-aqueous electrolyte, diffuse to the anode, and react with Li metal chemically. The additional LiPSs make the Li metal anode protection in a Li–S battery with much more challenges.

Fortunately, the anode issue of Li metal batteries including Li–S batteries has recently caught the researchers’ attentions. The publications on the anode side have sharply increased since 2013. Some creative strategies to protect Li metal anode considering the effect of LiPSs have been proposed, such as electrolyte additives, artificial solid electrolyte interphase (SEI), solid-state electrolyte, and structured composite Li anode. Though these strategies are designed based on each part of the cells, most of them will strengthen the interfacial stability between Li metal and the electrolyte, which is the
fundamental requirement for a long-lifespan Li metal anode. When LiPSs exist in the electrolyte, interfacial stabilization of Li metal anode becomes rather complicated.\(^{42}\) Usually, the shuttled LiPSs can etch the interfacial films and deteriorate the cycling performances. Surprisingly, researchers recently found that some specific kinds of LiPSs (such as Li$_2$S$_5$ and Li$_2$S$_8$) at a certain concentration can heal the dead Li$_2$S and Li$_2$S$_2$,\(^{43,44}\) facilitating the formation of a stable SEI when synergizing with LiNO$_3$ additives.\(^{45,46}\) Consequently, it is of primary importance to clearly investigate the surface chemistry of Li metal anode with the existence of LiPS species.

Recently, our group comprehensively reviewed the mechanism, model, and protecting strategies of SEI film and dendrite issues of Li metal anode.\(^{47}\) In this review, we do not reiterate the Li metal anode issue in the conventional Li metal batteries again, but focus on the Li metal anode in Li–S batteries. Here, we attempt to summarize the surface chemistry and interfacial stabilization of Li metal anode with the influence of LiPSs. Firstly, the importance and dilemma of Li metal anode issues are illustrated, aiming to arouse the attentions to Li metal anode protection. Specific attentions are paid to the surface chemistry of Li metal anode in LiPS-rich Li–S batteries. Then, lately proposed strategies to stabilize SEI film and protect Li metal anode are reviewed. Finally, a general conclusion and a perspective on the current limitations, as well as recommended future research directions of the Li metal anode in Li–S batteries are presented.

**The Significance of Li Metal Anode in Working Li–S Batteries**

Li metal anode plays a significant role in the service life of a Li–S battery.\(^{37}\) However, its role is severely neglected in a coin cell with the excess of Li metal and electrolyte. When we adopt the pouch-cell format to evaluate Li–S batteries, the role of anode will be prominent. In the pouch-cells, the areal sulfur loading is very large to render a cell with a high energy density. However, this induces both serious LiPS shuttle and a large current on the surface of metallic Li anode. Considering a 2000 mAh pouch cell as a typical example (an average format to evaluate Li–S pouch cell. The loss of interconnected ionic channels directly leads to the cell failure.\(^{53}\) However, it is not the decisive reason for the cell failure. When fresh electrolyte is injected into the failed cell, the cell regains discharge capacity (Figure 3a).\(^{39}\) However, the fresh electrolyte still cannot preserve the high capacity and this ‘twice born’ cell gets rapid capacity decay. Another ‘twice-born’ cell with cycled cathode vs. fresh anode is fabricated. The cell indicates an improved discharging capacity from 314 to 1030 mAh g$^{-1}$ (Figure 3b) at 0.1 C and remains stable in the following cycles (999 mAh g$^{-1}$ at 15th cycle).\(^{50}\) Therefore, Li metal anode itself is the fundamental factor to decide the cell failure.
Further analyzing the cycling performance of the Li–S battery, an obvious relation is observed between the discharging capacity and voltage evolution. The time point for rapid capacity decay is the same with that of voltage fall-off (Figures 3c and 3d). Consequently, the large polarization induced by powdery and dead Li is the primary reason for the cell failure. A similar conclusion has been reached by Xiao and colleagues through comparing the Li anodes cycling at different rates after 100 cycles (Figure 4).54 When the current density increases from 0.2 to 0.5, 1, and 2 C, the thickness of porous Li layer expands from 100 to 160, 223, and 270 μm, respectively, hence leading to the polarization aggravation and capacity decay. A novel failure mechanism of Li metal anodes is found that porous layer of the dead Li grows inward to the bulk (fresh) Li metal anode, evolving to a highly resistive layer with mossy Li. This porous dead Li layer leads to huge transfer resistance and cell polarization.55 Before the dendrite-induced short circuit, the impedance of the battery sharply escalates and hence the service life is early terminated.

Therefore, Li metal anode is critical to the degradation of a practical Li–S battery, especially in the pouch-cell format. Dendritic Li growth induced by the large currents is mainly responsible for the cell failure.56 Other than the usually prevailing theory of the failure caused by dendrite-induced short-circuit, the practical cell is more possible to be failed by the large polarization caused by powdery and dead Li in the porous layer. In a Li metal battery with the highly stable cathode (such as lithium iron phosphate and lithium titanate), the large capacity decay of Li metal battery is primarily due to the considerable polarization resulting from the porous and highly resistant layer in the Li metal anode. This conclusion is especially valid in a Li–S battery, where the LiPSs can readily react with Li dendrites to obtain the powdery, mossy, and dead porous Li layer.57 Consequently, it is rather indispensable to construct a stable and compact SEI film to protect the Li metal anode in a Li–S battery from the corrosion of LiPSs and electrolyte.

### The SEI on Li Metal Anode in Li–S Batteries

The SEI film formed by the parasitic reactions of electrolyte and Li was firstly observed by Dey in 197058 and named by Peled in 1979.59 Since then, knowledge on SEI film have evolved perpetually. Some conclusions on the SEI component and structure have been recognized as follows.60,61 (1) The customarily accepted description pattern on the SEI structure is the mosaic model, meaning that the SEI film is not homogeneous (Figure 5a).62 Several reductive decompositions proceed on the negatively charged anode surface simultaneously, and a mixture of insoluble multiphase products deposits on the anode. The formed SEI with a mosaic morphology allows the Li ions to migrate through it rapidly. (2) The SEI film in thickness direction is heterogeneous, with a dual-layer configuration and various ingredients (Figure 5b).63 The layer close to the Li metal anode is comprised of inorganic species with low oxidation states, including Li2N, LiF, Li2O, LiOH, and Li2CO3, etc, which is named as the inorganic layer. The outer part of the SEI film contains species with higher oxidation...
Figure 4. The thickness analysis of Li electrode harvested from the cycled cells. Cross-sectional SEM images of the Li anodes obtained from the cells after 100 cycles at (a) 0.2 C charge/1 C discharge, (b) 0.5C charge/discharge, (c) 1 C charge/discharge, and (d) 2 C charge/discharge. (a–d) Reproduced with permission from Ref. 54.

Figure 5. Scheme of SEI structure. (a) Mosaic structure in the top view. (b) Dual-layer structure in the cross-section view. (a) Reproduced with permission from Ref. 62. (b) Reproduced with permission from Ref. 63.

states, such as ROLi, ROCO2Li, and RCOO2Li, etc (R is the organic group related to the solvent molecules), named as the organic layer. (3) If a solvated Li ion intends to be reduced and deposit on the Li metal anode, it must go through two different diffusion routes (Figure 5b). One is the pore diffusion in the organic layer, during which the solvated Li ion gradually sheds its solvent molecules. After that, the other one is the interstitial knock-off diffusion in the inorganic layer of SEI film. Finally, the Li ion reaches the Li metal surface to receive the electrons and complete the plating process.

With the presence of LiPSs in the electrolyte, the Li metal anode of a Li–S battery presents a fundamentally unique surface-chemistry in contrast to the routine Li metal battery with an intercalated cathode. Indeed, LiPS species in the organic electrolyte leads to the formation of sulfur-containing components, such as Li2S and Li2SO4. The variation induced by LiPSs on the surface chemistry of Li metal anode in a Li–S battery can be divided into the following three categories.

1) SEI components. Take the commonly adopted electrolyte of Li–S battery (lithium bis(trifluoromethane sulfonimide) (LiTFSI)–1,3-dioxolane (DOL) with Li2S6) as an example (Figure 6a).54 The LiTFSI salts decompose into LiF, Li2CF3, Li2NSO2CF3, and Li2SO2CF3, while LiPSs are reduced to Li2S/Li2S2. The synergy of LiTFSI and LiPSs generates Li2SO4. DOL is an effective solvent in Li–S batteries to protect Li metal anode, and it decomposes into HCO2Li and LiOR. It is found that DOL is easier to thermodynamically decompose than another solvent, 1,2-dimethoxyethane (DME).51 However, the decomposition products of DOL are effective to protect Li metal anode (Figures 6b and 6c). LiNO3 is the most frequently adopted additive in Li–S batteries. When LiNO3 is adopted as the Li salt, the SEI film formed in the electrolyte solution contains Li4NOy due to the strong oxidation of LiNO3. Xiong et al. investigated the structure and component of SEI film formed in the Li2S6–LiNO3–DOL/DME electrolyte and found a dual-layer pattern
Figure 6. Electrolyte decomposition mechanism in the LiTFSI-DOL/DME with Li$_2$S$_6$ and LiNO$_3$. (a) A schematic illustration of the contribution of the various components in Li$_2$S$_6$/LiNO$_3$/LiTFSI/DOL solutions to the surface chemistry on the Li metal anode. (b) HOMO and LUMO energy comparison between DOL and DME molecules. (c) Reaction network of DOL decomposition mechanism. (a) Reproduced with permission from Ref. 64. (b, c) Reproduced with permission from Ref. 51.

for the inorganic components (Figure 7a). During initial cycling, the reduced products of LiNO$_3$ and Li$_2$S$_6$ (Li$_x$NO and Li$_2$S/Li$_2$S$_2$) deposit on the Li electrode simultaneously. The coprecipitation of Li$_x$NO and Li$_2$S/Li$_2$S$_2$ leads to a smooth and compact substratum layer. After that, the LiPSs in electrolyte solution are oxidized to lithium sulfates (Li$_2$SO$_4$ and Li$_3$SO$_4$) by LiNO$_3$ and deposit above the previous layer. The top layer is stable against oxidation, which can prevent the direct contact between the polysulfides in organic electrolyte and reductive species on Li electrode (including Li metal and Li$_2$S/Li$_2$S$_2$). This SEI film with the unique structure and component is effective to protect Li metal anode.

The high resolution transmission electron microscopy (HRTEM) image of SEI film formed in the LiPS-rich electrolyte confirms the classical mosaic-like structure, where various inorganic nanocrystals, including Li$_x$S, Li$_x$O, Li$_x$N, LiNO$_3$, and LiF are embedded (Figure 7b). By the meticulous investigations into the role of LiPSs on the composition of SEI film, it is found that Li$_2$S/Li$_2$S$_2$ is the unique component, which has not been found in the SEI films induced by other sulfur-containing additives, while Li$_2$SO$_4$ can also be achieved by other sulfur-containing electrolyte. Notably, the sulfurized SEI film indicates a high Li ion conductivity. However, Li$_x$S itself is a poor ionic conductor. Thus, a conjecture is proposed that the SEI structure is regulated by Li$_x$S 'nanopins' and the resultant poor crystallinity and enriched grain boundaries improve the Li-ion conductivity synergistically (Figure 7c). Therefore, the sulfurized SEI (SEI containing Li$_2$S/Li$_2$S$_2$) film formed in the LiPS-rich electrolyte is expected to exhibit a high ionic conductivity and stable Li plating/stripping processes.

(2) LiPS species-depending behavior. Though LiPSs can synergize with LiNO$_3$ to construct a unique SEI film, it does not mean that all LiPS species can act well for Li metal anode protection. When different LiPSs (Li$_x$S$_x$, $x$ = 1, 2, 3, 4, 5, 6, 7, 8; [S] = 0.1 mol L$^{-1}$) are added into the electrolyte (LiTFSI (1.0 M)−LiNO$_3$ (1.0 wt%)−DOL/DME), Li$_2$S$_6$ demonstrates the highest Li metal utilization (Coulombic efficiency) (Figure 8). In another study, Cui and colleagues found that Li$_2$S$_6$ with a sulfur concentration of 1.44 mol L$^{-1}$ can achieve a
Figure 7. SEI film formed in LiPS-rich electrolyte. (a) Illustration of the surface film behavior on lithium anode cycling in different electrolytes. (b) HRTEM image for the SEI film. (c) Schematic diagram for the SEI film (sulfurized SEI) formed in the LiPS-rich electrolyte. (a) Reproduced with permission from Ref. 65. (b, c) Reproduced with permission from Ref. 66.

Figure 8. Li metal utilization rate (Coulombic efficiency in a Li-Cu half-cell) in a Li_{2}S_{x}-rich environment (x = 1, 2, 3, 4, 5, 6, 7, 8). The sulfur concentration is fixed at 0.1 mol L\(^{-1}\) for all LiPS electrolytes. Reproduced with permission from Ref. 45.
Figure 9. Li metal utilization in LiPS electrolytes with different sulfur concentrations. (a) Coulombic efficiency of a Li-Cu half-cell in Li$_2$S$_5$ electrolyte with sulfur concentration varying from 0.005 to 1.0 mol L$^{-1}$ (b) Coulombic efficiency of a Li-Cu half-cell in Li$_2$S$_8$ electrolyte with Li$_2$S$_8$ concentration varying from 0.006 to 0.18 mol L$^{-1}$. (c) Possible mechanisms for the effect of the sulfur concentration on Li metal protection. (a) Reproduced with permission from Ref. 67. (b) Reproduced with permission from Ref. 46. (c) Reproduced with permission from Ref. 67.

good cycling performance when co-operating with 5.0 wt% LiNO$_3$ in the LiTFSI (1.0 M)−DOL/DME electrolyte. As the LiPSs in the electrolyte solution are not in a stoichiometric equilibrium and the exact compositions are highly dependent on the concentrations of LiPS species. More systematic investigations are required to clearly discover the best LiPS species added to the electrolyte to introduce the proper sulfur-containing components and construct a stable SEI film. (3) LiPS concentration-depending behavior. When Li$_2$S$_5$ with different sulfur concentrations (0.005−1.0 mol L$^{-1}$) is added into electrolyte solution (LiTFSI (1.0 M)−LiNO$_3$ (5.0 wt%)−DOL/DME), the electrolyte with 0.02 mol L$^{-1}$ Li$_2$S$_5$ obtains the best Li utilization and maintains a Coulombic efficiency of 95% after 233 cycles (Figure 9a). A similar result is achieved for the Li$_2$S$_8$ additives in the electrolyte (LiTFSI (1.0 M)−LiNO$_3$ (1.0 wt%)−DOL/DME) and 0.18 M Li$_2$S$_8$ exhibits the best cycling performance (average Coulombic efficiency over 120 cycles is ∼98.1%) (Figure 9b). The optimal concentration for Li$_2$S$_8$ seems much higher than that of Li$_2$S$_5$, which is probably induced by the higher solubility of Li$_2$S$_8$ than that of Li$_2$S$_5$. Nevertheless, the two LiPSs both possess an optimal concentration and excessive or inadequate LiPSs cannot effectively construct a stable SEI film to protect Li metal anode. The reasons can be explained as follows.
When the LiPS is in very low concentration ([S] < 0.050 mol L⁻¹), the formation of a uniform SEI layer can be hardly achieved (Figure 9c). As Li₂S prefers to deposit on the Li (111) plane rather than Li (110) plane, the ultralow sulfur concentration cannot build a continuous SEI layer on Li metal. The mutable and cracked SEI layer exposes fresh Li metal surface, which serves as dendrite formation site on the anode. When the sulfur concentration is very high ([S] > 0.50 mol L⁻¹) in the ether electrolyte, the cell exhibits a severe decay in efficiency even under the protection from 5.0 wt% LiNO₃. A large amount of LiPSs severely corrodes Li metal, leading to the cracked SEI layer and severe dendrite growth. The Li metal is etched into black powders and the electrolyte is gradually consumed. Only a proper concentration of LiPSs can realize the balance between the intermittent protective film and the strong etching effect.

LiPSs are helpful to facilitate the formation of a particular SEI film on the anode of Li–S batteries, which is distinctive to that of the routine Li metal batteries. However, the structure and component of the formed SEI film and its role in the cell cycling performance closely relate to the LiPS species and concentrations. In a practical Li–S battery, the LiPS species and concentrations are ever-changing at different depths of charges and discharges. Therefore, it is extraordinarily difficult to adopt the protogenetic LiPSs to construct the stable SEI film. Strategically designing the electrolyte component and anode structure can probably realize the positive role of LiPSs in the anode protections.

**Li Metal Protection in Li–S Batteries**

Relative to the sulfur cathode, the investigation on the Li metal anode is scarce. Nevertheless, the Li metal anode is gradually becoming the bottleneck of a practical Li–S battery and more attentions are required to promote the performance of the whole devices. In this section, we present an overview on the current approaches aiming at protecting the Li metal anode in Li–S batteries. Herein four basic categories are briefly established: electrolyte additives, artificial interfacial layer, solid-state electrolyte, and composite metallic anode. As the shuttled LiPSs in the anode side are corrosive to the Li metal anode, the strategies in suppressing LiPS shuttle, including cathode and separator design, are primarily helpful to protect Li metal anode. However, to focus on the working Li metal anode in Li–S batteries, herein we only summarize the strategies that fundamentally regulate the anode SEI film and metallic Li anode itself.

**Electrolyte additives.—** Among various electrolyte additives, LiNO₃ is the most popular one in the ether-based electrolyte (LiTFSI–DOL/DME) for Li–S batteries. In 2009, Aurbach et al. firstly introduced LiNO₃ co-salt to ether-based electrolyte, which can react with LiPSs to form the protective SEI film with Li₂S₄O₂ and LiNO₃ species. Zhang found that the discharge cutoff voltage must be higher than 1.6 V to avoid the irreversible consumption of LiNO₃. Nevertheless, LiNO₃ consumption is still unavoidable in Li–S batteries with a working voltage higher than 1.6 V. In the coin-cell with a low sulfur loading, LiNO₃ is effective to inhibit the side reactions between LiPS intermediates and Li metal anode by constructing a stable SEI film, leading to a high Coulombic efficiency of ~ 99%. Further researches demonstrate that the compact SEI film is generated by the synergetic reactions between LiPSs and LiNO₃, rather than the sole LiNO₃. However, when the sulfur loading and content in the cathode are increased, LiNO₃ fails to prevent the continuous corrosion of the anode caused by LiPSs. Therefore, some other novel additives are requested urgently to protect the Li metal anode in a working Li–S battery.

Considering the existence of LiPSs in the electrolyte, these electrolyte additives in Li–S batteries are inevitable to react with LiPSs. Liu et al. introduced lanthanum nitrate into Li–S battery to stabilize the surface of lithium anode (Figure 10a). After activation, the lanthanum element transforms into lanthanum sulfides on the anode surface. The resulting lanthanum sulfides are incorporated into Li₂S₂/LiS and LiS/Li₂O₃, forming a stable protective film on the surface of Li anode. Zu and Manthiram firstly investigated the role of copper acetate additives in protecting Li metal anode by generating a passivation film consisting of mainly Li₃Sₓ(CuS/Cu₂S) and other electrolyte decomposition products. In combination of elaborately designed characterization methods, Zu et al. further proposed a universal mechanism for the role of the metal ion additives. These electrolyte additives containing metal ions that have lower reactivity with sulfur than lithium (e.g., Cu, Ag, Au) are able to reduce the long-range crystallinity of the deposited impurity phases (SEI film), rendering more grain boundaries. These structures can lead to a higher Li⁺ conductivity, and hence a more stable lithium-metal anode. Lin et al. investigated the role of P₂S₅ as an additive into liquid electrolytes on the cycling performance of Li–S batteries. P₂S₅ is found to exhibit bifunctionality in Li–S batteries. One is to promote the dissolution of Li₂S, thus mitigating the capacity loss resulting from the irreversible precipitation of Li₂S. The other one is to passivate the surface of Li metal anode and achieve a stable SEI film to suppress the Li dendrite growth. The formed SEI film is about 3 to 5 μm thick with the Li₁₀PS₂₃ granular particles less than 100 nm. Due to the superior ionic conductivity of Li₁₀PS₂₃, the thick but highly conductive SEI film can enhance the Li ion transport rate, while significantly suppress LiPSs diffusion and the subsequent reactions with Li anode. Consequently, both the discharging capacity and Coulombic efficiency are promoted.

Besides the attempts to stabilize the SEI film in Li–S batteries, electrolyte additives are also designed to protect Li anode in general Li metal batteries. These additives include Cs⁺, LiF, and...
fluoroethylene carbonate (FEC), KNO₃, Li bis(oxalato)borate (LiBOB), AlCl₃, nanodiamond, a controlled trace amount of water, LiTFSI—lithium bis(fluorosulfonyl)imide (LiFSI) dual salt, and 0.05 M LiPF₆ additive in LiTFSI—LiBOB dual-salt, etc. However, it should be noted that due to the etching nature of LiPS-rich electrolyte in the Li−S battery, these electrolyte additives functioning well in other Li metal batteries are not always effective in the Li−S batteries. Some modifications are probably necessary to ensure their functionality in the Li−S batteries.

For the conventional electrolyte, it is generally acknowledged that 1.0 M is the most superior concentration for Li salt, which can achieve a proper balance among the cost, viscosity, and ionic conductivity. Highly concentrated electrolyte with a very high salt concentration has received broad attentions recently due to its effective role in stabilizing the SEI film and protecting the Li metal anode.

Zhang and co-workers adopted 4.0 M LiFSI−DME electrolyte to cycle Li metal anode. The enhanced availability of Li ions and increased solvent coordination in the electrolyte lead to a superior performance of Li metal anode. When this electrolyte is adopted in Li|Cu half-cells, very high Coulombic efficiencies are achieved: 99.1% for >1000 cycles at 0.2 mA cm⁻², 98.5% for >1000 cycles at 1.0 mA cm⁻², 98.4% for >1000 cycles at 4.0 mA cm⁻², and 97% for >500 cycles at 10.0 mA cm⁻². Suo et al. introduced a ‘Solvent-in-Salt’ electrolyte with an ultrahigh salt concentration and a high lithium ion transference number (0.73) to protect Li metal anode in a Li−S battery (Figure 10b). This electrolyte has two impacts on Li−S batteries: One is that LiPSs dissolution in the cathode is adequately inhibited. A Li ion conducting layer can be formed on the cathode by the highly concentrated electrolyte, acting as a barrier to inhibit LiPSs transport. The other is that it remarkably suppresses the Li dendrite growth and shape change of the metallic Li anode. When the highly concentrated electrolyte is adopted in the Li−S battery, a near 100% Coulombic efficiency and long cycling stability are achieved. Pan et al. found that even dimethyl sulfoxide (DMSO) solvent, usually incompatible with the Li metal anode, can realize a stable Li plating/tripping behavior in the highly concentrated electrolyte. A stable capacity of around 1200 mAh g⁻¹ can be achieved at 0.2 C after 65 cycles with DMSO solvent in a Li−S battery. Besides the superior performance, it should be noted that Li ion diffusion in the highly concentrated electrolyte will be hindered due to the high viscosity and low ionic conductivity. Therefore, the power density is lowered. Additionally, the cost of electrolyte will substantially rise when Li salts are excessively added.

Modifying the components and concentrations of electrolytes is often regarded as one of the most convenient strategies to suppress Li dendrite growth. Small modifications can bring about obvious changes in the surface chemistry of Li metal anode in Li−S batteries. However, electrolyte modification itself is not efficient enough to suppress Li dendrite growth in the long run due to the weaker mechanical performance of the formed SEI relative to Li dendrites. It is a primary tailor for the Li metal anode and is hopeful to cycle a long-lifespan when it co-operates with other strategies described subsequently in the review.

**Artificial interfacial layer.**—As discussed in Section 3, LiPSs are helpful to protect Li metal anode when they work with LiNO₃ in the electrolyte, which has been demonstrated in the half coin-cells. However, the shuttled LiPSs from the cathode are with varied species and concentrations, which will generate adverse effects to the stable SEI formation. To avoid the negative effects, while preserve the functional roles of LiPSs in stabilizing SEI film, our team reported an implantable strategy to effectively maintain the protective role of LiPSs-induced SEI film (Figure 11). The electroplated implantable SEI is obtained by pre-cycling Li metal in LiTFSI−LiNO₃−Li₂S₅ ternary salt electrolyte. After that, the routine Li metal is encapsulated by a uniform and multifunctional layer. The as-obtained Li-metal anode with protection of the implantable SEI can efficiently match sulfur cathode without any other additives. A Li−S coin cell assembled by the implantable SEI modified Li metal anode exhibits a high initial discharge capacity of 891 mAh g⁻¹ and a very large capacity retention rate of 76% after 600 cycles at 1.0 C with a Coulombic efficiency of 98.6% after 600 cycles. Li−S pouch cell with the implantable SEI exhibits an improved discharge capacity from 156 to 917 mAh g⁻¹ and enhanced Coulombic efficiency from 12% to 85% at 0.1 C. Electrochemical pretreatment is a powerful approach to construct an implantable SEI film when it cannot be realized in situ in the cycling cells. Since the electrolyte adopted in the activation stage (electrochemical pretreatment) can be different from that in the cycling stage, the selection of electrolyte additives is free from the cycling electrolyte. Other than LiPSs, FEC and AlII₃ based electrolytes are also adopted to build a stable SEI film before the cell cycling.
The electrochemically pretreating strategy can stabilize the electrolyte/Li metal interface, while the process is a bit complicated. In contrast, chemically liquid or gas processing seems much simpler. Li metals pretreated by polyphosphoric acid and styrene-butadiene rubber (Cu₃N + polymerized styrene butadiene rubber (SBR)) indicate a superior stability against the liquid electrolytes in the subsequent cycles. Wen’s group proposed several efficient agents to protect Li metal anode in Li−S batteries, such as Li₃N layer through in-situ reaction between Li and N₂, (CH₃)₂SiCl₄ or tetrahydrofuran (THF) solvent, oxygen atmosphere, and (CH₃)₂SiCl₄ liquid in sequence. The Li−S battery with a Li₃N protective layer on Li anode exhibits a discharge capacity of 773 mAh g⁻¹ after 500 cycles with an average Coulombic efficiency of 92.3% at 0.5 C without LiNO₃ additive (Figure 12).

Surface coating is another facile and cost-effective method to deposit a protective layer onto Li metal anode, which can be conveniently applied in the practical Li−S batteries. Due to its simplicity, various coating methods have been proposed and nearly all the coating materials can suppress Li dendrite growth under certain conditions. The coating materials include Al₂O₃, carbon, some polymers and some alloys, etc. The Li−S battery with a thin Li−Al alloy coating layer on the Li anode exhibits a better cycling performance than the one with pure Li anode.

This artificial interfacial layer can functionally prevent the contact between Li metal and LiPS to avoid the side reactions, and strengthen the electrolyte/Li metal interface to relieve the volume change during Li plating/stripping and retard Li dendrite growth. However, the artificial interfacial layer must be thin and ionically conductive. Briefly, these pretreatment strategies can protect Li metal before cell cycling, which afford a possibility to protect Li metal in the whole life cycle of Li−S batteries.

**Solid-state electrolyte.**—The routine liquid electrolyte is widely employed in current Li−S batteries. However, these liquid electrolytes display several safety issues including leakage, poor chemical stability, and flammability. The employment of solid inorganic/polymer electrolyte can totally or partly relieve these safety issues. More importantly, these electrolytes with a high modulus can efficiently suppress Li dendrite growth. Replacing liquid electrolytes with solid-state electrolytes has been considered as a most powerful strategy to avoid the safety hazards, especially in large-scale applications. In a Li−S cell, the solid-state electrolytes can additionally suppress the LiPS shuttle from the cathode to the anode, leading to an improved cathode utilization and hence a high discharge capacity and energy density. Therefore, the application of solid-state electrolyte into Li−S batteries is very attractive.

Relative to the conventional non-aqueous electrolyte, the primary dilemma of the solid-state electrolyte is the sharply reduced Li ion channels between the sulfur cathode and Li metal anode, leading to a large polarization as well as low Coulombic/energy efficiency in practical cells. To handle this trouble, the current researches of solid-state electrolyte focus on two aspects: (1) Continuously enhancing the ionic conductivity of solid-state electrolyte by developing novel solid-state electrolyte, such as LiₓGeP₂S₁₂, ipn-PEA electrolyte, three-dimensional (3D) ceramic/polymer network, in-situ plasticized polymer electrolyte, and composite polymer electrolyte with well-aligned ceramic nanowire (Figure 13a), etc. (2) Adequately reducing the interfacial impedance between the solid-state electrolyte and Li anode by the surface coating layer (Figure 13b), including Al₂O₃, Li−Al alloy, amorphous Si, ZnO, flexible polymer, in-situ formed Li₂PS₅, and liquid electrolyte wetting. It should be noticed that the coating layer must be thin and ionically conductive, which renders a high energy and power density at a cell level. These strategies shed fresh lights on the practical applications of solid-state electrolyte in the Li metal batteries.

So far the solid-state electrolytes have been tested in Li−S batteries. Polymeric electrolyte has a superior mechanical flexibility and can tightly contact with the sulfur cathode and Li metal.

![Figure 12.](image-url)
Figure 13. Li ion channel enhancement in a solid-state battery. (a) The ionic conductivity of solid-state electrolyte improved by the composite polymer electrolytes with well-aligned ceramic nanowire. (b) Interfacial modification by the surface coating layer. (a) Reproduced with permission from Ref. 130. (b) Reproduced with permission from Ref. 131.

The conventional Li–S batteries take elemental S as the cathode, while Li is stored in the anode. These above-mentioned hosts are merely matrixs without Li in them and most of conceptual advancements are mainly accomplished in Li metal anode half cells or full cells with the routine lithium-containing oxide or phosphate counter electrodes. The exploitation of a facile method to fill Li into the host as the anode of Li–S batteries is necessary. Our group demonstrated a 3D fibrous Li-B6 matrix as an inert host for elemental Li, which was derived from the high temperature alloying reaction of Li and B.175 Even at 10.0 mA cm$^{-2}$, no Li dendrite is observed, enabling a 2000-cycle long lifespan in Li–S batteries with a Coulombic efficiency higher than 90%. Cui’s group pioneered the fabrication of a composite Li metal anode by a melting strategy (Figure 15a).176–178 Firstly, a lithiophilic layer are coated onto the matrix to reduce the interfacial tension between Li metal and the matrix. Then this matrix is immersed into the molten Li (usually higher than 200°C) and the molten Li is adsorbed into the matrix to obtain the composite Li anode.179 With the help of LiF surface passivation on 3D layered Li-RGO electrode, Lin et al. achieved a composite Li metal anode and rendered Li–S cells with a significantly improved safety, cyclability, Coulombic efficiency, and excellent rate capability (≈800 mAh g$^{-1}$ at 2 C).180 Nevertheless, the method of filling molten Li into the pores of host materials is complicated. The current material processing is conducted at a high temperature, which requests a very sensitive regulation considering the safety issues. Additionally, the filling process is easily conducted.
when the lithiophilic hosts are applied, while the lithiophobic hosts have to be further modified with a lithiophilic barrier.

Another method to fabricate the composite anode for Li–S batteries is to electrochemically pre-deposit Li into the matrix. Jin et al. fabricated a covalently connected carbon nanostructure with CNTs growing on ultrathin graphite foam (CNT-UGF), which served as current collector for both sulfur cathode and lithium anode (Figure 15b). A novel Li–S full battery adopting sulfur/CNT-UGF cathode (47 wt% sulfur content in the whole cathode and 2.6 mg cm\(^{-2}\) sulfur loading) and lithium/CNT-UGF anode (20 wt% lithium content in the whole anode) exhibits a high capacity of 860 mAh g\(^{-1}\) at 12 C (52 mA cm\(^{-2}\)) and a very low cycling capacity decay rate of 0.057% at 2.0 C (8.7 mA cm\(^{-2}\)) after 400 cycles. For practical applications, the engineering development on the complicated routes of electrochemically pre-plating is further requested to achieve composite Li anode with dendrite-free plating/stripping behavior.

Contrast to the complicated routes to fabricate the composite Li metal anode, the introduction of an interlayer between the Li metal anode and membrane is a relatively simple method to regulate the Li ion depositing behavior on the Li metal anode. A novel Li–S battery using electrically connected graphite and Li metal as a hybrid anode is proposed. Lithiated graphite in front of Li metal anode acts as an artificial, self-regulated SEI film. This functional SEI can effectively suppress Li dendrite growth and prominently minimize the deleterious side reactions between Li metal, LiPSs, and electrolyte, rendering a significant performance improvement. Li–S batteries assembled with this hybrid anode exhibit a discharge capacity of >800 mAh g\(^{-1}\) at a high current of 1737 mA g\(^{-1}\) with a Coulombic efficiency >99% and only 11% capacity decay for 400 cycles. The introduction of porous interlayers and modified separator into the cathode with the functional entrapping of LiPSs or full rejection of LiPSs are another effective routes to avoid the direct contact of LiPSs with Li metal anode. Li metal is therefore protected in a stable Li metal anode at a current density and capacity of up to 10 mA cm\(^{-2}\) and 20 mA cm\(^{-2}\), an efficient composite Li metal anode is still scarce and the practical utilization of 3D lithium metal anode in Li–S batteries is very limited. Emerging strategies to easily and efficiently obtain a composite Li metal anode with high electrochemical performance is undoubtedly important for developing Li–S batteries with high discharging capacity and long lifespan.

Conclusions and Perspective

Li–S batteries with a high theoretical energy density of 2600 Wh kg\(^{-1}\) are under extensive investigations recently. Compared to the significant progresses obtained on the cathode and separators, advances and researches on Li metal anode are very rare. However, for a practical Li–S battery with a high areal sulfur loading and large operation current density, its lifespan is highly depended on the stability of Li metal anode. Relative to the Li metal anode matching with the stable oxide and phosphate cathode, Li metal anode in Li–S batteries has to be protected against the corrosion of LiPSs shuttling from the cathode, which results in a much more sophisticated surface chemistry on Li metal anode. In addition to the cell failure caused by dendrite-induced short circuit, powdery and dead Li created by dendrite growth can increase the cell polarization, hence leading to large capacity decay and cell failure.

To cope with this new failure mechanism, strategies of electrolyte additives, artificial interfacial layer, solid-state electrolyte, and composite metallic anode are proposed to protect the Li metal anode in a LiPS-rich environment. However, Li metal protection is a complicated issue. The modification aimed at healing one part of the electrode is far from adequate. The effective Li metal anode adopted in a practical Li–S battery should include several features as following. (1) 3D host is necessary to suppress Li dendrite growth and relieve the volume change during Li plating/stripping processes. The host should present good electronic conductivity and superior Li affinity. (2) If the composite anode is operated in non-aqueous electrolytes, there should be a protective film on the composite anode that is constructed through an artificial route before cell cycling and/or in-situ
formation during cell cycling. (3) If the composite anode is operated in solid-state electrolytes, enough ionic channels within the composite anode are required. A surface film between the composite anode and solid-state electrolyte is extremely imperative to reduce the interfacial impedance. It is the optimal choice if the ionic channels in and between the cathode and anode can be provided by one kind of solid-state electrolyte.

Frankly speaking, there is still a long route to realize the practical applications of Li–S batteries, especially an efficient Li metal anode with a very long lifespan. Aiming at this target, some principles are required to be considered in the future researches. (1) Similar to the situation of sulfur cathode before 2009, more attentions and research activities on Li metal anode are highly demanded from scientific and engineering groups. (2) Fundamental understanding on the mechanisms of SEI formation and de-solution of Li ion in the LiPS-rich environment needs to be intensively studied. (3) For a high-energy-density Li–S battery, the mass of Li in the anode should properly match the mass of sulfur in the cathode. Excess Li in the anode reduces the energy density based on the whole cell. (4) The effective methods to obtain a satisfactory composite Li metal anode with 3D host are still rare beyond high-temperature melting Li and electrochemical pre-lithiation. Developing emerging strategies to synthesize the composite anode is therefore quite necessary. (5) The rapid growth on insights into the Li plating/stripping behavior with solid-state electrolyte is an effective route to avoid the complex formation during cell cycling. (3) If the composite anode is operated with a very long lifespan. Aiming at this target, some principles are required to be considered through the continuous investigations on the science and engineering of Li metal anode.

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