Chemical Innovation & Technology
ISSN: 3078-7351
DOI: https://doi.org/10.61784/cit3004

FUNCTIONALIZED SEPARATORS FOR LITHIUM-SULFUR BATTERIES: MECHANISMS, MATERIALS, AND PERFORMANCE OPTIMIZATION

ShuYu Cheng
Strait Institute of Flexible Electronics (SIFE, Future Technologies), Fujian Key Laboratory of Flexible Electronics, Fujian Normal University and Strait Laboratory of Flexible Electronics (SLoFE), Fuzhou 350117, Fujian, China.
Corresponding Email: QSX20221464@student.fjnu.edu.cn

Abstract: Lithium-sulfur batteries, with ultrahigh energy density(2600 Wh kg^{-1}) and cost efficiency, face critical challenges hindering commercialization: poor conductivity of S/Li_2S, polysulfide shuttling, Li dendrite growth, and severe volume expansion. Functionalized separators emerge as a pivotal solution, integrating ion-sieving architectures, catalytic conversion, electrostatic repulsion, and chemisorption to suppress polysulfide migration while ensuring Li^+ transport. Advanced materials-carbon-based frameworks(graphene, CNTs), conductive polymers(PPy, PANI), porous MOFs/COFs, and inorganic compounds (transition metal oxides/sulfides)—synergistically enhance conductivity, anchor polysulfides, and accelerate redox kinetics. Heteroatom doping and heterostructure designs optimize adsorption and catalytic activity, achieving capacities >900 mAh g^{-1} and cyclability >1000 cycles. Flexible architectures demonstrate practical viability under mechanical stress. Future priorities include scalable fabrication of ultrathin separators, multifunctional integration (polysulfide suppression, dendrite inhibition), and compatibility with high-sulfur-loading cathodes. Bridging lab-scale innovations to industrial deployment requires harmonizing material design, electrolyte optimization, and advanced characterization to address interfacial instability and energy loss mechanisms.
Keywords: Lithium-sulfur batteries; Functionalized separators; Polysulfide shuttling; Catalytic conversion

1 INTRODUCTION

With the rapid progress of human society and the high-speed growth of the economy, traditional non-renewable fossil fuels are increasingly depleting and causing serious environmental pollution and other problems. There is an urgent need to develop sustainable clean energy to solve the current energy crisis[1,2]. Therefore, it is particularly urgent to replace fossil energy with clean and renewable energy. However, intermittent renewable energy requires an efficient energy storage system[3,4]. Batteries, as an effective means of electrochemical energy storage and release, play a crucial role[5](Figure 1).

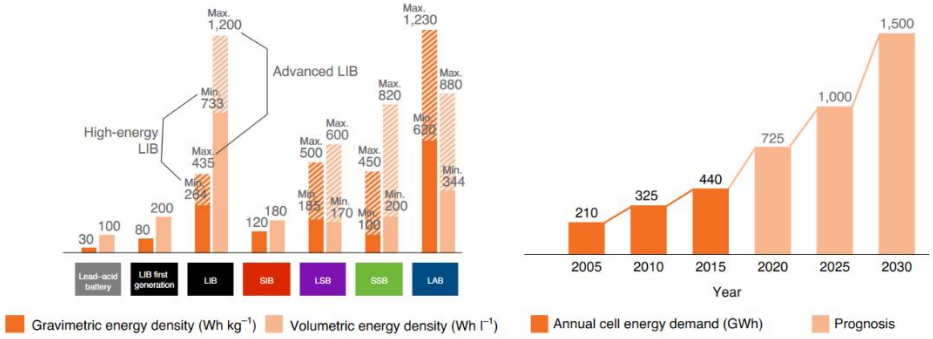

Figure 1 Comparison of Energy Densities among Different Secondary Battery Systems and the Evolution of Battery Energy Requirements over Time[13]

Secondary batteries, as clean and efficient portable energy storage devices, have become the main power source for new energy electric vehicles. Among them, lithium-ion batteries (LIBs) have surpassed traditional lead-acid batteries and nickel-metal hydride batteries in the market share of portable electronic products and are one of the most popular secondary batteries in current commercial applications[6]. However, limited by the energy storage mechanism of LIBs, that is, inserting lithium ions into layered electrode materials such as graphite anodes and lithium metal oxide cathodes[7,8], since lithium ions can only be inserted into some specific positions topologically, its theoretical energy density is only 387 Wh kg^{-1}, resulting in an actual energy density of less than 200 Wh kg^{-1}[9,10], which cannot meet the energy demands of new energy vehicles and others in the long term. In addition, the expensive cathode materials of LIBs limit their application in large-scale storage systems. Therefore, surpassing LIBs undoubtedly requires exploring new energy storage systems with higher energy density and lower cost[11-13].
Lithium-sulfur batteries(LSBs) are a new type of lithium secondary battery, using sulfur and its composite materials as the cathode and lithium metal as the anode. Compared with the "intercalation-deintercalation mechanism" of LIBs, the

working principle of LSBs is not intercalation but is based on the metal electroplating and stripping on the lithium anode side and the conversion reaction on the sulfur cathode side[9,11]. This non-topological nature of the reaction endows the Li anode and S cathode with high theoretical specific capacities of 3860 mAh g^{-1} and 1673 mAh g^{-1}, respectively[14]. In addition, elemental sulfur has the advantages of environmental friendliness, low cost, and abundant reserves. Therefore, LSBs are considered a particularly attractive low-cost energy storage technology[15,16].

LSBs are one of the battery systems developed earlier, dating back to the 1960s. Herbert and Ulam[17] first proposed the concept of Li-S batteries in 1962, assembling a Li-S battery using alkaline perchlorate as the electrolyte, metallic lithium as the anode, and elemental sulfur as the cathode. Since then, the research on LSBs has mainly focused on the selection and use of electrolytes(Figure 2). In 1983, the team of E. Peled[18] studied the complex electrochemical conversion behavior of sulfur in organic electrolytes, which laid an important foundation for the subsequent screening of suitable organic electrolyte components for Li-S batteries. Despite decades of research, the problems of low discharge capacity and rapid cycling capacity decay of LSBs have not been well solved. At the same time, as LIBs showed more stable cycling performance and then became commercialized, the research on LSBs once entered a stagnation period[19]. After 2000, with the rapid development of new applications such as electric vehicles, the energy density of traditional LIBs relying on intercalation chemistry has reached its limit, and there is an urgent need for batteries with higher specific energy[20-22]. In 2009, a major breakthrough was achieved in the research of LSBs. The team of Nazar[23] used CMK-3 (a mesoporous carbon) as a nanoscale channel to carry sulfur and achieved a high discharge capacity with stable cycling for more than 20 times. Since then, the research on LSBs has experienced a significant increase, and major progress has been made in specific capacity and cycling performance. So far, as one of the hotspots in the field of electrochemical energy storage, the research on LSBs focuses on optimization strategies to improve battery performance: composite sulfur cathode design[24], separator optimization[25], binder improvement[26], electrolyte optimization[27], and lithium metal protection[28].

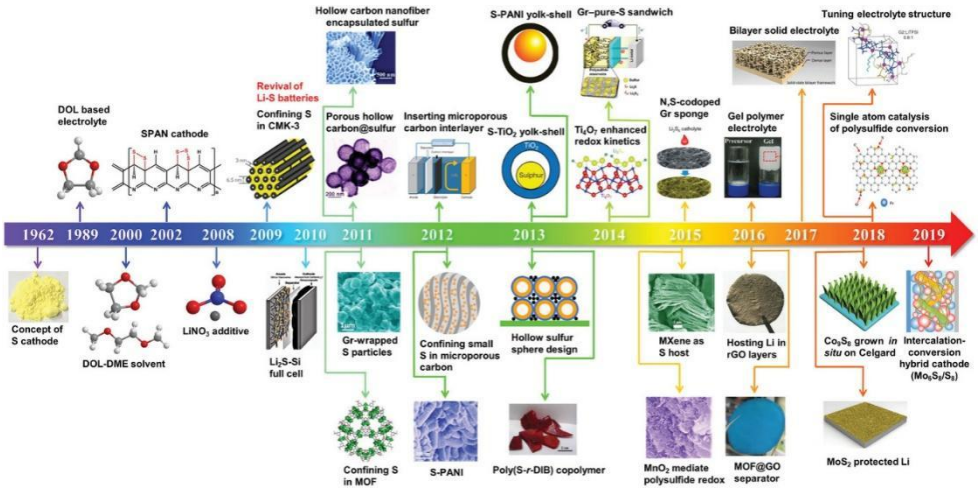

Figure 2 Timeline of Performance Improvements and Representative Design Strategies for LSBs[29]

LSBs are composed of an anode, electrolyte, separator, cathode, and current collector. The cathode is composed of elemental sulfur and a conductive framework. Elemental sulfur has more than 30 allotropes, among which S_8 has a crown-like structure (including 8 sulfur atoms), giving it excellent thermodynamic stability[30,31]. However, due to the poor conductivity of elemental sulfur, the cathode generally coats elemental sulfur or a composite material added with a conductive material on the conductive current collector[32].

The working principle of LSBs is the electrochemical reaction $S_8+16Li \leftrightharpoons 8Li_2S$. During the discharge process, metallic lithium (anode) is oxidized to form lithium ions and electrons. Lithium ions pass through the electrolyte to reach sulfur (cathode). At the same time, electrons also reach sulfur(cathode) through the external circuit, generating electrical energy. In the cathode part, sulfur undergoes a reduction reaction with lithium ions and electrons to form lithium sulfide. During the charging process, lithium ions and electrons return to the anode through the electrolyte and the external circuit respectively, and the electrical energy is converted into chemical energy and stored[7-9].

(1)Discharge process:

Anode: $Li \rightarrow Li+ + e^-$

Cathode: $S_8 + 16Li^+ \rightarrow 16e^- + 8Li_2S$

(2)Charging process:

Cathode: $Li^+ + e^- \rightarrow Li$

Anode: $8Li_2S \rightarrow S_8 + 16Li^+ + 16e^-$

LSBs exhibit a dual-platform charge-discharge curve. During the discharge process, sulfur is first lithiated to form a series of long-chain polysulfide intermediate species, corresponding to $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4$. These intermediate species are easily soluble in the ether-based electrolyte, which is manifested as a high voltage platform(2.3 V), and the

discharge specific capacitance is 418 mAh g^{-1}(this process contributes 25% of the theoretical capacity of sulfur). Then, sulfur is further lithiated, and the soluble long-chain polysulfides are reduced to insoluble short-chain sulfide species, corresponding to $Li_2S_4 \rightarrow Li_2S_2 \rightarrow Li_2S$, which is manifested as a low voltage platform(2.1 V), and the discharge specific capacitance is 1255 mAh g^{-1}(this process contributes the remaining 75% of the theoretical capacity of sulfur). The opposite situation occurs during the charging process[7-9]. In short, LSBs will undergo a solid → liquid → solid transformation during the discharge process, which is also different from other batteries.

2 CHALLENGES AND OPTIMIZATION STRATEGIES FOR LSBS

Although LSBs have many advantages, the following challenges still need to be overcome for commercialization:

2.1 Low Electrical Conductivities of Elemental Sulfur and Lithium Sulfide

The electrical conductivities of elemental sulfur and lithium sulfide at room temperature are only 5×10^{-30} and 1×10^{-13} S cm^{-1}, respectively. This will limit the redox kinetics on the sulfur cathode side, reducing the utilization rate of active sulfur and ultimately resulting in a low specific capacity of the battery [33,34]. The insulating property of lithium sulfide makes it difficult for solid-state(Li_2S_2) to transform into solid-state(Li_2S), manifested as incomplete conversion of higher-order lithium polysulfides(LiPSs) into Li_2S, with the final product being a mixture of Li_2S_2 and Li_2S. In addition, the precipitation during the discharge also leads to the passivation of the cathode surface, which also reduces the discharge capacity of the battery[35-37]. Therefore, adding conductive functional host materials to form composites with sulfur[38], and optimizing the deposition of reduction products Li_2S_2 and Li_2S at the interface[39] are important methods to improve sulfur utilization.

2.2 Shuttle Effect of Polysulfides

During the cycling process, the formed long-chain LiPSs(Li_2S_4 to Li_2S_8) dissolve in the ether-based electrolyte, resulting in the loss of active substances. In addition, LiPSs will diffuse through the separator to the lithium anode and undergo chemical reduction (rather than electrochemical reduction)[35]. The electrochemical reduction reaction is a direct chemical reaction between polysulfides and lithium ions without outputting charge to the circuit, leading to energy loss. Subsequently, the lower-order LiPSs diffuse back to the sulfur cathode and are re-oxidized into higher-order LiPSs, completing the re-migration of LiPSs. The phenomenon of LiPSs shuttling back and forth between the anode and cathode and undergoing irreversible chemical reactions is the shuttle effect[40,41]. The shuttle effect of polysulfides is essentially an internal short circuit of the battery, which is the root cause of the battery's self-discharge and low Coulombic efficiency. Therefore, research on suppressing the shuttle effect mainly focuses on the material optimization of the sulfur cathode[42], the construction of a barrier for the separator[43], and the effective protection of lithium metal[44].

2.3 Volume Expansion of Sulfur During Lithiation

The densities of sulfur and lithium sulfide are 2.03 and 1.66 g cm^{-3}. When sulfur is completely converted into lithium sulfide, the volume will expand by about 80% of the original, causing irreversible damage to the electrode[45].

2.4 Uneven Solid Electrolyte Interface(SEI)

Metallic lithium is very reactive and will react with the electrolyte to form an unstable SEI on the surface of metallic lithium. This SEI can only conduct ions but not electrons. In addition, the unevenness of the SEI leads to continuous side reactions between the electrolyte and lithium, constantly consuming the electrolyte and lithium, ultimately resulting in a decrease in battery capacity and unstable performance[46].

2.5 Dendrite Growth of Lithium Metal

The uneven deposition of lithium ions on the surface of lithium metal leads to the formation of lithium dendrites. Uneven lithium dendrites can pierce the separator, causing a short circuit in the battery and even safety accidents[47,48]. In addition, the growth of lithium dendrites will cause continuous rupture and reconstruction of the SEI, resulting in continuous loss of lithium metal and electrolyte and increasing the polarization of the battery[49,50]. The broken lithium dendrites will detach from the anode and become "dead lithium", reducing the utilization rate of lithium metal and further decreasing the Coulombic efficiency[51]. Therefore, artificially constructing a uniform SEI layer[52] and optimizing electrolyte additives[53] are effective measures to protect lithium metal.

3 OPTIMIZED SEPARATOR REQUIREMENTS FOR LSBS

As one of the core components of the battery, the separator is used to separate the anode and cathode to prevent internal short circuits of the battery and is required to have the ability to transport ions through its internal pores. Currently commercialized battery separators include porous polymers such as single-layer polypropylene separators(PP), single-

layer polyethylene separators(PE), and three-layer PP/PE/PP composite separators[54]. However, commercial separators have large pore gaps. While allowing lithium ions to pass through, polysulfides can also penetrate, leading to a serious shuttle effect. In addition, the poor wettability of commercial separators is also an important factor affecting battery performance, which will seriously deteriorate the cycling performance of the battery[55]. Studies have found that designing functionalized separators can effectively inhibit the shuttle effect and achieve uniform lithium nucleation growth[56,57]. The optimization strategy of the separator for LSBs can help enhance the interfacial performance between the cathode and the separator, thus achieving the effect of stabilizing the metal anode. In addition, the conductive modified separator on the sulfur cathode side can be regarded as a "secondary electrode" to improve the conductivity of the sulfur cathode, reactivate the "dead sulfur" during the cycling process, minimize the loss of active sulfur, and ultimately achieve the goal of improving the utilization rate of active substances[58].
An ideal functionalized separator should meet the following requirements(Figure 3):

3.1 Optimal Separator Thickness

The thickness of the separator is a key characteristic affecting battery impedance, ion transport, and mechanical strength[59]. Currently, the thickness of commercial polyolefin separators is less than 25 micrometers, and the thickness of inorganic coating layers such as metal-organic frameworks[60], metal oxides[61], and polymers[62] can exceed 25 micrometers, and the thickness of carbon-based coating layers and even some composite coating layers[63] can exceed 100 micrometers. Optimizing the conductive materials of the separator is beneficial for the reactivation of LiPSs. At the same time, with the increase in conductive materials, the problem of increased battery thickness requires more electrolyte. Therefore, finding the optimal conditions between the addition of conductive materials and thickness control is an effective way to maximize battery performance[64].

3.2 Excellent Electrolyte Wettability

Wettability is an important characteristic affecting the relative permeability and ionic conductivity of the battery. Currently, commercial polyolefin separators have low surface energy and strong hydrophobicity, resulting in poor electrolyte wettability, which in turn affects the ionic conductivity and lithium ion transference number of the battery[65].

3.3 Reasonable Structural Design

Reasonable structural design is one of the effective ways to maximize the role of functionalized separators. In the design process, parameters such as porosity, pore volume, and pore size distribution need to be considered[65].

3.4 Stable Safety Performance

Stable safety performance plays an important guarantee role in the battery. The structure and physical and chemical properties of the separator directly determine the safety of the battery. In LSBs, special attention needs to be paid to safety hazards such as the lithium metal anode and flammable electrolytes. In addition, polyolefin separators are prone to thermal shrinkage in high-temperature environments, which may lead to local penetration of the separator, causing the electrodes to come into direct contact and triggering battery short circuits and other consequences[66,67]. Therefore, to achieve a safe battery, it is crucial to construct and optimize materials with high heat resistance, flame retardancy, and mechanical stability as the materials for functionalized separators[68].

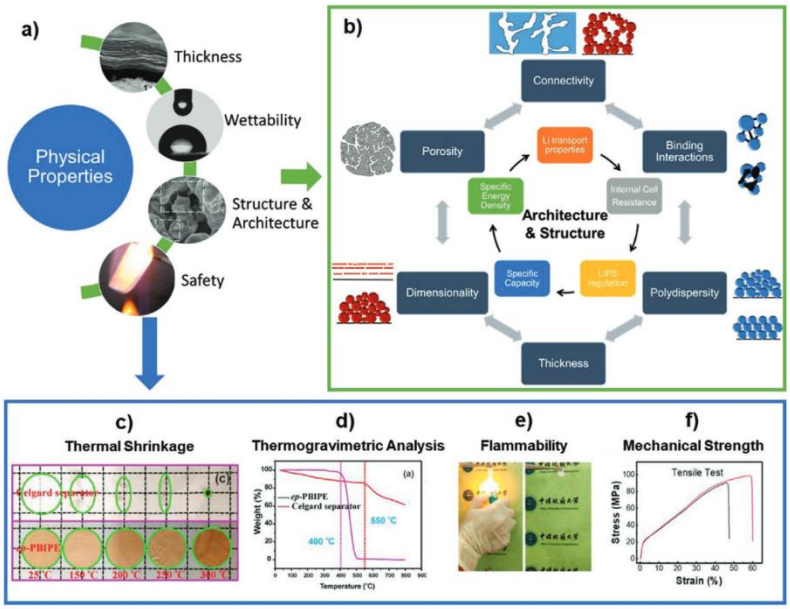

Figure 3 (a) The Physical Properties of the Functionalized Separator; (b) The Influence of the Structure of the Functionalized Separator on LSBs; (c-f) The Importance of Safety for LSBs and the Related Characterizations[69]

4 MECHANISMS OF FUNCTIONALIZED SEPARATORS IN LSBS

Current research has physically and chemically modified commercial separators. The action mechanisms of functionalized separators are mainly divided into the following four types: ion sieving, catalytic conversion, electrostatic repulsion, and surface chemical adsorption, as shown in Figure 4a-d.

4.1 Ion Sieving

Cover the large pore structure of the separator surface with functionalized materials, allowing the separator to allow lithium ions to pass through while preventing polysulfides from passing through, achieving the purpose of ion sieving[70]. High microporous volume with appropriate curvature is beneficial for inhibiting the migration of polysulfides, and the high surface area provides a "secondary capture" site for polysulfides. Due to its advantages of high specific surface area, adjustable pore structure, and excellent electrical conductivity, porous carbon is used as a material for designing functionalized separators[71,72]. The team of Manthiram[71] first reported a porous multi-walled carbon nanotube paper inserted between the cathode and the separator. Due to size exclusion, it can effectively block the passage of polysulfide intermediates, thereby improving the cycling stability of the battery(Figure 4e). Yang[72] et al. designed a hybrid coating composed of graphene and $Li_4Ti_5O_{12}$ nanospheres. The space between the nanospheres acts as a Li^+ transport channel and also plays the role of ion sieving, effectively preventing the migration of polysulfides. In addition to carbon-based functionalized separators, the ion sieving effect also widely exists in porous intermediates composed of other materials. He[73] et al. designed a Celgard interlayer modified with a hollow Co_9S_8 array. The Co_9S_8 array, as an efficient polysulfide capture agent, enables the battery to provide a high initial discharge capacity and stable cycling performance(Figure 4f).

4.2 Catalytic Conversion

The "solid-liquid-solid" conversion mechanism in the sulfur cathode of LSBs leads to the slow redox kinetics of the conversion from the liquid phase (soluble LiPSs) to the solid phase (lithium sulfide) in the second stage. Therefore, adding an electrocatalyst to the functional separator is a favorable means to improve the sulfur redox kinetics[74,75]. Studies have shown that introducing carbon nanotubes and graphene into the conductive network can accelerate electron transfer, accelerate LiS_2 nucleation, and reduce the reaction activation energy, ultimately promoting the redox kinetics of polysulfides[76]. Metal sulfides have been proven to be materials for catalytic conversion. Li[77] et al. anchored vertical MoS_2 nanosheets on conductive carbon nanotubes using the Mo-O-C covalent coupling method. MoS_2 enhances the affinity with polysulfides, accelerates the reaction kinetics of polysulfide conversion, and thus exhibits efficient electrochemical performance(Figure 4g). In addition, metal oxides also exhibit high catalytic activity for the reduction reaction of polysulfides. Song[78] et al. designed to coat MnO_2 on a PE separator. MnO_2 not only adsorbs polysulfides but also catalyzes the conversion of soluble polysulfides, greatly inhibiting the lithium polysulfide shuttle effect and improving the cycling performance of the battery(Figure 4h).

4.3 Electrostatic Repulsion

Designing functional groups with negative charges on the separator surface can generate electrostatic repulsion against polysulfides, thereby suppressing the polysulfide shuttle effect. Xu[79] et al. reported a sulfonic acid group-rich COF and applied it to modify the separator of Li-S batteries. Due to its strong electronegativity, it repels polysulfide anions via electrostatic interactions, strongly inhibiting the shuttle effect(Figure 4i). Huang et al.[80] introduced Nafion into the Celgard separator. The sulfonate groups, being negatively charged, allow Li+ to pass while repelling negatively charged polysulfide species. This forms a charge shield in the interlayer, preventing the shuttle of polysulfides(Figure 4j).

4.4 Chemical Adsorption

In the process of designing functionalized separators, adding modifiers to utilize chemical interactions (such as polarity-polarity interactions, Lewis acid-base interactions, and chain-like interactions) can achieve the fixation of polysulfides. Therefore, selecting materials with strong affinity for polysulfides is a key strategy for using chemical adsorption[81]. Polar molecules can adsorb and fix polysulfides through strong polarity-polarity interactions. Doping heteroatoms into carbon materials can achieve strong polarity-polarity interactions[82]. Per[83] et al. prepared a G@PC/PP functionalized separator by nitrogen-doping porous carbon nanotubes. The nitrogen-doped carbon nanotubes exhibit polarity-polarity interactions with polysulfides, thereby inhibiting the shuttle of polysulfides. In addition, transition metal sulfides are also used as coatings for functional separators due to their excellent electrocatalytic activity. Ghazi[84] et al. designed a MoS_2/Celgard composite separator, which has good lithium ion conductivity and can significantly inhibit the shuttle of polysulfides, ensuring the long lifespan and charge-discharge performance of the battery(Figure 4k).

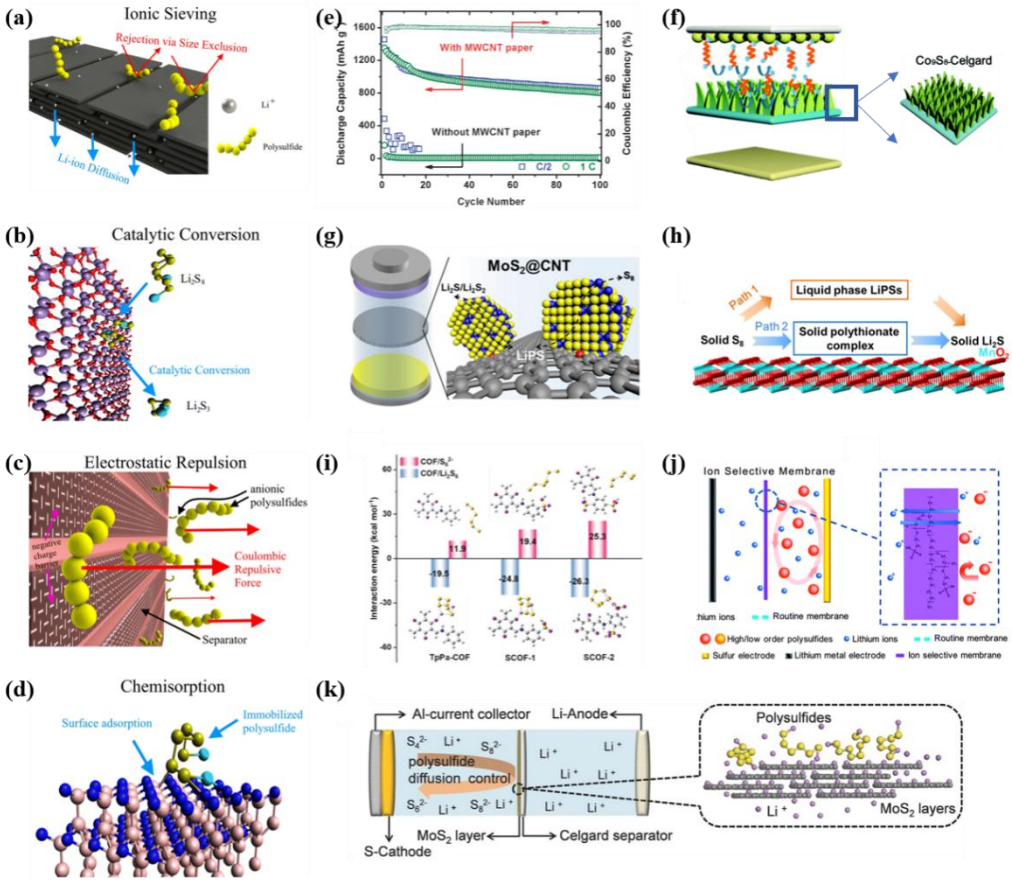

Figure 4 (a-d) Ion Sieving, Catalytic Conversion, Electrostatic Repulsion, and Surface Chemical Adsorption Mechanisms[85]; (e) The Cycling Performance Diagrams of LSBs with and without the MWCNT Interlayer[71]; (f) The Mechanism Diagram of the Co_9S_8-Celgard Separator during the Charging/Discharging Process[73]; (g) The Schematic Diagram of the Catalytic Conversion of Polysulfides by MoS_2@CNT[77]; (h) The Catalytic Process Schematic Diagram of the MnO_2@PE Separator[78]; (i) The Interaction Between Polysulfides and Different COF Monomers[79]; (j) The Schematic Diagram of the Cation-Selective Membrane Inhibiting the Shuttle of Polysulfides[80]; (k) The Schematic Diagram of Using the MoS_2/Celgard Separator[84]

5 MODIFYING MATERIALS OF FUNCTIONALIZED SEPARATORS

5.1 Modification with Carbon Materials

Carbon-based materials can achieve the purpose of ion sieving for LiPSs by reducing the pore size. In addition, due to their excellent electrical conductivity, they are beneficial for electron transfer and can improve the utilization rate of cathode active materials. Introducing heteroatoms into carbon materials can significantly enhance the chemical affinity for LiPSs, thereby improving battery performance[86,87]. On the other hand, carbon materials can improve the conversion kinetics of LiPSs by increasing the conductivity of the separator and enhancing the electron mobility, and reduce the formation of Li dendrites by decreasing the local current density and Li surface reactions.

Graphene, as a two-dimensional(2D) material, has excellent properties such as electrical conductivity, mechanical strength, thermal stability, and high functionalization. It can effectively adsorb LiPSs and transfer electrons better, thus improving battery performance[88]. Ou[89] et al. reduced the pore size of the PP/PE/PP membrane by transferring a graphene layer onto the Celgard membrane. The battery cycling performance of the separator modified with graphene was significantly improved. Graphene is usually modified by doping heteroatoms(N/S) to better adsorb LiPSs. Qi[90] et al. performed nitrogen doping on graphene. As shown in Figure 5a-b, the battery assembled with the designed PP/NG functionalized separator showed a higher capacity retention rate. Theoretical calculations proved that nitrogen doping significantly improved the adsorption ability for LiPSs. Composites composed of graphene and polar metal oxides/sulfides have been proven to be helpful for the chemical capture of LiPSs. Jing[91] et al. added vanadium nitride(VN) nanoparticles to enhance the reduction and oxidation kinetics of LiPSs. The test results showed that the addition of VN could promote the nucleation and growth of Li_2S, and thus promote the redox kinetics of LiPSs(Figure 5c). In addition, graphene can also greatly improve the utilization rate of active sulfur. Mo[92] et al. integrated vertical graphene nanosheets and continuously filled macropores. The hierarchical fibers have high electrical conductivity and large pore volume, which can significantly enhance electron transfer and effectively improve the storage capacity of sulfur species(Figure 5d).

Carbon nanotubes, due to their excellent electrical conductivity, can promote electron transfer to accelerate the conversion of LiPSs. However, carbon nanotubes alone cannot effectively adsorb LiPSs, while metal oxides/sulfides can adsorb LiPSs well, thus making full use of active substances and improving redox kinetics. Therefore, carbon nanotubes are often composited with them. Wang[93] et al. uniformly deposited three-dimensionally ordered macroporous N, Co-doped titanium oxide on the CNFs network to form a dense-structured adsorption/catalytic multifunctional interlayer(N, Co-TiO_x/NCNT@CNFs). This functional layer not only provides an effective physical barrier for the diffusion of polysulfides but also promotes the catalytic conversion kinetics. In addition, carbon nanotubes can be easily functionalized with other groups, thereby improving the adsorption force with other groups. Yang[94] et al. grafted the organic small molecule tris(hydroxypropyl)phosphine(THPP) onto hydroxylated multi-walled carbon nanotubes(CNT-OH) as a functional intercalation material. As shown in Figure 5e-g, it can accelerate the catalytic conversion of polysulfides, effectively inhibit the shuttle effect of polysulfides, and reduce the formation of lithium dendrites.

Carbon nanofibers have a special interwoven structure, so they have strong mechanical strength and flexibility. In addition, their electrical conductivity is beneficial for the effective transfer of electrons[95]. However, the fiber surface is smooth and has a low surface energy, which is not conducive to the adsorption of LiPSs[96]. Therefore, research efforts are dedicated to introducing functional groups to increase the adsorption energy of LiPSs[97]. For the self-supporting CNF interlayer with polar oxygen-containing functional groups, calculations show that CNF has a high adsorption energy for Li_2S_6. These results confirm that the oxygen-containing groups of the CNF separator have a strong chemical interaction with LiPSs, and the CNF separator can effectively inhibit the migration of polysulfides through steric hindrance and chemical anchoring(Figure 5h) [98].

Porous carbon materials have good adsorption for LiPSs and can improve the transfer of electrons and Li^+, showing a good synergistic effect[100]. Low-cost carbon black is also used to coat the separator or cathode due to its high surface area characteristics, so as to improve the electrochemical performance of the battery[101]. In addition, many other carbon materials are also applied to the modification of the interlayer.

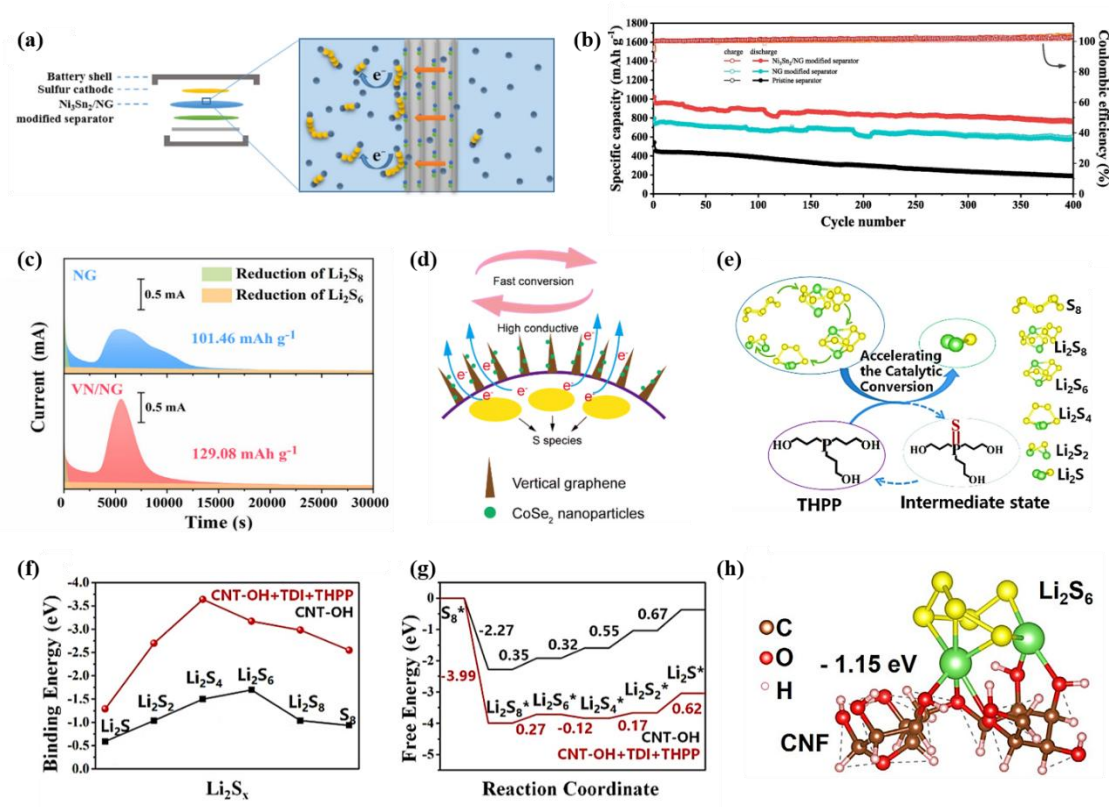

Figure 5 (a-b) The Battery Schematic Diagram of the Ni_3Sn_2/NG Modified Separator and the Comparison Diagram of the Cycling Performance of the Modified Separator[90]; (c) The Potentiostatic Discharge Curve of the Battery with the NG/VN Separator at a Voltage of 2.05 V[91]; (d) The Mechanism Diagram of VGMFs@$CoSe_2$[92]; (e-g) The Conversion Schematic Diagram of Lithium Polysulfide on THPP, the Comparison Diagram of the Adsorption Energy of Various Materials for Polysulfides, and the Free Energy Diagram of the Conversion of S_8 to Li_2S[94]; (h) The Adsorption Schematic Diagram of Li_2S_6 and CNF[99]

5.2 Modification with Conductive Polymers

The abundant charged functional groups on the surface of polymers can enhance the interfacial electrical conductivity and mechanical properties. The adjustable structure can inhibit the shuttle effect of LiPSs, and the affinity for the electrolyte can significantly improve the wettability of the separator and facilitate ion transport[102].

Polypyrrole(PPy) is widely used in the modification of separators due to its strong affinity for the electrolyte and excellent adsorption ability for LiPSs, which can improve the physical/chemical properties of the interface and inhibit the shuttle effect of LiPSs. Li[103] et al. introduced an ultrathin and lightweight PPy functional layer on the surface of the Celgard separator through a simple vapor phase polymerization method. As shown in Figure 6a, the modified separator can ensure the uniform flow of lithium ions on the one hand, thus achieving the uniform deposition and stripping of metallic lithium on the lithium anode, and can effectively anchor lithium polysulfide on the other hand, inhibiting the shuttle effect of lithium polysulfide.

Polyaniline(PANi), as a typical conjugated conductive polymer, can expand its conjugated structure by combining with certain heteroatoms, such as protonic acids, inorganic metal compounds, and other molecules with inherent conductivity, thereby enhancing its ionic conductivity[104]. Jo[105] et al. designed a polyaniline-coated hollow cobalt-iron Prussian blue analogue(CFP@PANI) for separator modification. As shown in Figure 6b, the CFP@PANI-PP had a capacity retention rate of 83.5% after 100 cycles at 1 A g^{-1}, indicating that the modified layer effectively inhibited LiPSs and thus improved the electrochemical performance.

Poly(3,4-ethylenedioxythiophene)(PEDOT) is often used together with polystyrene sulfonate(PSS) to produce a conductive polymer called PEDOT:PSS[106]. PEDOT can also form a chelating structure with LiPSs. Abbas[107] et al. sprayed a layer of PEDOT:PSS on the cathode side of the commercial separator. As shown in Figure 6c, since the surface of the modified membrane is negatively charged, it can effectively alleviate the shuttle effect through Coulombic repulsion, reducing the charge decay rate by 67%. In addition, the hydrophilicity increases with the modification of PEDOT:PSS, resulting in improved electrolyte wettability and a 14% reduction in the charge transfer resistance of the LSB.

5.3 Modification with Organic Frameworks

Both metal-organic frameworks(MOFs) and covalent organic frameworks(COFs) exhibit highly porous structures. MOFs have various properties, including strong functionality, large porosity and specific surface area, adjustable pore

size, biomimetic catalysis, and biocompatibility. Similar to MOFs, COFs, as a class of organic polymers, contain a certain porosity and a large number of polar groups[108].

MOFs with appropriate pore sizes can be introduced into the battery as ion sieves to regulate ion transport. Bai[109] et al. first reported the application of MOFs as separators for LSBs. The MOF@GO separator was prepared by a simple filtration method, and its pore size distribution is approximately 0.9 nm, which can fully play the role of an ion sieve. As shown in Figure 6d, this composite separator can effectively inhibit the shuttle of polysulfides to the anode without affecting the transport of Li^+, and the cycling test shows a very low capacity decay rate(0.019% per cycle after 1500 cycles). However, during the cycling process, GO may be partially reduced to conductive rGO, leading to a short circuit. At the same time, the mechanical properties of the composite separator are poor and cannot meet the requirements of practical applications. Therefore, on this basis, a new type of MOF@PVDF-HFP separator that can both capture polysulfides and protect the lithium metal anode was prepared using a similar method[110]. Compared with the MOF@GO separator, the MOF@PVDF-HFP separator has better flexibility. As shown in Figure 6f-g, the fabricated pouch battery can still provide a high capacity of 936 mAh g^{-1} after 200 cycles at 0.1 C, which further proves the practicality of this separator. Chang[111] et al. decorated the MOF channels with a negatively charged sulfonic acid polymer(NSP), which can simultaneously change the charge environment of the MOF channels Figure 6e. By forming a repulsive force between polysulfides and NSP, it promotes the transport of lithium ions, thus greatly reducing the initial "sulfur loss" and voltage polarization. This not only reveals the influence of the pore size and metal position on the performance of MOF-based separators but also proposes a new strategy for improving the performance of MOFs.

COFs exhibit high chemical adsorption ability for LiPSs. The adsorption mechanism is attributed to the uniform coexistence of electron-rich atoms and electron-deficient atoms, which can adsorb Li^+ and S_x^{2-} respectively. In addition, the ordered structure of COFs allows for a higher heteroatom doping ratio, as well as more uniform sulfur distribution and redeposition, resulting in good electrode kinetics[112]. Yan[113] et al. synthesized a C@COF coated separator using a simple sonochemical method. As shown in Figure 6i-g, C@COF has strong chemical adsorption and electron-ion co-conductivity on the surface of LiPSs, giving full play to the "absorption-conversion" catalytic effect. The COF containing boroxyl groups provides rich sulfur-philic and lithium-philic sites, while carbon nanotubes promote electron transfer. Therefore, the barriers for the deposition and decomposition of Li_2S are reduced, thus achieving the bidirectional catalytic conversion of LiPSs.

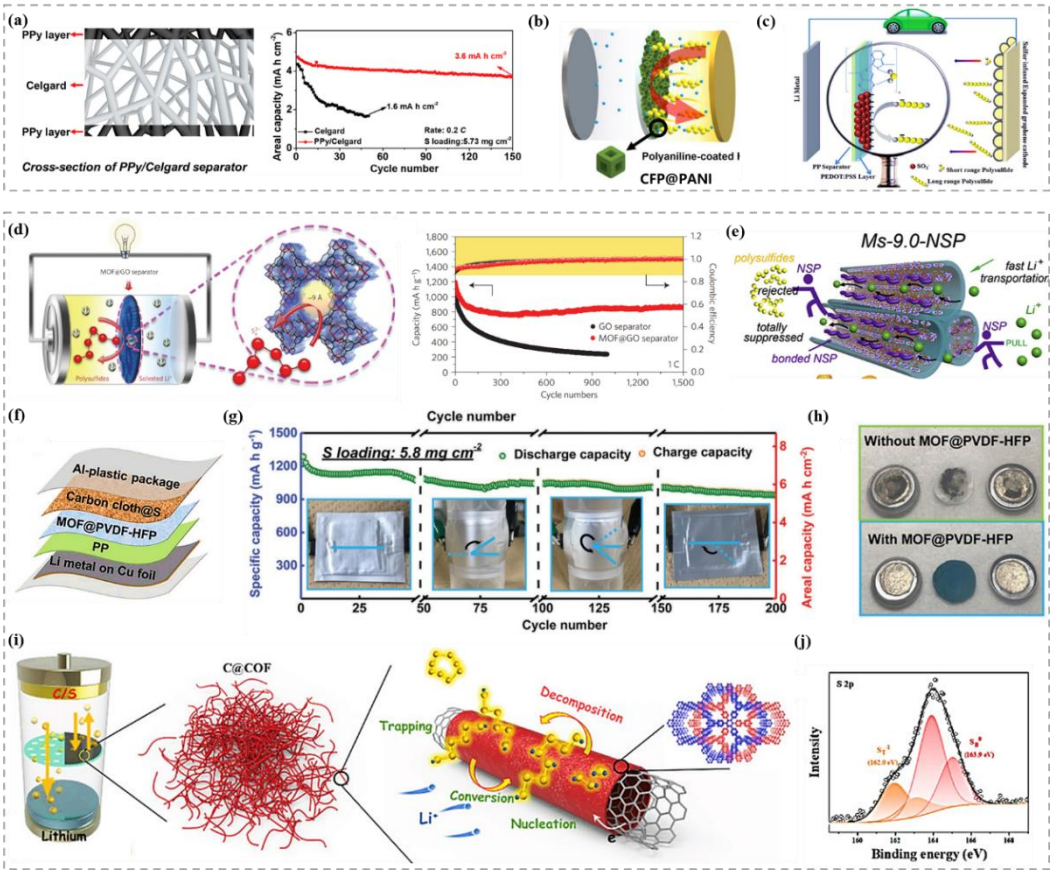

Figure 6 (a) The Structure Schematic Diagram of the PPy/Celgrad Separator and the Comparison Diagram of the Cycling Performance[103]; (b) The Schematic Diagram of the CFP@PANI Functional Separator[105]; (c) The Mechanism Diagram of the Separator Modified with PEDOT:PSS[107]; (d) The Mechanism Diagram of the MOF@GO Separator and the Comparison Diagram of the Cycling Performance[109]; (e) The Mechanism Diagram of Ms-9.0-NSP[111]; (f-h) The Battery Structure Schematic Diagram of the MOF@PVDF-HFP Separator, the Cycling Performance of the Flexible Li-S Pouch Battery, and the Digital Photos of Different Separators after 1000 cycles[110];

(i-j) The Battery Working Process Schematic Diagram of the C@COF Improved Separator and the Adsorption Energy Diagram between COFs and LiPSs[113]

5.4 Modification with Inorganic Materials

Inorganic materials with polar sites exhibit strong adsorption ability for polar LiPSs, which can effectively inhibit the shuttle effect of LiPSs. In addition, some inorganic materials can also increase the transference number of Li^+, thereby improving the electrochemical performance.

Transition metal oxides have excellent environmental stability and high catalytic activity. They can catalyze the conversion of LiPSs through Lewis acid-base interactions and oxygen vacancy fixation and exhibit excellent electrochemical performance when modifying separators[114]. Xiao[115] et al. designed a graphene/TiO_2 functionalized separator. The porous graphene nanosheets establish a highly conductive framework and can physically limit LiPSs, and the strong adsorption ability of TiO_2 for LiPSs can further inhibit the shuttle effect of LiPSs. However, metal oxides with poor electrical conductivity have slow redox kinetics, which will reduce the utilization rate of active substance S. Introducing highly conductive metal-based catalysts is a favorable way to improve conductivity and accelerate catalytic conversion. Zhou[116] et al. proposed a TiO_2-TiN heterojunction structure, which combines the advantages of highly adsorptive TiO_2 and conductive TiN to achieve the capture-diffusion-conversion process of LiPSs at the interface. By loading this heterostructure onto graphene as a physical barrier, a dense film was prepared on the separator, which can greatly inhibit the shuttle of LiPSs even under high sulfur loading. The test shows that the capacity retention rates at sulfur loadings of 3.1 and 4.3 mg cm^{-2} are 73% and 67% respectively after 2000 cycles. Using the bimetallic oxide strategy can give full play to the synergistic reaction of chemical interactions and catalytic activity. Lv[117] et al. designed a functionalized separator of metal oxide composite material($NiCo_2O_4$@rGO). The calculated energy barrier on the surface of $NiCo_2O_4$ is 0.15 eV, as shown in Figure 7a-b. Compared with ordinary PP or rGO/PP separators, the $NiCo_2O_4$@rGO/PP separator shows a significantly higher Li^+ diffusion coefficient. The metal oxide composite material $NiCo_2O_4$@rGO/PP separator with a low Li^+ diffusion energy barrier enables the LSBs to achieve a capacity retention rate of 92% after 400 cycles. The heterostructure composed of multi-metal oxides contains abundant oxygen vacancy defects, thus exhibiting strong adsorption for LiPSs.

Transition metal sulfides possess abundant metal centers for polymer adsorption. Figure 7c shows the adsorption energies of various LiPSs on MoS_2 nanosheets[118]. Transition metal sulfides exhibit high affinity for LiPSs, as evidenced by their highly negative adsorption energies. Liu[119] et al. modulated the d-band electronic structure of molybdenum disulfide electrocatalysts through p/n doping to promote polysulfide conversion and inhibit polysulfide migration in LSBsies. As shown in Figure 7d, the p-type V-MoS_2 catalyst demonstrates more pronounced bidirectional catalytic effects. Electronic structure analysis(Figure 7e-f**)** further reveals that the excellent anchoring and electrocatalytic activity originate from the upward shift of the d-band center and the optimized electronic structure induced by bimetallic coupling.

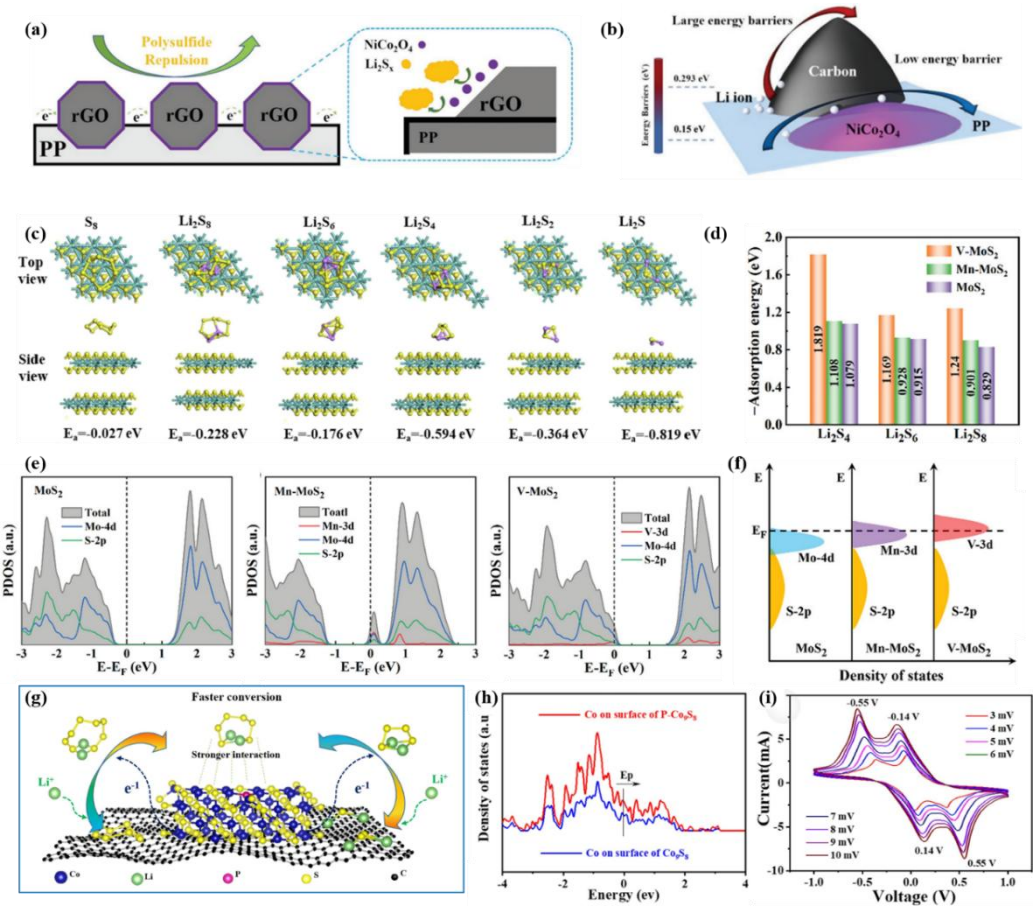

Figure 7 (a) The Detailed Schematic Diagram of $NiCo_2O_4$@rGO/PP during Charging; (b) The Schematic Diagram of the Lithium Ion Diffusion Energy Barrier on the Surface of Nickel-Cobalt Oxide and Carbon materials[117]; (c) The Adsorption Energy of S_8 and Li_2S_x ($2<x<8$) on MoS_2[118]; (d) The Calculated Adsorption Energy of Soluble LiPSs(Li_2S_4, Li_2S_6, and Li_2S_8) on the Surfaces of MoS_2, Mn-MoS_2, and V-MoS_2; (e) The PDOS of MoS_2, Mn-MoS_2, and V-MoS_2 Respectively; (f) The Conceptual Illustration of the d-Band Shift after Doping Various Foreign Atoms[119]; (g) The Schematic Diagram of the Interaction between P-Co_9S_8@SC and Polysulfides; (h) The Density Of States(DOS) of Co on the Surfaces of Co_9S_8 and P-Co_9S_8; (i) The CV Curve of P-Co_9S_8@SC[120]

Co_9S_8, with its metallic properties and abundant active centers, can facilitate polysulfide conversion in LSBs. Zhang[120] et al. investigated P-doping in Co_9S_8 to further enhance electrocatalytic and adsorption performance(Figure 7g**)**. On one hand, the polar surface exhibits strong affinity for polysulfides, enabling effective anchoring and inducing rapid nucleation of Li_2S_2/Li_2S. On the other hand, the abundant catalytic sites in P-Co_9S_8 accelerate polysulfide conversion and mitigate the shuttle effect(Figure 7h**)**. The retention of reduction-oxidation peaks in symmetric cell CV scans with increasing scan rates indicates rapid redox reactions of polysulfides(Figure 7i**)**. The assembled battery demonstrates an initial capacity as high as 961 mAh g^{-1} and maintains stable performance over 1000 cycles at 1C.

6 SUMMARY

This review systematically examines LSBs from material design, mechanistic insights, and performance optimization perspectives. It focuses on functionalized separator strategies to address critical challenges, including polysulfide shuttling, poor conductivity, and interfacial instability. Key advancements in catalytic conversion, ion regulation, and multifunctional integration are highlighted, alongside future directions for scalable and practical LSB development.

6.1 Challenges

LSBs suffer from insulating S/Li_2S, polysulfide shuttling (causing self-discharge, low Coulombic efficiency), Li dendrite risks, and 80% volume expansion during cycling. Unstable SEI exacerbates electrolyte degradation.

6.2 Separator Mechanisms

Ion-sieving blocks polysulfides via microporous structures; catalytic materials (e.g., Co_9S_8, MoS_2) lower redox activation energy; electrostatic layers repel anions; polar groups enable chemisorption.

6.3 Material Strategies

Carbon frameworks enhance conductivity and act as secondary current collectors; conductive polymers improve wettability; MOFs/COFs offer tunable pores for selective ion transport; inorganic compounds (e.g., TiO_2, VN) synergize adsorption and catalysis.

6.4 Performance Advances

Optimized separators enable >900 mAh g^{-1} initial capacity, >1000 cycles, and flexible designs (e.g., MOF@PVDF-HFP) for practical cells. Heterostructures (TiO_2-TiN) and doped catalysts (P-Co_9S_8) boost conversion efficiency.

6.5 Future Directions

Scalable fabrication of ultrathin, robust separators; multifunctional integration (thermal stability, dendrite suppression); compatibility with lean electrolytes and high-sulfur cathodes; in situ characterization to guide interfacial engineering.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

REFERENCES

[1] Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. Nature, 2012, 488(7411): 294-303. DOI: 10.1038/nature11475.
[2] Turner J A. Sustainable hydrogen production. Science, 2004, 305(5686): 972-974. DOI: 10.1126/science.1103197.
[3] Dunn B, Kamath H, Tarascon J M. Electrical energy storage for the grid: a battery of choices. Science, 2011, 334(6058): 928-935. DOI: 10.1126/science.1212741.
[4] Cao R, Xu W, Lv D, et al. Anodes for rechargeable lithium-sulfur batteries. Advanced Energy Materials, 2015, 5(16): 1402273. DOI: 10.1002/aenm.201402273.
[5] Dahn J R, Zheng T, Liu Y, et al. Mechanisms for lithium insertion in carbonaceous materials. Science, 1995, 270(5236): 590-593. DOI: 10.1126/science.270.5236.590.
[6] Chen Binglin, Zhao Jingquan. Research progress on factors affecting cycle life and mechanism of lithium-ion batteries. Chinese Journal of Power Sources, 2025, 49(01): 57-66. DOI: 10.3969/j.issn.1002-087X.2025.01.006.
[7] Goodenough J B, Park K S. The Li-ion rechargeable battery: a perspective. Journal of the American Chemical Society, 2013, 135(4): 1167-1176. DOI: 10.1021/ja3091438.
[8] Whittingham M S. Ultimate limits to intercalation reactions for lithium batteries. Chemical Reviews, 2014, 114(23): 11414-11443. DOI: 10.1021/cr5003003.
[9] Yang Y, Zheng G, Cui Y. Nanostructured sulfur cathodes. Chemical Society Reviews, 2013, 42(7): 3018-3032. DOI: 10.1039/c2cs35256g.
[10] Adelhelm P, Hartmann P, Bender C L, et al. From lithium to sodium: cell chemistry of room temperature sodium-air and sodium-sulfur batteries. Beilstein Journal of Nanotechnology, 2015, 6(1): 1016-1055. DOI: 10.3762/bjnano.6.105.
[11] Bruce P G, Freunberger S A, Hardwick L J, et al. Li-O2 and Li-S batteries with high energy storage. Nature Materials, 2012, 11(1): 19-29. DOI: 10.1038/nmat3191.
[12] Bruce P G, Scrosati B, Tarascon J M. Nanomaterials for rechargeable lithium batteries. Angewandte Chemie International Edition, 2008, 47(16): 2930-2946. DOI: 10.1002/anie.200702505.
[13] Duffner F, Kronemeyer N, Tübke J, et al. Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure. Nature Energy, 2021, 6(2): 123-134. DOI: 10.1038/s41560-020-00748-8.
[14] Adelhelm P, Hartmann P, Bender C L, et al. From lithium to sodium: cell chemistry of room temperature sodium-air and sodium-sulfur batteries. Beilstein Journal of Nanotechnology, 2015, 6(1): 1016-1055. DOI: 10.3762/bjnano.6.105.
[15] Manthiram A, Fu Y, Chung S H, et al. Rechargeable lithium-sulfur batteries. Chemical Reviews, 2014, 114(23): 11751-11787. DOI: 10.1021/cr500062v.
[16] Zheng D, Zhang X, Wang J, et al. Reduction mechanism of sulfur in lithium-sulfur battery: From elemental sulfur to polysulfide. Journal of Power Sources, 2016, 301: 312-316. DOI: 10.1016/j.jpowsour.2015.10.002.
[17] Feng Zhiwei, Fang Xinzuo. Research progress of modified materials for lithium-sulfur battery separators. Shandong Chemical Industry, 2024, 53(13): 134-136+142. DOI: 10.19319/j.cnki.issn.1008-021x.2024.13.049.
[18] Yamin H, Peled E. Electrochemistry of a nonaqueous lithium/sulfur cell. Journal of Power Sources, 1983, 9(3): 281-287. DOI: 10.1016/0378-7753(83)87029-3.
[19] Yin Y X, Xin S, Guo Y G, et al. Lithium-sulfur batteries: electrochemistry, materials, and prospects. Angewandte Chemie International Edition, 2013, 52(50): 13186-13200. DOI: 10.1002/anie.201304762.
[20] Evarts E C. Lithium batteries: To the limits of lithium. Nature, 2015, 526(7575): S93-S95. DOI: 10.1038/526s93a.
[21] Cano Z P, Banham D, Ye S, et al. Batteries and fuel cells for emerging electric vehicle markets. Nature Energy, 2018, 3(4): 279-289. DOI: 10.1038/s41560-018-0108-1.
[22] Schmuch R, Wagner R, Hörpel G, et al. Performance and cost of materials for lithium-based rechargeable automotive batteries. Nature Energy, 2018, 3(4): 267-278. DOI: 10.1038/s41560-018-0107-2.

[23] Ji X, Lee K T, Nazar L F. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. Nature Materials, 2009, 8(6): 500-506. DOI: 10.1038/nmat2460.
[24] Wang N, Zhang X, Ju Z, et al. Thickness-independent scalable high-performance Li-S batteries with high areal sulfur loading via electron-enriched carbon framework. Nature Communications, 2021, 12(1): 4519. DOI: 10.1038/s41467-021-24873-4.
[25] Kim J H, Lee Y H, Cho S J, et al. Nanomat Li-S batteries based on all-fibrous cathode/separator assemblies and reinforced Li metal anodes: towards ultrahigh energy density and flexibility. Energy & Environmental Science, 2019, 12(1): 177-186. DOI: 10.1039/c8ee01879k.
[26] Hou L P, Li Y, Li Z, et al. Electrolyte design for improving mechanical stability of solid electrolyte interphase in lithium-sulfur batteries. Angewandte Chemie International Edition, 2023: e202305466. DOI: 10.1002/anie.202305466.
[27] Elabd A, Kim J, Sethio D, et al. Dual functional high donor electrolytes for lithium-sulfur batteries under lithium nitrate free and lean electrolyte conditions. ACS Energy Letters, 2022, 7(8): 2459-2468. DOI: 10.1021/acsenergylett.2c00874.
[28] Zhao C, Xu G L, Yu Z, et al. A high-energy and long-cycling lithium-sulfur pouch cell via a macroporous catalytic cathode with double-end binding sites. Nature Nanotechnology, 2021, 16(2): 166-173. DOI: 10.1038/s41565-020-00797-w.
[29] Chen Y, Wang T, Tian H, et al. Advances in lithium-sulfur batteries: from academic research to commercial viability. Advanced Materials, 2021, 33(29): 2003666. DOI: 10.1002/adma.202003666.
[30] Choi Y J, Chung Y D, Baek C Y, et al. Effects of carbon coating on the electrochemical properties of sulfur cathode for lithium/sulfur cell. Journal of Power Sources, 2008, 184(2): 548-552. DOI: 10.1016/j.jpowsour.2008.02.053.
[31] Song M K, Cairns E J, Zhang Y. Lithium/sulfur batteries with high specific energy: old challenges and new opportunities. Nanoscale, 2013, 5(6): 2186-2204. DOI: 10.1039/c2nr33044j.
[32] Ng S F, Lau M Y L, Ong W J. Lithium-sulfur battery cathode design: tailoring metal-based nanostructures for robust polysulfide adsorption and catalytic conversion. Advanced Materials, 2021, 33(50): 2008654. DOI: 10.1002/adma.202008654.
[33] Liu G, Sun Q, Li Q, et al. Electrolyte issues in lithium-sulfur batteries: development, prospect, and challenges. Energy & Fuels, 2021, 35(13): 10405-10427. DOI: 10.1021/acs.energyfuels.1c00990.
[34] Zhang J, You C, Lin H, et al. Electrochemical kinetic modulators in lithium-sulfur batteries from defect-rich catalysts to single atomic catalysts. Energy & Environmental Materials, 2022, 5(3) 731-750. DOI: 10.1002/eem2.12250.
[35] Zhang S S. Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions. Journal of Power Sources, 2013, 231: 153-162. DOI: 10.1016/j.jpowsour.2012.12.102.
[36] Wang Q, Zheng J, Walter E, et al. Direct observation of sulfur radicals as reaction media in lithium sulfur batteries. Journal of the Electrochemical Society, 2015, 162(3): A474. DOI: 10.1149/2.0851503jes.
[37] Yin Y X, Xin S, Guo Y G, et al. Lithium-sulfur batteries: electrochemistry, materials, and prospects. Angewandte Chemie International Edition, 2013, 52(50): 13186-13200. DOI: 10.1002/anie.201304762.
[38] Zhu J, Cao J, Cai G, et al. Non-trivial contribution of carbon hybridization in carbon-based substrates to electrocatalytic activities in Li-S batteries. Angewandte Chemie International Edition, 2023, 62(3): e202214351. DOI: 10.1002/anie.202214351.
[39] Jiang Y, Liu S, Gao X, et al. Morphology control of Li2S deposition via geometrical effect of cobalt-edged Nickel Alloy to improve performance of lithium-sulfur batteries. Advanced Functional Materials, 2304965. DOI: 10.1002/adfm.202304965.
[40] Kaiser M R, Chou S, Liu H K, et al. Structure-property relationships of organic electrolytes and their effects on Li/S battery performance. Advanced Materials, 2017, 29(48): 1700449. DOI: 10.1002/adma.201700449.
[41] Ma L, Hendrickson K E, Wei S, et al. Nanomaterials: Science and applications in the lithium-sulfur battery. Nano Today, 2015, 10(3): 315-338. DOI: 10.1016/j.nantod.2015.04.011.
[42] Haldar S, Wang M, Bhauriyal P, et al. Porous dithiine-linked covalent organic framework as a dynamic platform for covalent polysulfide anchoring in lithium-sulfur battery cathodes. Journal of the American Chemical Society, 2022, 144(20): 9101-9112. DOI: 10.1021/jacs.2c02346.
[43] Zhang Y, Guo C, Zhou J, et al. Anisotropic ally hybridized porous crystalline Li-S battery separators. Small, 2023, 19(5): 2206616. DOI: 10.1002/smll.202206616.
[44] Guo W, Han Q, Jiao J, et al. In situ construction of robust biphasic surface layers on lithium metal for lithium-sulfide batteries with long cycle life. Angewandte Chemie International Edition, 2021, 133(13): 7343-7350. DOI: 10.1002/anie.202015049.
[45] Evers S, Nazar L F. New approaches for high energy density lithium-sulfur battery cathodes. Accounts of Chemical Research, 2013, 46(5): 1135-1143. DOI: 10.1021/ar3001348.
[46] Zhang X, Yang Y, Zhou Z. Towards practical lithium-metal anodes. Chemical Society Reviews, 2020, 49(10): 3040-3071. DOI: 10.1039/c9cs00838a.
[47] Cheng X B, Zhang R, Zhao C Z, et al. Toward safe lithium metal anode in rechargeable batteries: a review. Chemical Reviews, 2017, 117(15): 10403-10473. DOI: 10.1021/acs.chemrev.7b00115.

[48] Wu H, Zhuo D, Kong D, et al. Improving battery safety by early detection of internal shorting with a bifunctional separator. Nature Communications, 2014, 5(1): 5193. DOI: 10.1038/ncomms6193.
[49] Liu Y, Lin D, Liang Z, et al. Lithium-coated polymeric matrix as a minimum volume-change and dendrite-free lithium metal anode. Nature Communications, 2016, 7(1): 10992. DOI: 10.1038/ncomms10992.
[50] Ni X, Qian T, Liu X, et al. High lithium-ion conductivity LiF/GO solid electrolyte interphase inhibiting the shuttle of lithium polysulfides in long-life Li-S Batteries. Advanced Functional Materials, 2018, 28(13): 1706513. DOI: 10.1002/adfm.201706513.
[51] Pope M A, Aksay I A. Structural design of cathodes for Li-S batteries. Advanced Energy Materials, 2015, 5(16): 1500124. DOI: 10.1002/aenm.201500124.
[52] Li Z, Li Y, Bi C X, et al. Construction of organic-rich solid electrolyte interphase for long-cycling lithium-sulfur batteries. Advanced Functional Materials, 2023: 2304541. DOI: 10.1002/adfm.202304541.
[53] Cui Y, Liu S, Wang D, et al. A facile way to construct stable and ionic conductive lithium sulfide nanoparticles composed solid electrolyte interphase on Li metal anode. Advanced Functional Materials, 2021, 31(3): 2006380. DOI: 10.1002/adfm.202006380.
[54] Arora P, Zhang Z. Battery separators. Chemical Reviews, 2004, 104(10): 4419-4462. DOI: 10.1021/cr020738u.
[55] Wang J, Yi S, Liu J, et al. Suppressing the shuttle effect and dendrite growth in lithium-sulfur batteries. ACS Nano, 2020, 14(8): 9819-9831. DOI: 10.1021/acsnano.0c02241.
[56] Yao W, Zheng W, Xu J, et al. ZnS-SnS@ NC heterostructure as robust lithiophilicity and sulfiphilicity mediator toward high-rate and long-life lithium-sulfur batteries. ACS Nano, 2021, 15(4): 7114-7130. DOI: 10.1021/acsnano.1c00270. DOI: 10.1021/acsnano.1c00270.
[57] Xu J, An S, Song X, et al. Towards high performance Li-S batteries via sulfonate-rich COF-modified separator. Advanced Materials, 2021, 33(49): 2105178. DOI: 10.1002/adma.202105178.
[58] Yao W, Xu J, Ma L, et al. Recent progress for concurrent realization of shuttle-inhibition and dendrite-free lithium -sulfur batteries. Advanced Materials, 2023: 2212116. DOI: 10.1002/adma.202212116.
[59] Huang J Q, Zhuang T Z, Zhang Q, et al. Permselective graphene oxide membrane for highly stable and anti-self-discharge lithium-sulfur batteries. ACS Nano, 2015, 9(3): 3002-3011. DOI: 10.1021/nn507178a.
[60] Wu X, Zhou C, Dong C, et al. Polydopamine-assisted in-situ formation of dense MOF layer on polyolefin separator for synergistic enhancement of lithium-sulfur battery. Nano Research, 2022, 15(9): 8048-8055. DOI: 10.1007/s12274-022-4423-2.
[61] Yan J, Liu F Q, Gao J, et al. Low-cost regulating lithium deposition behaviors by transition metal oxide coating on separator. Advanced Functional Materials, 2021, 31(16): 2007255. DOI: 10.1002/adfm.202007255.
[62] Zhang Q, Huang Q, Hao S M, et al. Polymers in lithium-sulfur batteries. Advanced Science, 2022, 9(2): 2103798. DOI: 10.1002/advs.202103798.
[63] Fan B, He Q, Wei Q, et al. Anchoring and catalyzing polysulfides by rGO/MoS2/C modified separator in lithium-sulfur batteries. Carbon, 2023: 118361. DOI: 10.1016/j.carbon.2023.118361.
[64] Yu X, Wu H, Koo J H, et al. Tailoring the pore size of a polypropylene separator with a polymer having intrinsic nanoporosity for suppressing the polysulfide shuttle in lithium-sulfur batteries. Advanced Energy Materials, 2020, 10(1): 1902872. DOI: 10.1002/aenm.201902872.
[65] Lagadec M F, Zahn R, Wood V. Characterization and performance evaluation of lithium-ion battery separators. Nature Energy, 2019, 4(1): 16-25. DOI: 10.1038/s41560-018-0295-9.
[66] Zhang X, Yang Y, Zhou Z. Towards practical lithium-metal anodes. Chemical Society Reviews, 2020, 49(10): 3040-3071. DOI: 10.1039/c9cs00838a.
[67] Zhang X, Sahraei E, Wang K. Li-ion battery separators, mechanical integrity and failure mechanisms leading to soft and hard internal shorts. Scientific Reports, 2016, 6(1): 32578. DOI: 10.1038/srep32578.
[68] Dai J, Shi C, Li C, et al. A rational design of separator with substantially enhanced thermal features for lithium-ion batteries by the polydopamine-ceramic composite modification of polyolefin membranes. Energy & Environmental Science, 2016, 9(10): 3252-3261. DOI: 10.1039/c6ee01219a.
[69] Jovanović P, Mirshekarloo M S, Hill M R, et al. Separator design variables and recommended characterization methods for viable lithium-sulfur batteries. Advanced Materials Technologies, 2021, 6(10): 2001136. DOI: 10.1002/admt.202001136.
[70] Tang W, Chen Z, Tian B, et al. In situ observation and electrochemical study of encapsulated sulfur nanoparticles by MoS2 flakes. Journal of the American Chemical Society, 2017, 139(29): 10133-10141. DOI: 10.1021/jacs.7b05371.
[71] Su Y S, Manthiram A. A new approach to improve cycle performance of rechargeable lithium-sulfur batteries by inserting a free-standing MWCNT interlayer. Chemical Communications, 2012, 48(70): 8817-8819. DOI: 10.1039/c2cc33945e.
[72] Zhao Y, Liu M, Lv W, et al. Dense coating of Li4Ti5O12 and graphene mixture on the separator to produce long cycle life of lithium-sulfur battery. Nano Energy, 2016, 30: 1-8. DOI: 10.1016/j.nanoen.2016.09.030.
[73] He J, Chen Y, Manthiram A. Vertical Co9S8 hollow nanowall arrays grown on a Celgard separator as a multifunctional polysulfide barrier for high-performance Li-S batteries. Energy & Environmental Science, 2018, 11(9): 2560-2568. DOI: 10.1039/c8ee00893k.
[74] Guo D, Ming F, Su H, et al. MXene based self-assembled cathode and antifouling separator for high-rate and dendrite-inhibited Li-S battery. Nano Energy, 2019, 61: 478-485. DOI: 10.1016/j.nanoen.2019.05.011.

[75] Imtiaz S, Ali Zafar Z, Razaq R, et al. Electrocatalysis on separator modified by molybdenum trioxide nanobelts for lithium-sulfur batteries. Advanced Materials Interfaces, 2018, 5(15): 1800243. DOI: 10.1002/admi.201800243.
[76] Lai Y, Wang P, Qin F, et al. A carbon nanofiber@mesoporous δ-MnO2 nanosheet-coated separator for high-performance lithium-sulfur batteries. Energy Storage Materials, 2017, 9: 179-187. DOI: 10.1016/j.ensm.2017.07.009.
[77] Li Y, Yan Q, Zhu J, et al. Covalent coupled sulfur-deficient MoS2 nanosheets on carbon nanotubes toward polysulfide catalytic conversion in a lithium sulfur battery. ACS Sustainable Chemistry & Engineering, 2023, 11(3): 1019-1026. DOI: 10.1021/acssuschemeng.2c05699.
[78] Song X, Chen G, Wang S, et al. Self-assembled close-packed MnO2 nanoparticles anchored on a polyethylene separator for lithium-sulfur batteries. ACS Applied Materials & Interfaces, 2018, 10(31): 26274-26282. DOI:10.1021/acsami.8b07663.
[79] Xu J, An S, Song X, et al. Towards high performance Li-S batteries via sulfonate-rich COF-modified separator. Advanced Materials, 2021, 33(49): 2105178. DOI: 10.1002/adma.202105178.
[80] Huang J Q, Zhang Q, Peng H J, et al. Ionic shield for polysulfides towards highly-stable lithium-sulfur batteries. Energy & Environmental Science, 2014, 7(1): 347-353. DOI: 10.1039/c3ee42223b.
[81] Zhang X, Li G, Zhang Y, et al. Amorphizing metal-organic framework towards multifunctional polysulfide barrier for high-performance lithium-sulfur batteries. Nano Energy, 2021, 86: 106094. DOI: 10.1016/j.nanoen.2021.106094.
[82] Shao H, Ai F, Wang W, et al. Crab shell-derived nitrogen-doped micro-/mesoporous carbon as an effective separator coating for high energy lithium-sulfur batteries. Journal of Materials Chemistry A, 2017, 5(37): 19892-19900. DOI: 10.1039/c7ta05192a.
[83] Pei F, Lin L, Fu A, et al. A two-dimensional porous carbon-modified separator for high-energy-density Li-S batteries. Joule, 2018, 2(2): 323-336. DOI: 10.1016/j.joule.2017.12.003.
[84] Ghazi Z A, He X, Khattak A M, et al. MoS2/celgard separator as efficient polysulfide barrier for long-life lithium-sulfur batteries. Advanced Materials, 2017, 29(21): 1606817. DOI: 10.1002/adma.201606817.
[85] Kim A, Oh S H, Adhikari A, et al. Recent advances in modified commercial separators for lithium-sulfur batteries. Journal of Materials Chemistry A, 2023 ,11, 7833-7866. DOI: 10.1039/d2ta09266b.
[86] Wang X, Yang L, Li Q, et al. TiO2@chlorella-based biomass carbon modified separator for high-rate lithium-sulfur batteries. Industrial & Engineering Chemistry Research, 2022, 61(4): 1761-1772. DOI: 10.1021/acs.iecr.1c04510.
[87] Yao H, Yan K, Li W, et al. Improved lithium-sulfur batteries with a conductive coating on the separator to prevent the accumulation of inactive S-related species at the cathode-separator interface. Energy & Environmental Science, 2014, 7(10): 3381-3390. DOI: 10.1039/c4ee01377h.
[88] Liu X, He Q, Liu J, et al. Dual single-atom moieties anchored on N-doped multilayer graphene as a catalytic host for lithium-sulfur batteries. ACS Applied Materials & Interfaces, 2023, 15(7): 9439-9446. DOI: 10.1021/acsami.2c21620.
[89] Ou X, Yu Y, Wu R, et al. Shuttle suppression by polymer-sealed graphene-coated polypropylene separator. ACS Applied Materials & Interfaces, 2018, 10(6): 5534-5542. DOI: 10.1021/acsami.7b17251.
[90] Qi X, Huang L, Luo Y, et al. Ni3Sn2/nitrogen-doped graphene composite with chemisorption and electrocatalysis as advanced separator modifying material for lithium sulfur batteries. Journal of Colloid and Interface Science, 2022, 628: 896-910. DOI: 10.1016/j.jcis.2022.08.031.
[91] Jing E, Chen L, Xu S, et al. Dual redox catalysis of VN/nitrogen-doped graphene nanocomposites for high-performance lithium-sulfur batteries. Journal of Energy Chemistry, 2022, 64: 574-582. DOI: 10.1016/j.jechem.2021.05.015.
[92] Mo Y, Yang K, Lin J, et al. CoSe2 anchored vertical graphene/macroporous carbon nanofibers used as multifunctional interlayers for high-performance lithium-sulfur batteries. Journal of Materials Chemistry A, 2023, 11(12): 6349-6360. DOI: 10.1016/j.cej.2023.144338. DOI:10.1039/d2ta10020g.
[93] Wang H, Xu C, Du X, et al. Ordered porous metal oxide embedded dense carbon network design as high-performance interlayer for stable lithium-sulfur batteries. Chemical Engineering Journal, 2023: 144338. DOI: 10.1016/j.cej.2023.144338.
[94] Yang B, Guo D, Lin P, et al. Hydroxylated multi-walled carbon nanotubes covalently modified with tris (hydroxypropyl) phosphine as a functional interlayer for advanced lithium-sulfur batteries. Angewandte Chemie International Edition, 2022, 61(28): e202204327. DOI: 10.1002/anie.202204327.
[95] Zhao Q, Zhu Q, An Y, et al. A 3D conductive carbon interlayer with ultrahigh adsorption capability for lithium-sulfur batteries. Applied Surface Science, 2018, 440: 770-777. DOI: 10.1016/j.apsusc.2018.01.162.
[96] Maihom T, Kaewruang S, Phattharasupakun N, et al. Lithium bond impact on lithium polysulfide adsorption with functionalized carbon fiber paper interlayers for lithium-sulfur batteries. The Journal of Physical Chemistry C, 2018, 122(13): 7033-7040. DOI: 10.1021/acs.jpcc.7b09392.
[97] Chung S H, Manthiram A. A hierarchical carbonized paper with controllable thickness as a modulable interlayer system for high performance Li-batteries. Chemical Communications, 2014, 50(32): 4184-4187. DOI: 10.1039/c4cc00850b.

[98] Kaewruang S, Chiochan P, Phattharasupakun N, et al. Strong adsorption of lithium polysulfides on ethylenediamine-functionalized carbon fiber paper interlayer providing excellent capacity retention of lithium-sulfur batteries. Carbon, 2017, 123: 492-501. DOI: 10.1016/j.carbon.2017.07.096.
[99] Li J, Dai L, Wang Z, et al. Cellulose nanofiber separator for suppressing shuttle effect and Li dendrite formation in lithium-sulfur batteries. Journal of Energy Chemistry, 2022, 67: 736-744. DOI: 10.1016/j.jechem.2021.11.017.
[100] Park G D, Lee J, Piao Y, et al. Mesoporous graphitic carbon-TiO2 composite microspheres produced by a pilot-scale spray-drying process as an efficient sulfur host material for Li-S batteries. Chemical Engineering Journal, 2018, 335: 600-611. DOI: 10.1016/j.cej.2017.11.021.
[101] Shao H, Wang W, Zhang H, et al. Nano-TiO2 decorated carbon coating on the separator to physically and chemically suppress the shuttle effect for lithium-sulfur battery. Journal of Power Sources, 2018, 378: 537-545. DOI: 10.1016/j.jpowsour.2017.12.067.
[102] Ma G, Huang F, Wen Z, et al. Enhanced performance of lithium sulfur batteries with conductive polymer modified separators. Journal of Materials Chemistry A, 2016, 4(43): 16968-16974. DOI: 10.1039/c6ta07198h.
[103] Li Y, Wang W, Liu X, et al. Engineering stable electrode-separator interfaces with ultrathin conductive polymer layer for high-energy-density Li-S batteries. Energy Storage Materials, 2019, 23: 261-268. DOI: 10.1016/j.ensm.2019.05.005.
[104] Zhang Y, Liu X, Wu L, et al. A flexible, hierarchically porous PANI/MnO2 network with fast channels and an extraordinary chemical process for stable fast-charging lithium–sulfur batteries. Journal of Materials Chemistry A, 2020, 8(5): 2741-2751. DOI: 10.1039/c9ta12135h.
[105] Jo H, Cho Y, Yoo T, et al. Polyaniline-encapsulated hollow Co-Fe Prussian blue analogue nanocubes modified on a polypropylene separator to improve the performance of lithium-sulfur batteries. ACS Applied Materials & Interfaces, 2021, 13(40): 47593-47602. DOI: 10.1021/acsami.1c12855.
[106] Bubnova O, Khan Z U, Malti A, et al. Optimization of the thermoelectric figure of merit in the conducting polymer poly (3, 4-ethylenedioxythiophene). Nature Materials, 2011, 10(6): 429-433. DOI: 10.1038/nmat3012.
[107] Abbas S A, Ibrahem M A, Hu L H, et al. Bifunctional separator as a polysulfide mediator for highly stable Li-S batteries. Journal of Materials Chemistry A, 2016, 4(24): 9661-9669. DOI: 10.1039/c6ta02272c.
[108] Chakraborty G, Park I H, Medishetty R, et al. Two-dimensional metal-organic framework materials: Synthesis, structures, properties and applications. Chemical Reviews, 2021, 121(7): 3751-3891. DOI: 10.1021/acs.chemrev.0c01049.
[109] Bai S, Liu X, Zhu K, et al. Metal-organic framework-based separator for lithium-sulfur batteries. Nature Energy, 2016, 1(7): 1-6. DOI: 10.1038/nenergy.2016.94.
[110] He Y, Chang Z, Wu S, et al. Simultaneously inhibiting lithium dendrites growth and polysulfides shuttle by a flexible MOF-based membrane in Li-S batteries. Advanced Energy Materials, 2018, 8(34): 1802130. DOI: 10.1002/aenm.201802130.
[111] Chang Z, Qiao Y, Wang J, et al. Fabricating better metal-organic frameworks separators for Li-S batteries: Pore sizes effects inspired channel modification strategy. Energy Storage Materials, 2020, 25: 164-171. DOI: 10.1016/j.ensm.2019.10.018.
[112] Yoo J T, Cho S J, Jung G Y, et al. COF-net on CNT-net as a molecularly designed, hierarchical porous chemical trap for polysulfides in lithium-sulfur batteries. Nano Letters, 2016, 16(5): 3292-3300. DOI: 10.1021/acs.nanolett.6b00870.
[113] Yan W, Gao X, Yang J L, et al. Boosting polysulfide catalytic conversion and facilitating Li+ transportation by ion-selective COFs composite nanowire for Li-S batteries. Small, 2022, 18(11): 2106679. DOI: 10.1002/smll.202106679.
[114] Cheng H, Liu H, Jin H, et al. Suppression of polysulfide shuttling with a separator modified using spontaneously polarized bismuth ferrite for high performance lithium-sulfur batteries. Journal of Materials Chemistry A, 2020, 8(32): 16429-16436. DOI: 10.1039/d0ta05181k.
[115] Xiao Z, Yang Z, Wang L, et al. A lightweight TiO2/graphene interlayer, applied as a highly effective polysulfide absorbent for fast, long-life lithium-sulfur batteries. Advanced Materials, 2015, 27(18): 2891-2898. DOI: 10.1002/adma.201405637.
[116] Zhou T, Lv W, Li J, et al. Twinborn TiO2-TiN heterostructures enabling smooth trapping-diffusion-conversion of polysulfides towards ultralong life lithium-sulfur batteries. Energy & Environmental Science, 2017, 10(7): 1694-1703. DOI: 10.1039/c7ee01430a.
[117] Lv X, Lei T, Wang B, et al. An efficient separator with low Li-ion diffusion energy barrier resolving feeble conductivity for practical lithium-sulfur batteries. Advanced Energy Materials, 2019, 9(40): 1901800. DOI: 10.1002/aenm.201901800.
[118] Gong Y, Wang Y, Fang Z, et al. Constructing a catalytic reservoir using cobalt nanoparticles-MoS2@ nitrogen doped carbon nanotubes on the separator to immobilize polysulfides and accelerate their conversion for lithium-sulfur batteries. Chemical Engineering Journal, 2022, 446: 136943. DOI: 10.1016/j.cej.2022.136943.
[119] Liu G, Zeng Q, Sui X, et al. Modulating d-Band electronic structures of molybdenum disulfide via p/n doping to boost polysulfide conversion in lithium-sulfur batteries. Small, 2023: 2301085. DOI: 10.1002/smll.202301085.
[120] Li Y, Lei D, Jiang T, et al. P-doped Co9S8 nanoparticles embedded on 3D spongy carbon-sheets as electrochemical catalyst for lithium-sulfur batteries. Chemical Engineering Journal, 2021, 426: 131798. DOI: 10.1016/j.cej.2021.131798.