Mechanistic understanding of the role separators playing in advanced lithium-sulfur batteries

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Abstract
The lithium-sulfur battery is considered one of the most promising candidates for portable energy storage devices due to its low cost and high energy density. However, many critical issues, including polysulfide shuttling, self-discharge, lithium dendritic growth, and thermal hazards need to be addressed before the commercialization of lithium-sulfur batteries. To this end, tremendous efforts have been made to explore battery configurations and components, such as electrodes, electrolytes, and separators, among which the separator plays an especially critical role in addressing aforementioned issues. Thus, this review analyzes the mechanisms and interactions of these critical issues and summarizes both the function of separators and recent progress made towards remedying such issues. Additionally, promising directions for the development of separators in lithium-sulfur batteries are proposed.

KEYWORDS
lithium dendrite, lithium-sulfur batteries, self-discharge, separator, shuttle effect, thermal hazards

1 | INTRODUCTION

With merits of high energy density, low cost, and abundant reserves, lithium-sulfur batteries have garnered increasing attention for their potential in portable energy storage applications.1-4 However, many critical issues hinder the practical application (Figure 1A), including polysulfide shuttling,5-8 self-discharge,9-11 lithium dendrite formation,12-15 and thermal hazards.16-18 During discharge, cathodic sulfur is gradually reduced to polysulfides (Li$_2$S$_n$, 4 $\leq$ n $\leq$ 8) and low-order sulfides (Li$_2$S and Li$_2$S$_2$). These polysulfide intermediates dissolve in the electrolyte and shuttle between the cathode and anode, reacting spontaneously with the lithium anode, resulting in the loss of cathodic active components, passivation of the lithium electrode, and reduction in energy efficiency. Solvation

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and migration of polysulfides also leads to self-discharge.\textsuperscript{19-21} Under the static state, solvated polysulfides are continuously consumed by the lithium electrode via chemical reactions, causing a low open-circuit voltage and a quick capacity degradation.

Lithium dendrite growth is inevitable on the lithium anode. During the charging process, the nonuniform electric field and/or lithium flux results in the uneven electrodeposition, which forms dendritic structures on the lithium electrode surface. After that, electrons tend to gather at peaks on the uneven surface, intensifying preferential electrodeposition, which leads to the self-propagating dendrite growth. The lithium dendrites then lead to uneven surfaces, which consumes more electrolyte through parasitic reactions, resulting in high internal resistance. Concurrently, dendrites can also penetrate the separator and cause an internal short-circuit, leading to capacity loss and safety hazards.

Thermal safety is also of critical concern. The internal heat accumulation will cause thermal shrinkage of commonly used polyolefin separators due to their limited deformation temperature. The severe deformation of the separator may lead to direct contact between the anode and cathode, which results in thermal runaway and even an explosion in some cases.\textsuperscript{22,23} Therefore, inhibiting the separator thermal shrinkage will be helpful to improve the thermal safety of the battery.

These above-mentioned issues plaguing lithium-sulfur batteries interact with each other to constitute a sophisticated battery system (Figure 1B). Meanwhile, they are all related to separators and thus the separators are crucial to solve these issues (Figure 1C). In the past few years, several constructive reviews have summarized the progress of separator in lithium-sulfur batteries but only focused on the shuttle effect.\textsuperscript{24-26} This review summarizes the functional mechanisms and major breakthroughs in separators for lithium-sulfur batteries on both inhibiting polysulfide shuttling, limiting self-discharge, suppressing lithium dendrites, and improving safety. Furthermore, the challenges of separators in achieving widespread applications of lithium-sulfur batteries are discussed.

2 | SEPARATORS TO RESTRAIN POLYSULFIDE SHUTTLE EFFECT

2.1 | Separators with trapping effect to polysulfide

2.1.1 | Working mechanism and material design principle

Polysulfide species are first adsorbed on the surface of the trapping material through physical/chemical interactions and then reduced and fixed on the surface. Therefore, an efficient polysulfide trapping separator should be constructed with the physical, chemical, and catalytic adsorption effects, as shown in Figure 2.

The physical trapping effect mainly depends on the nonselective Van der Waals force between the trapping material and the polysulfide molecules. There is a slight physical adsorption heat and a swift adsorption speed. However, the adsorption of polysulfides is also easy to reverse. Once a dynamic balance is established between
adsorption and desorption, the physical adsorption is disabled on a macroscopic level.

The chemical trapping effect mainly depends on the chemical bonding force created by the electron transfer and exchange or coexistence between polysulfide molecules and the surface atoms of adsorption materials. Compared to physical adsorption, chemical adsorption has a stronger adsorption force and greater selectivity.

The catalytic trapping effect can immobilize polysulfides on the trapping material's surface by facilitating the polysulfide electrochemical reduction reaction. Therefore, the catalytic adsorption occurs after physical/chemical adsorption and is positively correlated with the physical/chemical adsorption capability.

In conclusion, to capture polysulfides, trapping separators should have a high specific surface area, an appropriate porous structure, strong interaction with polysulfides, high conductivity, and high catalytic activity. Based on these specifications, different trapping separators have been developed and applied in lithium-sulfur batteries.

2.1.2 Separators with physical trapping effect

Key considerations for physical trapping materials are micropore volume and specific surface area. High micropore volume, with decent tortuosity, is favorable for inhibiting polysulfide migration, while a high surface area provides abundant trapping sites for polysulfides. Due to the naturally porous structure, most separators have strong or weak physical trapping effect.

Benefitting from its high specific surface area, tunable pore structure, and excellent electronic conductivity, porous carbon is a suitable physical barrier for polysulfides. Chang et al. coated single-wall carbon nanotubes (SWCNTs) as a polysulfide physical trapping material on a polypropylene (PP) separator via a simple vacuum-filtration method. SWCNTs have a high specific surface area (527 m² g⁻¹) and a large pore volume (1.30 cm³ g⁻¹), with the abundant micropores providing the total surface area of 189 m² g⁻¹ and the pore volume of 0.10 cm³ g⁻¹ (Figure 3A), allowing for an excellent polysulfide trapping efficiency (Figure 3B). With a SWCNT-coated separator, the lithium-sulfur battery exhibits a high discharge capacity of 1132 mAh g⁻¹ (0.2 C) and a low capacity decay rate of 0.18% per cycle (0.2 C, 300 cycles), showing much improvement over the commercial separator (630 mAh g⁻¹, 1.3% per cycle) (Figure 3C,D).

In addition to the nonpolar carbon trapping layer, the physical trapping effect also widely exists in the porous separators composed of other materials and coexists with chemical adsorption. Deng et al. prepared a porous F-doped poly-m-phenyleneisophthalamide (PMIA) separator via an electrospinning approach. By adding a certain amount of tetrabutylammonium chloride in the spinning solutions, a tree-like nanofiberal separator is formed with high porosity and good physically trapping effect to polysulfides. At the same time, the doped F endues the PMIA membranes with chemical binding force to polysulfides. With this novel separator, a lithium-sulfur battery can deliver an initial discharge capacity of 1222.5 mAh g⁻¹ at 0.5 C with a capacity fade rate of 0.049% per cycle over 800 cycles. He et al. modified the Celgard separator with hollow Co₉S₈ arrays through an in-situ conversion reaction. The Co₉S₈ arrays on the achieved separator work as both the physical and the chemical trapping layers, enabling the battery to provide an high initial discharge capacity of 1385 mAh g⁻¹ at 0.1 C and a capacity fade rate of 0.07% per cycle over 200 cycles.

Although the physical trapping effect exists in most porous separators, its trapping strength and trapping capability are not satisfactory. On the basis of the physical trapping effect, chemical adsorption is further developed to fix polysulfides through the chemical bond between polysulfides and trapping materials.

2.1.3 Separators with chemical trapping effect

Due to relatively weak trapping efficiency, the physical trapping effect is far from meeting the requirements of lithium-sulfur batteries. In order to improve the overall trapping effect, chemical trapping has been introduced to separators.
Surface functionalization, which generates surface functional groups on carbon materials, can enhance the trapping effect through chemical interactions with polysulfide species. Ponraj et al. prepared a hydroxyl functionalized-CNT (CNTOH)-coated separator via a vacuum filtration method. The hydroxyl groups generate a strong interaction with lithium polysulfides on the CNTOH surface, which is indicated by the color change of the Li$_2$S$_4$ solution (Figure 4A,C). On the contrary, the CNT shows weak adsorption with no changes in color (Figure 4B,D). The X-ray photoelectron spectroscopy (XPS) test of the CNTOH after the adsorption detects the thiosulfate and polythionate peaks (Figure 4E), further illustrating the strong chemical interaction between the CNTOH and $S_4^{2-}$. The binding energy for polysulfide adsorption onto CNT and CNTOH is also confirmed by the DFT calculations (Figure 4F). Polysulfides bind more tightly to CNTOH than to CNT, which is mainly attributed to the additional interactions between Li and O elements within the CNTOH. Consequently, the lithium-sulfur battery with the CNTOH-coated separator delivers a capacity of 1057.6 mAh g$^{-1}$ at the current density of 0.5 C with a capacity fade rate of 0.11% per cycle over 400 cycles.

Doping heteroatoms into carbons can create a non-uniform electron distribution on the carbon surface, therefore generate chemical adsorption sites for polysulfides and enhance the carbon-polysulfide interactions. For example, nitrogen doping can improve the trapping effect of carbon-based materials: pyridinic-N...
and pyrrolic-N enhance the polysulfides adsorption capacity while graphitic-N improves the electronic conductivity of the trapping layer. Pyridinic-N and pyrrolic-N show high polysulfide trapping efficiency on the N-doped carbon through Li-N interactions, which is proven by the detected N-Li bond (Figure 5A). Balach et al prepared an N-doped microporous carbon (NDMC) by a hard template method with resorcinol, melamine, and formaldehyde precursors. A UV-Vis absorption spectroscopy test was conducted to detect the polysulfide trapping capability of Super P (SP) carbon, mesoporous carbon, and NDMC. As the results shown in Figure 5B, in 0.1 M Li2S6 solution, SP carbon and mesoporous carbon can trap 21% to 65% of the Li2S6 while the NDMC can trap approximately 93% of the Li2S6. Thus, nitrogen doping greatly enhances the polysulfide trapping capability of carbon materials. A lithium-sulfur battery with an NDMC-coated Celgard separator delivers a discharge capacity of 1364 mAh g⁻¹ at 0.2 C with a higher capacity decay rate of 0.48% per cycle during 100 cycles. Hu et al prepared a porous Co–N–C decorated separator to confine the polysulfide. This Co–N–C material exhibits three characteristic XPS peaks of metallic Co, Co–N, and Co–O (Figure 5C). With electron donation from Co to N in the Co–N bond, the electron-rich N can efficiently trap Li⁺ and the neighboring Co can trap the polysulfide species through Co-S bonds (Figure 5D). With the strong synergy between S-Co and N-Li-S bonds, this hybrid separator boosts the battery performance to high capacities of 1406 and 1203 mAh g⁻¹ at 0.2 C and 1 C, respectively, with a capacity fading rate of 0.31% per cycle at 1 C during 100 cycles.

Although surface functionalization and heteroatom doping can introduce polar groups into carbon materials, this polarity change is relatively limited because of the nonpolar nature of carbon. Therefore, several kinds of noncarbon-based materials, including oxides, carbides, sulfides, nitrides, and conductive polymers are used for the polysulfide trapping layer in lithium-sulfur batteries. Lin et al reported a Ti3C2
nanosheet-coated glass fiber (GF) separator. Due to the strong interaction between surface Ti and S cations, Ti$_3$C$_2$ can trap polysulfides as well as S and Li$_2$S. The ab-initio calculation results suggest that Ti$_3$C$_2$ has much higher binding energy with S species compared to graphene (Figure 6A,B), but the binding energy will be severely weakened when replacing the surface Ti atoms with F/OH groups in the preparation of Ti$_3$C$_2$ nanosheets. The experimental results demonstrate that the Ti$_3$C$_2$ nanosheet-coated GF separator only allows 10.9% Li$_2$S penetration after 24 hours, while 86.5% of Li$_2$S penetrates through the GF separator, as shown in Figure 6C-E. With the Ti$_3$C$_2$ nanosheet-coated GF separator, the lithium-sulfur battery exhibits a discharge capacity of 820 mAh g$^{-1}$ at the current density of 0.5 A g$^{-1}$ and a capacity decay rate of 0.12% per cycle during 100 cycles.

Generally, noncarbon materials have strong interactions with polysulfides but low electronic conductivity and specific surface area, whereas carbon materials have weak interactions with polysulfide but high electronic conductivity and specific surface area. Knowing this, composite materials with carbon/noncarbon trapping materials are expected to cause strong interactions with polysulfides and possess high specific surface areas for polysulfide trapping. Numerous noncarbon trapping materials, including oxides, sulfides, nitrides, carbides, and phosphides have been used to form a carbon/noncarbon composite trapping layer. Ali et al. used WS$_2$/carbon as the trapping material to modify the Celgard separator, in which polythionate and thiosulfate were detected by XPS at the binding energy of 167.3 and 169.2 eV, respectively (Figure 7A). These polythionate/thiosulfate groups are projected to trap polysulfides and convert them to lower-order polysulfides. Polysulfide adsorption tests show that a WS$_2$/C modified Celgard separator is more effective than the bare Celgard or carbon-modified Celgard separators for adsorbing polysulfides (Figure 7B). In addition to the polysulfide adsorption, the highly conductive carbon in the composite layer can provide electron pathways to promote the cathodic reaction and reduce charge transfer impedance (Figure 7C). The combination of these two beneficial factors leads to enhanced battery performance, including a discharge capacity of 996 mAh g$^{-1}$ at 1 C and a capacity decay rate of 0.045% per cycle during 1000 cycles (Figure 7D).

Beside modified commercial separators, new types of separators have also been developed to block the polysulfide with the chemical trapping effect. Wang
**FIGURE 6** Mechanism and polysulfides trapping performance of Ti$_3$C$_2$-coated separator: A, Calculated structures of different polysulfide adsorbed on Ti$_3$C$_2$. B, Comparison of calculated binding energies of different polysulfide with Ti$_3$C$_2$, Ti$_3$C$_2$(OH)$_2$, and graphene, respectively. C-E, Polysulfides penetration test of GF separator and Ti$_3$C$_2$ modified GF separator. Reproduced with permission: Copyright 2016, Royal Society of Chemistry.

**FIGURE 7** Polysulfides trapping performance of WS$_2$/carbon modified Celgard separator and its battery performance: A, S 2p XPS spectrum of cycled WS$_2$/carbon layer. B, Polysulfide trapping test for different separators. C, Electrochemical impedance spectra of batteries with different separators after discharge process. D, Cycle performance of lithium-sulfur batteries contains different separators. Reproduced with permission: Copyright 2018, American Chemical Society.
et al. prepared a graphdiyne (GDY)/polyimide composite separator. With an electron-rich structure, the GDY can form a strong electrostatic attraction with Li\(^+\) and result in trapping polysulfides by chemical interaction. A lithium-sulfur battery using this composite separator exhibits a high initial discharge capacity of 1648.5 mAh g\(^{-1}\) at 0.1 C and a capacity decay rate of 0.25% per cycle after 200 cycles.

### 2.1.4 Separators with catalytic trapping effect

After being physically/chemically absorbed, polysulfides will be further reduced to insoluble sulfides and fixed in the trapping layer. On the basis of the physical/chemical adsorption effect, some trapping materials also exhibit good catalytic activity for the polysulfide reduction reaction. Metal sulfides like Co\(_9\)S\(_8\), MoS\(_2\), VS\(_4\), and WS\(_2\) were used in lithium-sulfur batteries as catalytic trapping materials. Yu et al. developed an ultrathin and compact MoS\(_2\) film that contains a large amount of flake edges with high catalytic activity, which could promote the reduction reaction of polysulfides and lead to an improved capacity (1010 mAh g\(^{-1}\) at 0.5 C) and a lower decay rate (0.11% per cycle). Wang et al. applied VS\(_4\) nanorod anchored 3-D graphene to modify the separator, which could adsorb polysulfides and accelerate polysulfide redox kinetics, enabling the battery to exhibit excellent cyclability and rate performance. Besides metal sulfides, metal oxides including In\(_2\)O\(_3\), MoO\(_x\), MnO\(_2\), and HfO\(_2\) also have high catalytic activity for the polysulfide reduction reaction. Song et al. prepared a MnO\(_2\)-coated PE separator in which the MnO\(_2\) not only adsorbed polysulfides but also promoted the formation of an insoluble mediator through the catalytic effect. As a result, the MnO\(_2@\)PE can greatly suppress the lithium polysulfide shuttle effect, leading to a high reversible capacity and superior cycling stability.

### 2.2 Separators with shield effect to polysulfide

#### 2.2.1 Working mechanism and material design principle

Unlike the trapping effect, the charge-shield effect inhibits the polysulfide shuttle effect through electrostatic repulsion. The working mechanism of the charge-shield separator is illustrated in Figure 8. Because the polysulfide species carry negative charge, the same negatively charged functional groups (\(-\text{SO}_3\text{H}, \text{COOH}, \text{-OH}\) in the charge-shield separator can repel the polysulfide through electrostatic force, effectively inhibiting the shuttle effect. In addition, negatively charged functional groups can interact with positively charged Li\(^+\) through electrostatic attraction, improving Li\(^+\) transport. To realize the strong charge rejection to polysulfides, the adopted charge-shield separator should have high charge density, high electric field strength, and good chemical/electrochemical stability. With these working mechanisms and design principles, several kinds of separators have been developed and adopted in lithium-sulfur batteries.

#### 2.2.2 Separators with shield effect to polysulfide

Efforts have been made to introduce negative charge into separators. Li et al. used O\(_2\) plasma to generate oxygen-containing groups on the surface of a commercial Celgard separator, which are expected to suppress the polysulfide shuttle effect and improve cycling stability. When applied in lithium-sulfur batteries, the raw and O\(_2\) plasma-treated separators induce the discharge capacities of 973.8 and 1028.2 mAh g\(^{-1}\) at 0.2 C, respectively, and the capacity decay rates are 0.72% and 0.49% per cycle during 105 cycles, respectively. Gu et al. prepared a poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA)-modified separator through a layer-by-layer assembly method (Figure 9A). The charge density of the modified separator can be regulated easily by tuning the reaction solution pH value and the number of bilayers, leading to tunable polysulfide repulsion and Li\(^+\) selectivity. With a high negative charge density, the battery with a PAH/PAA modified separator delivers an increased discharge capacity from 1302 (bare PP separator) to 1418 mAh g\(^{-1}\) (modified PP separator), and the
cycle performance is also improved. Huang et al.\textsuperscript{130} modified Celgard separators with a Nafion thin layer, in which the sulfonate groups allow the hopping of Li\textsuperscript{+} and reject negatively charged polysulfide species. As a result, the Nafion layer on the Celgard separator builds a charge shield to completely suppress the polysulfide shuttle effect. However, a dense Nafion layer will decrease the battery performance due to relatively low Li\textsuperscript{+} conductivity.\textsuperscript{131} For lithium-sulfur batteries with commercial Celgard separators, the discharge capacity is 906 mAh g\textsuperscript{-1} at the current density of 1 C, with a capacity decay rate of 0.13% per cycle during 500 cycles. While for a Nafion-modified separator, although the discharge capacity is reduced to 781 mAh g\textsuperscript{-1} at the current density of 1 C, the capacity decay rate is reduced to 0.08% per cycle during 500 cycles at 1 C, suggesting the significant suppression of polysulfide effects. Unfortunately, the cost of Nafion greatly hinders its practical application. To decrease the cost, Babu et al.\textsuperscript{132} developed a thin sulfonated poly(ether-ether-ketone)/Nafion (SPEEK/Nafion) composite layer-coated Celgard separator. With the optimized SPEEK/Nafion (50:50) modified separator, the discharge capacity reaches 1300 mAh g\textsuperscript{-1} with a capacity decay rate of 0.1% during 500 cycles. Zhuang et al.\textsuperscript{133} prepared a PP/graphene oxide/Nafion ternary-layered separator for lithium-sulfur batteries (Figure 9B). In this separator, graphene oxide (GO) sheets can cover the macropores of PP separators as well as serve as a barrier for polysulfides. Therefore, the Nafion loading can be reduced to as low as 0.05 mg cm\textsuperscript{-2}. With this novel separator, the capacity decay rate is reduced to 0.18% per cycle. Yu et al.\textsuperscript{134} attached carboxyl groups onto the PP backbone through facile hydroxylation-grafting-hydrolysis processes (Figure 9B). With strong electronic repulsion effects to negatively charged polysulfide species, a lithium-sulfur battery with the modified PP separator shows a discharge capacity of 1250 mAh g\textsuperscript{-1} at 0.1 C and a capacity decay rate of 0.11%, better than those with the PP separator (1220 mAh g\textsuperscript{-1}, 0.30%). Yim et al.\textsuperscript{135} prepared a BaTiO\textsubscript{3} (BTO)-coated PE separator via a simple dip-coating process. After being placed in a 100 kV mm\textsuperscript{-1} electric field, permanent dipoles are generated in BTO particles to inhibit polysulfide shuttle effects through electrostatic repulsion (Figure 9C). As a result, a battery with the PE-poled BTO separator displays a discharge capacity of 1122.1 mAh g\textsuperscript{-1} at 0.5 C and a capacity decay rate of 0.34% during 50 cycles. By comparison, the batteries with

**FIGURE 9** Schematic diagram of separators with shield effect constructed using different materials: A, PAH/PAA multilayer modified PE separator. Reproduced with permission: Copyright 2014, RSC Publishing.\textsuperscript{129} B, Carboxyl functional group decorated separator. Reproduced with permission: Copyright 2016, Royal Society of Chemistry.\textsuperscript{134} C, Poled BTO-coated separator. Reproduced with permission: Copyright 2016, Wiley-VCH.\textsuperscript{135} D, Negative charged rGO/SL for separator modification: Reproduced with permission. Copyright 2018, Elsevier\textsuperscript{137}
PE-BTO and PE separators deliver discharge capacities of 1124.1 and 997.2 mAh g\(^{-1}\) with capacity decay rates of 0.56% and 0.81%, respectively. Zeng et al\(^{136}\) coated sulfonated acetylene black (AB-SO\(_3\)\(^{-}\)) on Celgard separators to promote Li\(^{+}\) transport and inhibit polysulfide crossover owing to the strong negative charges of the AB-SO\(_3\)\(^{-}\). With this selective effect, the Li\(^{+}\) transference number increases greatly from 0.39 to 0.96, suggesting the decent Li\(^{+}\) permeability. Consequently, the battery delivers a discharge capacity of 1262 mAh g\(^{-1}\) at 0.1 C with a capacity decay rate of 0.24% during 100 cycles. Lei et al\(^{137}\) developed a reduced graphene oxide (rGO)/sodium lignosulfonate (SL) composite layer-modified PP separator (Figure 9D). By combining highly negative charged SL with rGO, they created an rGO@SL layer to effectively retard the polysulfide shuttle effect, leading to an extraordinarily low capacity fading rate of <0.026% per cycle during 1000 cycles at 2 C.

Freitag et al\(^{138}\) prepared a polyvinylidene fluoride-hexafluoropropylene/polyvinylsulfate potassium salt (PVdF-HFP/PVSK)-blend separator for lithium-sulfur batteries. In this separator, the negatively charged PVSK generates electrostatic repulsion towards polysulfides and inhibits the shuttle effect via the charge-shield effect. Hence, porosity and charge density can be easily adjusted by controlling the PVSK concentration, both of which are important properties for inhibiting the polysulfide shuttle effect. Ma et al\(^{139}\) prepared a poly(ethylene glycol) dimethacrylate-vinylsulfonic acid salt copolymer (PV) separator through a simple UV-cross-linking process. In this separator, the SO\(_3\)\(^{-}\) groups lead to higher electrolyte uptake and dielectric constant, causing a higher conductivity (1.14 × 10\(^{-3}\) S cm\(^{-1}\)) and Li\(^{+}\) transfer number (0.98). To enhance the mechanical strength, a novel sandwich-type PV/Celgard/PV separator was developed, which led to a discharge capacity of ~1000 mAh g\(^{-1}\) at 0.5 C with a capacity decay rate of 0.08% per cycle during 100 cycles. Luo et al\(^{140}\) prepared a polyamide acid nanofiber separator via electrospinning. The negatively charged —COOH functional groups in PAA separators can promote Li\(^{+}\) transport while suppressing polysulfide migration. A battery with this porous separator delivers a discharge capacity of 1031 mAh g\(^{-1}\) at 0.2 C and a capacity decay rate of 0.12% per cycle during 200 cycles.

2.3 | Separators with sieve effect to polysulfide

2.3.1 | Working mechanism and material design principle

Although the above-mentioned method can effectively improve the battery performance, polysulfides can still permeate through pores in the separator and lead to the shuttle effect. To completely suppress the polysulfide shuttle effect, a dense Li\(^{+}\)-conductive separator is developed and used in lithium-sulfur batteries. This ion-sieve separator can conduct Li\(^{+}\) and completely block the shuttle effect of polysulfides due to its crystal structure and ionic conductivity (Figure 10). For this goal, ion-sieve materials should have high ionic conductivity, low porosity, and good film-forming properties. With these mechanisms and design principles, different ion-sieve materials are developed for separator modifications.

2.3.2 | Separators with sieve effect

Different solid-state Li\(^{+}\) conductive materials, such as V\(_2\)O\(_5\) and LiF, have been used to prepare ion-sieve separators. Li et al\(^{144}\) used dense V\(_2\)O\(_5\) ion-sieve layers to modify Celgard separators via spin-coating, which inhibits the polysulfide shuttle effect while permitting Li\(^{+}\) transportation. With this V\(_2\)O\(_5\) modified separator, a pouch cell can be cycled more than 300 times at a specific capacity of 800 mAh g\(^{-1}\) without any noticeable degradation. Li et al\(^{142}\) also used LiF as the ion-sieve layer for the PP separator modification. Interactions between LiF and the DME electrolyte lead to the formation of a dense and viscous sol-layer that acts as a physical barrier against the polysulfide shuttle effect. Simultaneously, the surface coating layer effectively migrates Li\(^{+}\) due to the low diffusion barrier energy of LiF. With this novel LiF modified separator, a lithium-sulfur battery exhibits a discharge capacity of 1064.6 mAh g\(^{-1}\) at a current density of 0.2 C with a remaining capacity of 69.3% after 200 cycles. Ni et al\(^{143}\) prepared a LiF-GO modified PP separator through a CaF\(_2\)-GO in-situ transformation process (Figure 11A), during which CaF\(_2\) reacts with Li\(^{+}\) to generate LiF (Figure 11B,C). In this ion-sieve layer, GO is adopted to overcome the brittleness of the LiF layer due to its good mechanical strength and high elastic modulus. A lithium-sulfur battery with this LiF/GO coated separator delivers a similar discharge capacity of 880 mAh g\(^{-1}\) at 1 C to that with a commercial separator, but demonstrates a dramatically decreased capacity decay rate of 0.09% per cycle (200 cycles, LiF/GO coated PP separator) compared to that of 0.59% per cycle (20 cycles, PP separator). Zeng et al\(^{144}\) prepared a graphite-modified separator in which a solid-electrolyte-interphase layer is formed to stabilize the graphite and sieve the polysulfides and Li\(^{+}\) ions after an in-situ generation process. With this novel ion-sieve layer, a lithium-sulfur battery retains 87% of its original capacity during 100 cycles at 0.2 C (Figure 11D).

Materials with proper pore sizes can also be used as the sieving layer for separators in lithium-sulfur batteries.
to block polysulfide shuttle effects. Du et al.\textsuperscript{145} used graphene as the polysulfide ion-sieve layer to modify Celgard PP separators (Figure 12A), in which graphene can selectively block polysulfides while maintaining Li\textsuperscript{+} conductivity (Figure 12B). With this graphene-modified PP separator, a capacity of 1035 mAh g\textsuperscript{-1} at 0.5 C with 11\% improvement and a decreased capacity decay rate of 0.026\% per cycle during 1500 cycles (Figure 12C,D) are obtained. Wu et al.\textsuperscript{146} prepared a Prussian blue (PB)-coated Celgard separator, through which the suitable lattice structure of PB permits Li\textsuperscript{+} transportation while hindering polysulfide migration. A battery with this PB-coated Celgard separator delivers a capacity of 1170.5 mAh g\textsuperscript{-1} at 0.2 C with a capacity decay rate of 0.3\% during 100 cycles, superior to those with commercial Celgard separators (1091.0 mAh g\textsuperscript{-1}, 0.6\%).

Besides using the modified commercial separators, functional separators also have been developed. Jin et al.\textsuperscript{147} applied a lithiated Nafion separator to lithium-sulfur batteries. As a single ion conductor, the lithiated Nafion separator can conduct Li\textsuperscript{+} with a transfer number of 0.986 while preventing the polysulfide from traveling...
through it. However, the low Li+ conductivity ($2.1 \times 10^{-5}$ S cm$^{-1}$) hinders the performance of this Nafion separator. To address this issue, they synthesized a new lithium perfluorinated sulfonyl dicyanomethide (Li-PFSD) single ion conductor, which has Li+ conductivity of about $1.2 \times 10^{-4}$ S cm$^{-1}$ and a transfer number of 0.958. With this new separator, a lithium-sulfur battery delivers a capacity of 1161 mAh g$^{-1}$ at 0.3 mA cm$^{-2}$ with a capacity decay rate of 0.285% during 100 cycles. Bai et al used MOF@GO as an ionic sieve separator. The pore size that is smaller than the diameter of polysulfides within the MOF can efficiently conduct Li+ and suppress the polysulfide shuttle effect. After compositing with GO, the mechanical strength of the as-prepared MOF@GO is enhanced greatly. From the polysulfide permeation measurements, the GO separators are unable to block polysulfides infiltration while the MOF@GO separator can block the polysulfides for at least 48 hours. Consequently, the separator delivers a high discharge capacity of 1207 mAh g$^{-1}$ at 1 C with a low capacity decay rate of 0.019% per cycle over 1500 cycles.

To maximize the inhibition effect of the separator on polysulfide migration, several materials have been developed with the combination of ion-trap, charge-shield, and ion-sieve effects. Huang et al prepared a GO-coated Celgard separator. In the GO layer, the nanocapillary network formed by carbon atoms works as the ion-sieve and the negatively charged surface group works as the charge-shield. With the combination of these two effects, a lithium-sulfur battery delivers a discharge capacity of 920 mAh g$^{-1}$ at 0.1 C, higher than that without the GO separator (860 mAh g$^{-1}$). Besides, the capacity decay rate is reduced from 0.49% to 0.23% per cycle during 100 cycles at 0.1 C, suggesting good suppression of the polysulfide shuttle effect. Abbas et al prepared a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) coated Celgard separator, in which the large amount of sulfonate groups in PSS effectively suppresses the shuttle effect of the negatively charged polysulfide molecules through electrostatic repulsion, while the PEDOT provides strong chemical interactions with polysulfides. The batteries incorporating this PEDOT/PSS modified separator exhibit a discharge capacity of 985 mAh g$^{-1}$ with a capacity decay rate of 0.0364% per cycle during 1000 cycles at 0.25 C, superior to those with commercial separators (981 mAh g$^{-1}$, 0.0932%). Zhu et al prepared a polyacrylonitrile-silica/MWCNT separator via electrospinning. In this separator, —C≡N and SiO$_2$ trap the polysulfide through chemical interaction and MWCNT provides electrons for the polysulfide reduction reaction. This separator makes the initial discharge capacity reach 1182 mAh g$^{-1}$ at 0.2 C and leads to a capacity decay rate of 0.37% per cycle during 100 cycles.

Among recent works, the research on inhibition performance to polysulfides shuttle effect is the most extensive. However, there are still two points that should be paid attention to in the future. First, separators with trapping and sieve effects may increase the transport resistance of Li+. In contrast, separators with the shield effect can...
suppress the shuttle effect and promote the transport of Li⁺ simultaneously. Therefore, the research on the shield effect of separators should be strengthened. Second, the coating layer on the separator can inhibit the shuttle effect but increases the weight and thickness of the separator, reducing the practical energy density of the battery. Thus, it is necessary to optimize the thickness of the coating layer.

3 | SEPARATORS FOR SELF-DISCHARGE SUPPRESSION

The self-discharge phenomenon is directly related to the transmembrane migration of polysulfides, meaning that increasing the polysulfide diffusion resistance of separators can significantly reduce the self-discharge rate. The self-discharge suppression mechanisms of separators can also be divided into three types, including ion-trap, charge-shield, and ion-sieve, and many separators have been designed based on these mechanisms to inhibit the self-discharge phenomenon.²⁹,⁷¹,⁷²,⁹³,¹⁰⁰,¹²⁷,¹⁴⁵,¹⁵²,¹⁵⁵-¹⁶⁸

Chung et al.²⁹ first reported the inhibition effect of the polysulfide barrier separators on the self-discharge behavior. With a decent polysulfide trapping property, the carbon-coated separator effectively inhibits the self-discharge phenomenon. For example, the pure sulfur cathode with a carbon-modified separator maintains 81% of its original capacity after being stored for 3 months. For comparison, the same cathode with a raw Celgard separator only maintains 49% of its original capacity after 1 month of storage. Wu et al.¹⁶⁴ tested the anti-self-discharge performance of the boron-functionalized reduced graphene oxide (B-rGO) coated separator. With the separator’s adeptness at polysulfide trapping, this B-rGO coated separator can prevent the polysulfide transmembrane migration and thus inhibits the self-discharge process (Figure 13A). The open circuit voltage (OCV) of a lithium-sulfur battery with the B-rGO coated separator shows a stable curve at 2.37 V for 14 days. In contrast, the OCV of the battery with a raw separator falls gradually (Figure 13B). In the self-discharge evaluation experiment, batteries with raw and B-rGO-coated separators were allowed to rest for 48 hours after the third charge process, after which the fourth charge-discharge performance was tested and compared with the third one. Due its good polysulfide adsorption capacity, the B-rGO decorated separator induces the discharge capacity retention of 80%, while the raw Celgard separator only induces the capacity retention of 63.04% (Figure 13C). Wang et al.¹⁶⁵ prepared a lithium aluminum germanium phosphate (LAGP)-carbon coated separator and investigated the catalytic trapping effect of LAGP particles in lithium-sulfur batteries. The
self-discharge experiment shows that the batteries with LAGP-carbon-coated, carbon-coated, and pristine separators maintain the discharge capacities of 84.3%, 66.1%, and 55.2%, respectively in their 11th cycles compared with their 10th cycles after resting for 72 hours. Li et al. prepared a TiO/MWCNT coated separator with strong adsorption capacity to polysulfides. TiO has high oxygen and titanium vacancies density and is therefore considered to be beneficial for trapping polysulfides. With this novel separator, the capacity maintaining rate of 12.4% is achieved after resting for 96 hours.

In addition to the modified Celgard separator, new functional separators also have been developed and investigated. Huang et al. tested the self-discharge inhibition performance of GO modified separators. Due to the highly negative charge density of GO, the as-prepared separator inhibits the polysulfide penetration through the charge-shield effect and the capacity retention rate is improved from 60.7% to 93.3% after resting for 24 hours. Suriyakumar et al. suppressed the self-discharge by the ion-sieve effect of a MOF-SiO2 modified separator. With the MOF-SiO2 coating layers, the capacity retention rate is improved from 66.5% to 86% after resting for 40 hours, suggesting the excellent self-discharge suppression ability of the functional layers. Zhu et al. prepared a PAN/GO nanofiber separator via an electrospinning method, in which the -C≡N group provides strong chemical adsorption with polysulfide and GO provides the electrostatic rejection to negatively charged polysulfides. Using this composite separator, the capacity lost rate can be reduced to 5% after a resting time of 24 hours, indicating the excellent anti-self-discharge capability of the PAN/GO nanofiber separator.

The self-discharge behavior of lithium-sulfur batteries is directly related to the polysulfides shuttle effect. Therefore, the barrier effect on polysulfide will help to reduce the self-discharge rate. Presently, the self-discharge rate of lithium-sulfur batteries is still much higher than that of lithium-ion batteries (capacity retention rate is 94.1% after 2 months' resting). To achieve a commercial lithium-sulfur battery, more research work should be conducted on the battery structures and materials, especially on the separators.

Both good mechanical strength and small pore sizes are considered to be beneficial for suppressing lithium dendrites penetration. Qu et al. prepared a porous inorganic Li_{6.4}La_{3}Zr_{1.4}Ta_{0.6}O_{12} (LLZTO) separator for lithium-sulfur batteries. The good mechanical strength and high porosity of this inorganic separator help to maintain a low overpotential of ~25 mV for 100 hours in symmetrical lithium batteries. In comparison, a 6-layer PP separator exhibits a large overpotential of 45 mV for 75 hours, suggesting that LLZTO separators are effective at lithium dendrite suppression. Xu et al. coated PP separators with a thin TiO2-carbon black layer to establish a mechanical barrier against lithium dendrites. Figure 14A shows the effective blockage of lithium dendrites by the TiO2-carbon black layer contrasted with the penetration of lithium dendrites through the pores of the PP separator. Ni et al. prepared a LiF/GO modified PP separator through an in-situ Ca-Li replacement reaction. The LiF/GO layer not only inhibits the shuttle of polysulfides but also suppresses lithium dendrite penetration with its good mechanical properties. The combination of these two effects leads to a smooth lithium surface, which is free of dendrites, whereas several dendrites are observed on the lithium surface with a bare PP separator. Chen et al. coated PP separators with CNTs and Al2O3 double coating layers as the physical barrier for lithium dendrite growth. The conjugation between Al2O3 and CNTs possesses sufficient mechanical strength and flexibility to prevent lithium dendrite penetration during cycling.

Uniform electric field/ion flux achieved by the separator also contributes to uniform lithium electrodeposition. Thus, strenuous efforts have been made under the guidance of this purpose. Kim et al. used a polydopamine (PD)-modified separator to facilitate uniform Li⁺ flux and enhance the separator-lithium contraction to diminish lithium surface tension (Figure 14B). Kim et al. replaced PP/PE separators with cellulose-based separators. The cellulose-based separator has a nanosized porous structure that leads to a uniform current density for lithium electrodeposition. Stable voltage profiles were observed from the symmetric lithium battery containing the cellulose-based separator whereas early failure occurred with the commercial Celgard 2500 separator. Wang et al. deposited CNF layers on both sides of the PP separator. The CNF layer not only restrains the polysulfide shuttle effect but also eliminates the tip-charge effect by providing a 3D skeleton (Figure 14C). With the 3D CNF layers, the as-prepared separator effectively inhibits lithium dendrite growth even at a high current density of 2 mA cm⁻² (Figure 14D,E). Jiang et al. coated the commercial PP separator with N-doped and porous carbon-decorated MXene nanosheets. In this separator, the homogeneously distributed N heteroatoms

4 | SEPARATORS FOR LITHIUM DENDRITE SUPPRESSION

The suppression of Lithium dendrites by separators is achieved by two main methods: inhibiting dendrite penetration with strong mechanical strength and promoting uniform lithium deposition. With these two methods, several types of separators have been developed for lithium dendrite suppression in lithium-sulfur batteries.
perform as lithiophilic sites to regulate the Li\(^+\) flux, and the decorated carbon greatly reduces the local current density for Li plating. The synergy effects lead to good lithium-dendrite inhibition performance under a current density of 1 mA cm\(^{-2}\). Lu et al\(^{188}\) created an electronegative coating layer on a Celgard separator with liquid-phase delaminated birnessite (H\(_x\)MnO\(_{2+x}\)) nanosheets, graphene, and carbon nanotubes. Besides rejecting the polysulfides, this electronegative coating layer suppresses lithium dendrite growth by regulating uniform Li\(^+\) fluxes, leading to highly stable cycling performance of 1000 cycles with greatly reduced dendrite inhibition for 1000 hours. Xiang et al\(^{190}\) introduced a Li\(^+\) pump to the separator with \(\beta\)-phase poly(vinylidene fluoride) in which piezoelectric potential is established near the electrode surface and serves as a driving force to regulate the migration of Li\(^+\). With this pump effect, the Li\(^+\) transfer number was greatly increased from 0.19 of PP/PE to 0.59. Abbas et al\(^{191}\) coated the commercial Celgard separator with a thin layer of graphite by sputtering. Due to the high ionic conductivity and mechanical strength, the graphite coating layer can minimize the dendrite growth by providing uniform ionic flux and physical barrier for dendritic lithium penetration.

The separator provides the physical barrier effect to lithium dendrites penetration and promotes the uniform lithium deposition on the electrode/seperator interface. Such an effect is mainly based on the enhanced mechanical strength, decreased pore size, and increased tortuosity of the separators. However, the physical barrier effect also increases the Li\(^+\) transportation resistance, leading to an adverse effect on battery performance. The promotion effect to uniform lithium deposition is achieved by adjusting the Li\(^+\) flux and the current distribution with separators. Compared with the physical barrier effect, this promotion effect is more effective. For future work, the researchers are suggested to pay more attention to the homogenization effect of separators on the Li\(^+\) flux and the current distribution.

**5 | SEPARATORS WITH HIGH THERMAL TOLERANCE**

Polyolefin-based separators have been widely used lithium-sulfur batteries. However, due to the low melting points of PE and PP, the polyolefin separators suffer from large thermal shrinkage at high temperatures.\(^{192,193}\) The thermal shrinkage rate of PP separator is tested to be 33.3% at 150°C for 2 hours,\(^{64}\) which will further increase the risk of internal short-circuit, causing the battery thermal runaway or even explosion.
Composites of heat-resistant materials can significantly reduce the thermal shrinkage in polyolefin-based separators by providing additional mechanical supports. Based on this principle, several PP/PE-based composite separators with low thermal shrinkage were prepared. For example, BTO nanoparticles were used as the thermally resistant material, and the PE/BTO separator exhibits a low thermal deformation rate of 45% compared to the PE separator (91.8%) after annealing at 150°C for 1 hour. Yang et al coated the separator with a laponite nanosheet (LNS)/CB layer to enhance the overall thermal stability in two different ways. First, the LNS/CB surface layer provides additional mechanical support to resist thermal shrinkage. Second, the laponite particles penetrate into the pores of the Celgard separator to further strengthen the separator’s structure. Therefore, the LNS/CB-coated Celgard separator shows no obvious thermal shrinkage after being kept at 160°C for 1 hour, whereas the Celgard separator shows serious thermal shrinkage.

GF-based separators have excellent thermal stability due to the intrinsic thermal resistance of the borosilicate structure. Zhu et al tested the performance of GF separators in lithium-sulfur batteries. Their results show that the GF separator can withstand a high temperature of 150°C for 2 hours without any apparent dimensional change, while the PP separator shows significant thermal shrinkage under the same condition. Although GF-based separators exhibit good thermal stability and low thermal shrinkage rates, the low mechanical strength/flexibility greatly limits its application in lithium-sulfur batteries.

New heat-resistant separators have been developed with high melting points and low thermal shrinkage. Zhu et al prepared a rGO-PVDF/PVDF composite nanofiber separator via electrospinning. The as-prepared separator shows no dimensional changes after being soaked in liquid electrolytes at 80°C for 24 hours. Conversely, the PP separator experiences a severe crimping deformation. Yang et al. prepared a core-shell structured polyacrylonitrile (PAN)/PVDF-HFP separator via a co-axial electrospinning method. Due to the high melting point of PAN (~317°C), the achieved PAN@PVDF-HFP separators show no obvious changes until 150°C. Zhu et al prepared a porous polyetherimide(PEI)/Al2O3 separator via a nonsolvent
induced phase separation technique. Owing to the high glass temperature of 217°C, no obvious shrinkage (1.9%) is observed for PEI/Al2O3 separators after storing even at the temperature of 200°C.

Incorporating inorganic materials can also improve the thermal tolerance of the separator. However, inorganic particles agglomerate easily in the preparation process of the separators and can result in separator inhomogeneity, which limits the application of this method. To address this issue, Ali et al.207 first incorporated colloidal Al2O3 into the PVDF-HFP separator, and citric acid was utilized to stabilize Al2O3 colloid in the PVDF-HFP solution (Figure 15A). The as-prepared separator exhibits a small shrinkage of 4.5% under 150°C while the Celgard separator and the PVDF-HFP separator shrink more than 50% and 20%, respectively (Figure 15B). This research provides a new direction for improving the separator thermal tolerance by using inorganic material composites. Wang et al.113 prepared a polyimide separator through a simple electrospinning-hot press-imidization. This prepared separator can maintain its room-temperature shape at a high temperature of 250°C due to the excellent thermal tolerance of polyimide. Lei et al.208 used PAN and ammonium polyphosphate (APP) as the precursors to prepare a multifunctional PAN@APP separator via electrospinning. Refractory APP ensures good thermal tolerance and allows the separator to withstand a high temperature of 200°C without shrinkage (Figure 15C). More importantly, the flame-retardant property of APP also improves the flammability resistance of the separator (Figure 15D).

Battery safety is a complex problem and the research based on separator can partially improve battery safety. Although the surface coating layer can provide additional mechanical support to against thermal shrinkage, the low melting point determines that the PP/PE separator is not the best choice for high-temperature applications. In contrast, the new types of high-melting-point separators are more suitable for lithium-sulfur batteries under high temperatures.

6 | ADDITIONAL FUNCTIONS TO IMPROVE BATTERY PERFORMANCE

6.1 | Improve electrolyte-separator wettability

The electrolyte wettability of the separator is an important parameter for batteries since good wettability can effectively improve the electrolyte uptake and facilitate Li+ transport. In lithium-sulfur batteries, the existing commercial PP/PE separators show insufficient electrolyte wettability, which greatly hinders the transmission of Li+ and subsequently increases the internal resistance of the battery. To this end, the separators exhibit good electrolyte wettability and excellent liquid absorption should be used to remedy this problem.94,127-129,199,209 Li et al.128 used an O2 plasma treatment to produce oxygen containing surface groups on the surface of the commercial Celgard separator. After treatment, the water-separator contact angle decreased from 125.4° to 64.9°, suggesting that increased polarity in the treated separator. The enhanced polarity of a separator can improve electrolyte wettability and electrode-separator interfacial adhesion, consequently improving overall battery performance. SiO2 has been applied for separator decoration through an in-situ hydrolysis reaction.62 The results show that the PP-SiO2 separator can be completely infiltrated by electrolytes, whereas the PP separator shows a contact angle of about 35° to electrolytes (Figure 16A). At the same time, PP-SiO2 separators can absorb more electrolytes (149%) than PP separators (93%).
The superior wettability and higher electrolyte uptake are expected to be beneficial for battery performance.

### 6.2 Provides an additional electron pathway for cathode reaction

Due to the low conductivity of sulfur, conductive carbon skeletons are always used to assist electron transport. However, carbon makes up a large amount of the cathode by mass and more binder is needed to unite the loose carbon, thereby compromising the gravimetric and volumetric energy densities. Decorating the separator with a conductive layer as an additional current collector will mitigate this cathode insulation dilemma. Peng et al. applied a highly conductive (100 S cm\(^{-1}\)) cellular graphene framework (CGF) coated PP separator in a high sulfur loaded lithium-sulfur battery. Their results show that with the high conductivity of CGF, the PP-CGF separator can alleviate ~50% of the charge transfer resistance encountered by PP separators. With this highly conductive separator, a cathode containing 80% sulfur with the loading of 5.3 mg cm\(^{-2}\) was applied, delivering an outstanding practical capacity of 5.5 mAh cm\(^{-2}\) at 0.1 C (Figure 16B).

### 6.3 Provides a buffer zone for cathode volume change

In lithium-sulfur batteries, sulfur undergoes a volume expansion of 80% to form Li\(_2\)S, which deconstructs the conductive skeleton, insulates the sulfur from electrons and thus leads to a dramatic fade in capacity during cycling. More seriously, such a large volume expansion generates local pressure that deforms or damages both the separator and the electrode. The porous coating layers on the separator can provide a buffer zone for the cathodic volume expansion and improve the cycling performance of the cathode.54,211,214,215

### 7 RESEARCH PROSPECTS

Many researchers have focused on solving critical issues in lithium-sulfur batteries from the perspective of separators due to their unique functions. Extensive efforts have been made to enhance the selective polysulfide blocking effect, self-discharge inhibition effect, lithium dendrite inhibition effect, and thermal stability. However, existing methods, materials, and structures cannot fully meet the requirements of lithium-sulfur batteries and breakthroughs in several critical areas are needed for further development.

First, the performance of separators needs to be studied further at different operating temperatures. The operating temperature is a crucial variable that influences the separator’s resistance to polysulfides, the mobility of polysulfides, and the growth of lithium dendrites. However, limited research focuses on the performance of separators under different working temperatures. For future work, researchers are strongly recommended to evaluate the effect of operating temperature on separators.

Second, the inert weight of the separator needs to be further reduced. Loading a functional layer onto the separator by slurry coating and vacuum filtration will increase the weight of the separator and compromise the energy density of the battery. Although thin functional layers loaded by in-situ self-assembly or Langmuir-Blodgett-scoping add little weight to the separator, their applications are limited to very specific materials. A new method that loads decent functional materials onto a thin support structure is required. Recently, Han et al. loaded a thin polymer separator (10 μm) on the electrode to produce an integrated electrode-separator structure by electrophoretic deposition, which has potentials for the weight reduction of lithium-sulfur batteries.

Third, new battery systems need to be further developed. Two kinds of lithium-sulfur batteries are suggested here with good prospects, which are quasi-solid-state and hybrid-electrolyte lithium-sulfur batteries. In quasi-solid-state ones, the gel-polymer electrolyte consists of liquid electrolyte and polymer matrix is considered to have good electrochemical performance. Qu et al. prepared a novel sandwich-structured gel-polymer electrolyte, which contains nanocarbon as the physical trapping material and the additional current collector, cellulose as the chemically trapping material, and poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) coating layer as the inhibition for lithium dendrite formation. This multifunctional gel-polymer electrolyte proposes novel research directions. Hybrid-electrolyte lithium-sulfur batteries, which use solid electrolyte to separate the electrodes and the liquid electrolyte to promote the polysulfide dissolution in the cathode electrode, can also eliminate both polysulfide shuttling and lithium dendrite growth. However, the development of hybrid-electrolyte lithium-sulfur batteries is still limited by the electrode-electrolyte interface, mechanical strength, and ionic conductivity of the solid electrolyte, which requires more research attention.

### 8 CONCLUSION

The separator is crucial for lithium-sulfur batteries to be viable for massive energy storage. Plenty of separators have been developed recently to address the perniciousness of...
polysulfide shuffling, self-discharge, lithium dendrite growth, and separator thermal shrinkage in lithium-sulfur batteries. This review analyzes these critical issues and their internal relationships in lithium-sulfur batteries, summarizes the functional mechanisms and recent progress of separators in addressing these issues, and proposes prospects in developing novel separators. According to the summarized achievements, it is strongly believed that all of the issues plaguing lithium-sulfur batteries can be solved by further development of separators.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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