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Polysulfide regulation vs anode modification: Perspectives on commercializing lithium–sulfur batteries

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INTRODUCTION

It is widely known that lithium–sulfur (Li–S) batteries are one of the most promising next-generation batteries due to their high theoretical energy density (2567 Wh kg\(^{-1}\)) and the abundance of sulfur.\(^1\) Since their introduction in 1962, Li–S batteries have gone through a series of developmental stages to overcome their limitations.\(^2\) For instance, the dissolution of discharged products (i.e., lithium polysulfides, Li\(_2\)S\(_x\)) during cycling causes poor battery life, lithium anode corrosion, and significant volume change during cycling.\(^3\) Thus, a large number of academic research studies have focused on understanding the behavior of polysulfides and improving the stability of the rechargeable cell. With the development of carbon nanomaterials, cathodes that are designed with carbon/sulfur composites were capable of mitigating the dissolution of polysulfides as well as alleviating the volume changes during cycling.\(^4\)-\(^12\) In addition, the recent advancements of separator modification,\(^13\),\(^14\) electrolyte tuning,\(^15\)-\(^18\) redox mediator,\(^18\) and anode protection\(^20\),\(^21\) have not only allowed Li–S cells to achieve over 1000 cycles but also facilitated the reversible capacities of over 1000 mAh g\(^{-1}\).

Despite the impressive electrochemical results that are achieved via various technological innovations, most of them are demonstrated with a coin cell configuration. Indeed, many laboratories employ a small-scale production for Li–S batteries using coin cells (e.g., CR2032 or CR2025), where the active areas of the electrodes are relatively small [Fig. 1(a)]. Pouch cells, on the other hand, exhibit a comparatively larger active area for both cathodes and anodes, which makes them more susceptible to unstable charge/discharge processes [Fig. 1(b)].\(^22\) Thus, the academic research into Li–S batteries has shown remarkable results in the past decades, while the actual product has failed to reach the market. Moreover, there are some controversies regarding the practical aspects and the cost of Li–S batteries at a large scale. For example, a high rate of over 40 C and a long cycle life of over 1500 cycles have been reported in many research papers using coin cells.\(^23\)-\(^26\) However, the rate capability for
pouch cells hardly surpasses 0.2 C and the cyclability (depending on how much sulfur is loaded) struggles beyond dozens of cycles.\textsuperscript{27–29} The huge performance gap between the two cell configurations can be attributed to the amount of electrolyte, sulfur, and lithium used during the assembly of cells. For example, the amount of lithium used in a coin cell is an excessive amount (over 200 μm thick lithium foil; 50–100 more than the cathode).\textsuperscript{22} In contrast, the amount of lithium for practical Li–S pouch cells should be just enough (<50 μm thick) to warrant the cost for large-scale production as well as to meet the required energy density.\textsuperscript{30,31}

Considering that the most promising benefit of a Li–S battery is the high energy density, the electrochemical assessment of pouch cells should address the practical parameters, including high sulfur-loaded cathodes, low electrolyte-to-sulfur ratios (E/S ratios), and ultrathin lithium anodes. Academically, researchers have already met those parameters by using advanced techniques to solve the polysulfide shuttle effect and the corrosion of lithium metal.\textsuperscript{32–34} Conversely, when considering the production cost and the viability of those techniques at a large scale, most of the methods can be barely applied to pouch cells. As shown in Fig. 1(c), it is evident that there is an exponential growth of publications concerning the performance aspect of Li–S batteries. However, the publication rate for the pouch cell implementation is disappointingly incremental. Indeed, it is important to understand that the exceptional performance observed in coin cells does not translate to a comparable result in pouch cells. Thus, the electrochemical evaluation based on a pouch cell level is considered a bottleneck for the commercialization of Li–S batteries.

**POLYSULFIDE REGULATION**

The electrochemical process for Li–S batteries primarily relies on the formation of soluble lithium polysulfides; as a result, regulating the dissolution of polysulfides has become a common goal for addressing the “shuttling effect” of polysulfides.\textsuperscript{35,36} There are several strategies to control polysulfides upon their generation, such as confinement, redox mediation, and absorption. Moreover, polysulfide regulation potentially improves the utilization of the negative electrode by reducing the deposition rate of polysulfides on the Li metal. Accordingly, this section covers three types of strategies that have been applied as a polysulfide regulator to demonstrate a functional pouch cell, including cathode design, separator/interlayer, and electrolyte tuning. In each type of strategy, we begin with the discussion of how the conventional coin cell methods hardly work at a pouch cell level; subsequently, we cover the most recent publications that have demonstrated Li–S pouch cells.
Cathode design

For the past decades, research into Li–S batteries is dominated by the development of cathode materials. Indeed, advanced carbon materials have been successfully utilized as a conductive matrix for insulating sulfur, such as graphene,37 porous carbon,38 carbon nanotubes,39 and carbon composites.40 Although most of the carbon materials are fabricated via a complex and high-cost process, this is hardly an issue for small-scale production (i.e., coin cell approach). As far as a pouch cell approach is concerned, commercially available carbon materials (e.g., acetylene black and activated carbon)41 are not suitable for the synthesis of large-scale sulfur cathodes due to their higher requirement of binders. For instance, commercial lithium-ion (Li-ion) batteries using a modern nickel-based cathode use only 1–3 wt. % of the binder.42 The amount of binders used in Li–S batteries, on the other hand, goes up to about 10 wt. %, which inevitably lowers the overall energy density of the pouch cells.43 Thus, it is imperative to optimize the structure of cathodes and the material synthesis process to minimize the cost and to maximize the practicality of Li–S pouch cells. Kensy et al. synthesized a highly porous cathode host with a commercially available carbon black material.44 The group employed a pyrolysis process to obtain the nitrogen-doped carbon materials, which enhanced the polysulfide adsorption as well as the active material utilization [Fig. 2(a)]. At a pouch cell level, this material facilitated a specific energy density of 238 Wh kg$^{-1}$45 for up to 170 cycles. Similarly, Xia et al. modified a different commercial carbon black (Super P) with FeP nanoparticles to introduce catalysis for polysulfide conversion reactions.46 As a result, the prepared Li–S pouch cells maintain up to 100 cycles with an areal sulfur loading of 7 mg cm$^{-2}$ at 0.2 C. The promising electrochemical results were ascribed to the efficient electrocatalysis for the liquid–liquid and liquid–solid transitions.

Several carbon materials could be used as a cathode host without any form of the doping element. However, they require an exotic process for successful synthesis. For instance, Wang et al. constructed a three-dimensional (3D) porous carbon out of a ZnO foam via the catalytic conversion of ethanol.47 This porous structure design not only provided an abundant space to store sulfur but also accommodated the volume expansion upon lithiation. When used as the cathode for Li–S pouch cells, this 3D porous carbon delivered the energy density of 382 Wh kg$^{-1}$ under the E/S ratio of 3.5 μl mg$^{-1}$. More recently, Yun et al. arranged the process of deriving a sustainable cathode host from hemp fibers.48 The group applied a two-step pyrolysis method to fabricate a carbon micro-tube, which involves the use of sulfuric acid to carbonize the raw hemp fibers [Fig. 2(b)]. Since the carbon micro-tubes mimic the water transport properties of a vascular plant, the prepared cathode was compact and robust enough to encapsulate a large amount of sulfur via capillary force. Accordingly, pouch cells with the hemp-derived cathodes managed a specific capacity of 1127 mAh g$^{-1}$ at the 50th cycle with an average Coulombic efficiency of 99.2%.

Although the ubiquitous use of carbon materials in Li–S batteries is undeniable, it is crucial to realize that carbon materials are nonporous and can only facilitate weak adsorption for polysulfides. Thus, the cycling performance of the pouch cells is not satisfactory for commercial use. This issue can be potentially resolved by modifying a carbon surface or by constructing a composite cathode structure specifically tuned to enhance the chemical affinity for polysulfides. Recently, Shao et al. demonstrated that Fe and N atoms on the surface of a modified hollow carbon sphere (Fe–N/MHCS) acted as Lewis acidic and basic sites to immobilize polysulfide molecules.49 As a result, the enhanced chemisorption promoted a favorable polysulfide conversion on the cathode while the merit of the large specific surface area of porous carbon spheres benefited high sulfur accommodation. Moreover, the potential for practical application is revealed through the Fe–N/MHCS pouch cell with the specific capacity of ∼970 mAh g$^{-1}$, which was sustained after 200 cycles. More recently, Yuan et al. designed a composite cathode consisting of the graphene-supported tin (IV) phosphate (SnP-G), which played a dual functional role of anchoring polysulfides and accelerating the kinetics for conversions [Fig. 2(c)]. With the merits of a stable layered structure and chemical stabilities, a pouch cell employing the SnP-G cathode delivered an improved capacity retention of 76.9% at 0.1 C for 100 cycles [Fig. 2(d)].

Apart from using carbon-based materials, other organic materials (e.g., conductive polymers) and inorganic 2D materials were also used to design composite cathodes. Owing to their diverse range of functional groups, conductive polymers are especially useful for polysulfide trapping; in addition, the elastic and flexible properties of a polymer are beneficial for high volume variation during cycling. To take advantage of these features, Li et al. assembled a flexible Li–S pouch cell by introducing the poly(3,4-ethylene dioxythiophene) conductive polymer to the composite cathode (CP@g-C3N4@CC).50 As shown in Fig. 3(a), the flexible pouch cell maintained a relatively consistent impedance at various angles with a sulfur loading of 4.7 mg cm$^{-2}$. On a larger scale, Wang et al. utilized the hexaaza-trinaphthylene (HATN) polymer to construct a functional pouch cell, which exhibits specific and volumetric energy densities of 303 Wh kg$^{-1}$ and 392 Wh l$^{-1}$, respectively.51 The group has also demonstrated a real-life use by powering a drone with the pouch cell assembled with a HATN polymer/S cathode [Fig. 3(b)]. It is worth noting that the conductivity of conductive polymers is not as good as the carbon materials. Thus, composite cathodes using conductive polymers are usually paired with some form of carbon to enhance the overall conductivity of the electrode. Moreover, the low thermal stability of most polymers is ill-suited for the sulfur melt-diffusion process. Composite cathodes using inorganic 2D materials are generally robust enough to handle the melt-diffusion process. However, just like conductive polymers, 2D materials are combined with carbon materials to increase the overall conductivity rather than using their intrinsic conductivity to achieve the optimized performance for Li–S batteries. Indeed, the most extensively studied 2D materials, such as transition metal dichalcogenides (TMDs), have been applied as robust sulfophilic anchors for carbon hosts.52 For instance, He et al. prepared a nanocomposite of 2D ReS$_2$ nanosheets on carbon nanotubes (ReS$_2$@CNTs), which was employed as an electrocatalyst to accelerate polysulfide redox reactions.53 Accordingly, pouch cells fabricated with ReS$_2$@CNT cathodes maintain a low capacity fading rate of 0.22% per cycle with the E/S ratio of 4.5 μl mg$^{-1}$. Similarly, mesoporous carbon spheres (MHCs) can be decorated with 2D MoS$_2$ nanosheets to accelerate sulfur reduction and polysulfide oxidation during cycling.54 Compared to the pouch cell with a bare MHCS cathode, the pouch cell using the MoS$_2$-modified MHCS cathode delivered a comparatively stable cycle life with the capacity retention of 960 mAh g$^{-1}$ after 170 cycles [Figs. 3(c) and 3(d)]. Apart from 2D TMDs, inorganic 2D MXene has emerged as a promising...
FIG. 2. Schematic diagrams illustrating (a) the nitrogen doping process for commercially available carbon black, (b) the two-step synthesis of a hemp fiber-based carbon scaffold, and (c) the synthesis route for the carbon-based composite cathode using SnP-G. (d) Cycling performances and Coulombic efficiencies of pouch cells prepared with the C–S and SnP-G cathodes. (a) Reproduced with permission from Kensy et al., Carbon 161, 190 (2020). Copyright 2020 Elsevier. (b) Reproduced with permission from Yun et al., J. Mater. Chem. A 9, 18260 (2021). Copyright 2021 Royal Society of Chemistry. (c) and (d) Reproduced with permission from Yuan et al., J. Energy Chem. 53, 99 (2020). Copyright 2020 Elsevier.
FIG. 3. (a) Digital images of the pouch cell (g-C$_3$N$_4$@CC cathode with conductive polymers) bent at various angles and the corresponding impedance spectra. Reprinted with permission from Li et al., Adv. Energy Mater. 10, 2001683 (2020). Copyright 2020 Wiley-VCH. (b) Digital image of a drone powered by the pouch cell using the HATN polymer/S cathode. Reprinted with permission from Wang et al., Angew. Chem., Int. Ed. 60, 11359 (2021). Copyright 2021 Wiley-VCH. (c) Cycling performance of pouch cells comparing bare and MoS$_2$-modified MHCS-S cathodes. (d) Schematic representation of the enhanced polysulfide reactions with the MHCS@MoS$_2$ cathodes. Reprinted with permission Shao et al., J. Energy Chem. 51, 262 (2020). Copyright 2020 Elsevier. (e) Long-term cycling performance of the Li–S pouch cell using MXene incorporated cathodes. Reprinted with permission Pai et al., Cell Rep. Phys. Sci. 2, 100480 (2021). Copyright 2021 Elsevier.
component for polysulfide regulations in pouch cells. MXene can either be coated onto a textile fabric or be functionalized to form a composite cathode.\textsuperscript{46} Recently, Pai et al. functionalized the surface of MXene nanosheets with ammonium chloride to improve the synthesis process for a high sulfur-loaded composite cathode.\textsuperscript{47} Further analysis revealed that the prepared cathode exhibited strong Lewis acid interactions to polysulfides, which enabled a practical pouch cell to deliver 770 mAh g\(^{-1}\) after 200 cycles at 0.2 C \textsuperscript{[Fig. 3(e)]}. The promising electrochemical performance is also attributed to the unique cathode design tuned to facilitate a metal-like conductivity for efficient ion transport.

**Separator/interlayer**

Modifying separators or introducing multi-functional interlayers to Li–S batteries usually serves two roles: (1) confining polysulfides on the cathode side to prevent the effects of shuttling behavior and (2) improving the utilization of sulfur during cycling.\textsuperscript{55} In general, commercially available separators (i.e., polypropylene Celgard membrane) are coated with adsorbent materials, such as activated carbon and polypyrrole nanotubes, to improve the performance of Li–S batteries.\textsuperscript{48} However, the electrochemical results are based on a coin cell configuration with a low amount of sulfur (<2 mg cm\(^{-2}\)). In a pouch cell configuration, the benefits of the modified separators are diminished by the limited adsorption capacity against higher loaded sulfur cathodes. Increasing the amount of modifying materials on separators may absorb more polysulfides, but this would reduce the overall energy density and potentially increase the cost for large-scale production. In addition, modifying separators at a large scale with powdered-forms of materials would cause them to become more susceptible to detachment during extended cycling. Thus, material selection must be carefully considered for separator modifications to ensure that pouch cells are operational for long-term use. Inserting a multi-functional interlayer between the cathode and the separator is intended to mitigate the shuttle effect as well as to promote ionic selectivity. In this regard, interlayers serve a similar role as the modified separators. This also means that they face similar issues with modified separators when they are configured into pouch cells. Likewise, introducing additional components with a specially designed interlayer may not only increase the cost but also add more weight to the large-scale assembly of Li–S pouch cells. Thus, the mass and thickness of interlayers should be optimized to enable a balance between energy capacity and cost.

To avoid losing the energy density of a Li–S pouch cell, researchers have opted for lightweight separators and interlayers by directly functionalizing a Celgard membrane instead of stacking more materials to it. For example, Fu et al. modified a Celgard membrane with a vapor-phase polymerization method, which resulted in a polypyrrole (PPy) functionalized separator that repelled the migration of polysulfide anions from cathodes.\textsuperscript{56} Indeed, the Li–S pouch cell with the PPy-functionalized separator demonstrated a flexible feature while retaining a discharge capacity of 1016 mAh g\(^{-1}\) at the initial stage \textsuperscript{[Figs. 4(a) and 4(b)]}. To further attain a higher energy capacity in a pouch cell configuration, Jovanovi\’c et al. took advantage of the self-assembly chemistry of polyelectrolyte complexation (PPX) and applied the functionalized nanoparticles to a separator \textsuperscript{[Fig. 4(c)]}.\textsuperscript{57} The porous nature of the PPX separator accommodated a dense amount of functional groups, which yielded a high adsorption capability to polysulfides. Moreover, the separator exhibited low weight and strength to bear the scale of a pouch cell synthesis. As a result, the cell with the PPX separator delivered an initial discharge capacity of 1281 mAh g\(^{-1}\) with the E/S ratio of 4.6 \(\mu l\) mg\(^{-1}\). Although modifying separators with the right approach can effectively improve the specific capacity in pouch cells, a large amount of electrolyte is typically used to ensure that the separators are thoroughly soaked, which is counterintuitive for enabling a practical energy density. To avoid using bulk electrolytes for pouch cells, Xue et al. decorated a separator with BiFeO\(_3\) (BFO) nanoparticles that can efficiently accelerate the transfer of Li ions.\textsuperscript{58} The ferroelectric properties of the BFO induced electric field on the separator not only facilitated a fast diffusion of Li ions but also anchored the dissolved polysulfides. Accordingly, the Li–S pouch cell using the BFO modified separator exhibited an initial capacity of 1408 mAh g\(^{-1}\) with a minimal electrolyte amount of 4 \(\mu l\) mg\(^{-1}\) for up to 150 cycles.

Besides using the functional groups to either repel or absorb polysulfides, applying a catalytic interface on the separator is another viable solution to regulate polysulfides without adding extra bulk. In this regard, Xue et al. reported the catalytic mechanism of Mo\(_5\)S\(_3\) and stacked an electrocatalytic interface on a separator that efficiently prevents the clogging of polysulfides while promoting a fast Li-ion transport.\textsuperscript{59} As illustrated in Fig. 4(d), a thin layer of the Li\(_3\)Mo\(_5\)S\(_3\) interface exhibits a low electronic resistance that contributes to additional capacity. Thus, the interlayer is considered an active material, which benefits the overall energy density of a Li–S battery. Indeed, the pouch cell with the Mo\(_5\)S\(_3\) interface delivered a sustained capacity of 1114 mAh g\(^{-1}\) after 39 cycles. Instead of stacking catalytic materials on a separator, Hu et al. configured a catalytic interlayer by incorporating CoIn\(_2\)S\(_3\) (CIS) particles into a separator that efficiently induces the redox reactions with a large number of polysulfides.\textsuperscript{60} As shown in Fig. 4(e), the CIS eliminates the conversion barriers of any incoming polysulfide species; hence, a thin interlayer of CIS can act as a “recycler” to maximize the usage of sulfur. Using the CIS coated separator for a pouch cell, the specific capacities of 1144 mAh g\(^{-1}\) at 50 mA and 711 mAh g\(^{-1}\) at 100 mA were achieved for up to 120 cycles with a sulfur loading of 4 mg cm\(^{-2}\) \textsuperscript{[Fig. 4(f)]}. These results demonstrate that the catalytic interlayer is effective in improving both the sulfur utilization and cycle life of a Li–S pouch cell.

**Electrolyte tuning**

An electrolyte is a critical component for Li–S batteries because it not only provides ion transport but also has a direct impact on the energy density depending on its quantity. Indeed, the relationship between the electrolyte amount and the energy density of Li–S batteries has been intensely studied in recent years.\textsuperscript{61,62} Chung and Manthiram have pointed out that a coin cell with the E/S ratio of 4.2 \(\mu l\) mg\(^{-1}\) and the sulfur loading of 57.6 mg cm\(^{-2}\) exhibited a promising specific capacity for up to 200 cycles.\textsuperscript{63} However, such an E/S ratio translated to the specific energy density of ~270 Wh kg\(^{-1}\) for pouch cells. Excessively increasing the electrolyte amount (>10 \(\mu l\) mg\(^{-1}\)) would drastically reduce the energy density to about 140 Wh kg\(^{-1}\), which is even lower than that of the current Li-ion batteries.\textsuperscript{63} Thus, it is vital to minimize the amount of electrolyte used in Li–S pouch cells to maximize their practicality.
FIG. 4. (a) Galvanostatic charge–discharge profiles comparing the normal and bent states of the Li–S pouch cell with the PPy coated separator. (b) The cycling performance of the flexible pouch cell (PPy@CS) at a bending angle of 90°. Reprinted with permission from Fu et al., Nanoscale 12, 5483 (2020). Copyright 2020 Royal Society of Chemistry. (c) Schematic illustrations outlining the chemistry behind the formation of polyelectrolyte complex nanoparticles. Reprinted with permission from Jovanović et al., ACS Appl. Energy Mater. 3, 7908 (2020). Copyright 2020 American Chemical Society. (d) Schematic of the Li$_x$Mo$_6$S$_8$ interlayer suppressing the migration of polysulfides and preventing the separator from clogging. Reprinted with permission from Xue et al., Matter 1, 1047 (2019). Copyright 2019 Elsevier. (e) Schematic representation of the CoIn$_2$S$_4$ (CIS) induced catalytic conversion for polysulfides. (f) Cycling performance of the pouch cell utilizing the CIS modified separator. Reprinted with permission from Hu et al., J. Mater. Chem. A 9, 9771 (2021). Copyright 2021 Royal Society of Chemistry.
Lowering the electrolyte amount not only results in a decreased dissolution of polysulfides but also leads to sluggish Li-ion transport as well as a low sulfur utilization. Consequently, modifying the electrolyte and optimizing the amount used are the crucial steps to maintain the balance between performance and energy densities of Li–S batteries. In this regard, introducing additives to the electrolytes is one way to boost their efficiency of sulfur utilization at a limited amount. Bai et al. tuned the electrolyte by utilizing the nitrogen-defective graphite-like carbon nitride (NGCN) as an additive, which prevented the loss of active polysulfides and improved the utilization rate of sulfur. As a result, the pouch cell with the NGCN containing electrolyte managed a stable cycling performance of 100 cycles with the areal sulfur loading of 5 mg cm$^{-2}$. Similarly, Guo et al. reported that the addition of 1,3,5-benzentrithiol (BTT) to a conventional 1,3-dioxolane (DOL)/DME-based ether electrolyte can play a dual role of protecting the electrodes and reducing the dissolution of polysulfides. Indeed, the high chemical reactivity of BTT to sulfur is beneficial for reducing the required amount of electrolyte for a stable operation [Fig. 5(a)]. By the virtue of this unique chemical property, the pouch cell with the BTT additives demonstrated an improved energy density of 441 Wh kg$^{-1}$ while operating at a reduced E/S ratio of 2.6 μl mg$^{-1}$. This work offers a new avenue into designing a practical Li–S pouch cell by tuning the bond chemistry of additives, which efficiently provides a positive reaction for both electrodes and electrolytes.

Instead of employing external additives, incorporating cosolvents or modifying the electrolyte concentrations may serve as an efficient method to modulate the solubility of polysulfides without adding extra electrolyte volume. For instance, Jiang et al. modified the concentration of the ether electrolyte by tuning a certain amount of lithium salt (LiTFSI) and the 1,3-dioxolane (DOL) solvent. As shown in Fig. 5(b), the modified electrolyte (MDHCE) enabled robust protection for the cathode to promote high flexibility and fast Li-ion transport. Due to the enhanced durability of the cathode, the sulfur utilization improved and the pouch cell achieved an areal capacity of 10 mAh cm$^{-2}$ under the reduced electrolyte volume (3 μl mg$^{-1}$). Zhang and co-workers proposed that the reactivity of polysulfides to Li is highly dependent on the reduction resistance of the solvent shells. By adding isopropyl ether (DIME) as a cosolvent to the electrolyte, the group discovered that polysulfides were encapsulated with anti-reductive solvent shells, which mitigated the parasitic effects of the shuttling behavior. As demonstrated in Figs. 5(c) and 5(d), the improved reduction resistance of the electrolyte with the DIME cosolvent prevented the corrosion of Li by polysulfides. By taking advantage of the reduction stability against polysulfides, the pouch cell with the E/S ratio of 3 μl mg$^{-1}$ delivered the specific energy density of 300 Wh kg$^{-1}$ for up to 23 cycles. Besides tuning the solvents to accelerate the redox kinetics of electrolytes, the overall density of an electrolyte can be reduced by incorporating reactive cosolvents to alter the salt solubility. For example, Liu et al. developed a method to reduce the electrolyte density by introducing a Li-compatible monoether to the conventional electrolyte. As a result, a reduction of over 30% in the electrolyte weight per volume was achieved while retaining the favorable traits for an effective polysulfide utilization (e.g., high ionic conductivity and moderate viscosity) [Figs. 5(e) and 5(f)]. Likewise, a Li–S pouch cell with the ultralight electrolyte reached a cell-level energy density of 393.4 Wh kg$^{-1}$ at the E/S ratio of 3 μl mg$^{-1}$. Liu et al. have recently...
demonstrated another solvent-mediated electrolyte density reduction by using a fluorinated silane solvent (TFMTMS). When mixed with the Li salt concentration of 0.5 M, the fluorinated electrolyte exhibited a low density of 1.0 g ml⁻¹, which benefited the practical conditions of the pouch cell by delivering the energy density of 276 Wh kg⁻¹. It was also found that the electrolyte formed robust solid-electrolyte interface layers on the electrodes. Hence, even under a lean electrolyte condition of 4.5 μl mg⁻¹, the cell managed to operate beyond 100 cycles with the improved polysulfide protection.

**ANODE MODIFICATION**

The Li metal is a preferred anode material for Li–S batteries due to its high theoretical capacity of 3860 mAh g⁻¹ and the low potential of −3.04 V against standard hydrogen electrodes. However, Li anodes are susceptible to the corrosive effects of polysulfides; additionally, they suffer from dendritic growths and rampant volume changes during cycling. It should be noted that the significant volume expansion is hardly an issue for coin cells since they use an excessive amount of Li with a stainless steel casing. Pouch cells, on the other hand, are more sensitive to the volume expansions due to their soft plastic/aluminum packaging; moreover, their anodes are comparatively larger in terms of the surface area, which leaves more room to side reactions between Li and the electrolyte. Another challenge that causes stability issues with the anodes in Li–S pouch cells is the use of thin Li foil to minimize the excess amount of the Li metal. Indeed, Zhu et al. observed a severe corrosion of Li foil (160 μm thick) in a pouch cell after several cycles. In this section, we will highlight the recent strategies to protect Li anodes against corrosions as well as to improve the stability for practical Li–S pouch cells. These strategies can be categorized into two types of anode modifications: protecting the surface of Li foil with an interface layer or accommodating Li with a host material.

**Interface protection**

A widely considered approach to stabilize the anodes is to form a multi-functional interface on the surface of the Li metal. The formation of the protective interface should not only promote a uniform Li-ion flux (which mitigates Li dendrite growths) but also minimize the contact between the electrolyte and the Li metal to prevent the consumption of active materials. This is especially important for Li–S pouch cells since the area of the electrode in pouch cells is considerably larger than that of coin cells. In this regard, the protective interface should be designed to efficiently handle the limited amount of electrolyte in a practical Li–S pouch cell. Luo and Manthiram protected the surface of Li foil with the in situ formed LiF-dominated interface. Due to its low diffusion energy barrier of Li transfer and excellent chemical stability against the electrolyte, the LiF interface diminished the corrosion of polysulfides on the anode while restraining the dendrite growths. As a result, the pouch cell using the protected anode maintained a discharge capacity of 136 mAh after 45 cycles. To further improve the Li-ion diffusion kinetics at the interface, Hu et al. utilized the combination of a lithium–antimony (Li₃Sb) alloy and LiF to passivate the surface of the Li anode. Such a hybrid approach not only eliminated the diffusion barrier for Li-ions during cycling but also provided an electron-blocking “shield” to prevent the electron tunneling from the anode into the solid electrolyte interphase (SEI). Thus, the consumption of the electrolyte is reduced by a dendrite-free Li deposition. Benefitting from these features, the LiF/Li₃Sb modified Li anode enabled a Li–S pouch cell to deliver the energy density of 325.28 Wh kg⁻¹ under a lean electrolyte condition (3 μl mg⁻¹) for up to 60 cycles [Fig. 6(a)].

Besides forming an interface layer directly on the surface of the Li metal, another method is to introduce an external protective coating for Li anodes, which potentially offers more options to control the components of the interface protection. For example, Wang et al. reported that the large numbers of atomic sites on the specially designed composite interface (SACo/ADFS) modulated the plating behavior of Li [Fig. 6(b)]. Due to the homogenous deposition/dissolution of Li, the interface maintained its structural integrity to prevent the exposure of the Li metal to the electrolyte. When the protected Li anode was assembled into a Li–S pouch cell, a high areal capacity of 3.78 mAh cm⁻² for over 60 cycles was attained with the sulfur loading of 5.4 mg cm⁻². Indeed, the stable interface layer not only reduced the rate of electrolyte decomposition but also prolonged the efficient utilization of sulfur.

**Host design**

The utilization of a host material has become a common practice to address the excessive volume change of Li metal anodes upon repeated cycling. Typically, a host material is composed of a 3D matrix that exhibits both lithiophilicity and the space to accommodate a large amount of Li. This feature is useful for a pouch cell application in which the anode can suffer from pulverization due to the significant volume change. However, careful discernment is required when designing the host to ensure that the anode is not unreasonably thick and heavy. Otherwise, the employment of a host material as the anode will reduce the overall energy density of Li–S pouch cells. To avoid this, constructing a host structure with a lightweight material (i.e., carbon nanomaterials) was considered to be a feasible approach for large-scale applications. Shi et al. employed a carbon fiber (CF) matrix as the host for Li and synthesized the anode through a one-step rolling method [Fig. 7]. The group also formed the lithiophilic LiC₆ layers on the surface of the CF host to establish the intercalation reaction between carbon and Li, which improved the wettability of Li throughout the matrix. Therefore, the excessive volume expansion and the dendrite growths were suppressed to enable a large-scale utilization of active materials in Li–S batteries. Indeed, the pouch cell with the Li/CF anode displayed a discharge capacity of 3.25 mAh cm⁻² and maintained a capacity retention of over 98% after 100 cycles at 0.1 C. In addition to the physical infusion of the Li metal into the host structure, a host material can also be pre-deposited with Li before applying it as an anode for Li–S pouch cells. In this case, the host matrix acts as a 3D current collector that can effectively modulate the lithiation behavior on an anode with a large surface area. For instance, Dharmasena et al. pre-lithiated the nanowires consisting of an alpha phase molybdate (α-MoO₃) to take advantage of its low-expansion property during cycling. The host material also showed stability against the electrolyte by maintaining a stable charge transference. Benefitting from these aspects, the group demonstrated the practicality of the host material by integrating an α-MoO₃ anode into the pouch cell, which delivered the energy density of 620 Wh kg⁻¹ for...
the first cycle. The subsequent cycling exhibited energy densities of at least 300 Wh kg\(^{-1}\) for up to 100 cycles.

Indeed, the host design proves to be an effective strategy to eliminate the volume instability issue in anodes; nevertheless, the open structure of the host renders it vulnerable to polysulfides. In this regard, the combinative modification of the anode with a protective interface and a robust host design seems to be the ideal solution to deal with the issue. Moreover, the method of predepositing a certain amount of Li to the host structure appears to be a sustainable strategy to use a finite amount of Li for large-scale Li–S battery production.

**CONCLUSION AND OUTLOOK**

Over the past few decades, remarkable progress has been made in the development of high-performance Li–S batteries with in-depth research and understanding of the fundamentals of battery chemistry. Indeed, the electrochemical performance (e.g., specific capacity and cycling performance) of Li–S batteries based on a coin cell level has significantly improved. However, researchers were hard-pressed to reproduce those promising results in a pouch cell configuration. This is due to the obvious difference in the assembly process and the scale between coin cells and pouch cells. Likewise, an
unfortunate gap between the real-world use and academic research in Li–S batteries exists, which presents as a huge bottleneck for the commercialization of Li–S batteries. To realize the main advantage of a Li–S battery (i.e., high energy density), more attention should be given to the implementation of pouch cells. Indeed, practical Li–S pouch cells are restricted to the key parameters, including high sulfur content, lean electrolyte, and minimal Li amount. Those restrictions, however, present challenges and redefine the research boundaries of Li–S batteries. In this regard, we suggest the following research directions to emphasize that there is room for improvement as well as new opportunities to explore:

(1) By this point, it is obvious that the amount of research into Li–S pouch cells employing the strategy of polysulfide regulation is more substantial than that of the anode modification. Indeed, handling Li anodes for a large-scale modification is not a simple task due to the high reactivity of the Li metal. While previous studies have assembled a functional Li–S pouch cell using modified anodes, they only discussed how the modification protected the anodes against dendrites and volume fluctuations. Hence, the interactions between a modified anode and polysulfides remain unclear. This presents an opportunity for the researchers to investigate the true cause of failure for the Li metal in Li–S pouch cells while developing an advanced anode that promotes a beneficial interaction with polysulfides.

(2) Ultimately, the use of a solid-state electrolyte for Li–S batteries is the best strategy to overcome all of the intrinsic challenges, such as Li instability, polysulfide shuttling, and weight issues. Since the development of an all-solid-state Li–S battery is still in its infancy, difficult challenges, such as low ionic conductivity, high interfacial resistance, and unstable compatibility, with Li–S chemistry remain unsolved. In addition, a pouch cell application for an all-solid-state Li–S battery is almost nonexistent in the current literature. Although there are some exceptions, the inadequate parameters (e.g., sulfur loading, energy densities, and cycle life) compromise their viability for real-world use. Therefore, more evidence is needed to prove that the use of solid-state electrolytes is a realistic approach for Li–S batteries.

(3) Stating just the specific capacity of the pouch cells does not provide a complete picture of the useable energy. Indeed, pouch cells have many components to function properly and a few of those components are inactive. Consequently, the weight of each component has a profound impact on the final energy density. In this case, research into Li–S batteries with pouch cell implementations should transparently state how the specific energy density is estimated and which cell components are considered. Additionally, pressure distribution in pouch cells should be checked and optimized for the respective mechanical properties of the internal components.

(4) With the right materials and parameters, the specific energy density \(W_E\) of Li–S batteries exceeds that of Li-ion batteries. However, the volumetric energy density \(W_V\) of Li-ion batteries still takes the lead over that of Li–S pouch cells. For portable applications, \(W_V\) should not be overlooked and the cell design should be adapted to operate in a tight space. Key factors that influence the \(W_V\) of Li–S pouch cells are the sulfur content, thickness/density of the cathode, and the electrolyte amount. Although increasing attention has been paid to boost \(W_V\) with a high sulfur-loaded cathode, high sulfur loadings will significantly compromise the ion transport and the cycle life of pouch cells. Thus, researchers are encouraged to introduce interdisciplinary technologies for cathode development instead of blindly pursuing high sulfur content.

Undoubtedly, there is a long way to go before we can safely say that Li–S batteries are ready for the mainstream market to compete against Li-ion batteries. This is evidenced by the fact that there are a limited number of publications for Li–S pouch cells. Based on the publications that presented a pouch cell application, two different strategies are observed to enhance the performance of Li–S pouch cells. These strategies are achieved by (1) regulating polysulfides with advanced cathodes, modified separators/interlayers, and optimized electrolytes and (2) modifying anodes with the protective interface and host materials. Here, we have reviewed those strategies with the most recent developments of Li–S pouch cells. We have also raised the importance of the pouch cell evaluation when introducing new materials and concepts for Li–S technology. In this regard, we hope that this perspective would encourage researchers to continue exploring new approaches to achieve the goal of producing practical Li–S batteries at a commercial scale.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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