

The multifunctional role of transition metal compounds in modification of separators for lithium-sulfur batteries: Applications and recent progress

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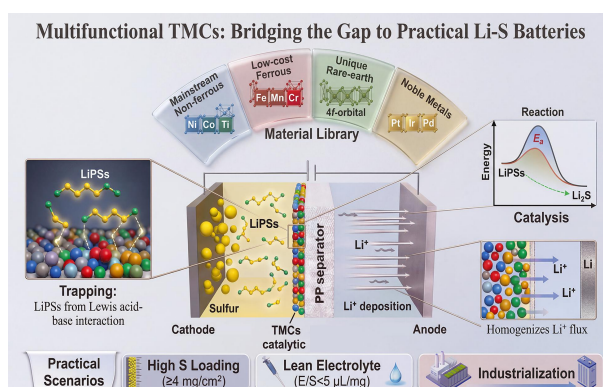
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This review presents a systematic framework for transition metal compound (TMC)-based separator modifications in lithium-sulfur batteries, encompassing non-ferrous, ferrous, rare-earth, and noble metal compounds. It elucidates their multifunctional synergy combining robust chemisorption, accelerated redox catalysis, and interfacial Li-ion flux regulation to effectively suppress the shuttle effect and enable high-performance energy storage.

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ABSTRACT: Lithium-sulfur (Li-S) batteries are widely recognized as promising candidates for high-energy-density storage systems owing to their theoretical specific capacity and energy density, environmental friendliness, and the natural abundance of sulfur. However, their commercialization is hindered by critical challenges, including the lithium polysulfide (LiPSs) shuttle effect, active material loss, sluggish redox kinetics, and uncontrolled lithium dendrite growth. Recently, transition metal compounds (TMCs) have been employed for the functional modification of separators in Li-S batteries, driven by their distinctive electronic structures and superior surface/interface activities. The rational design and application of TMCs as separator modification layers can not only effectively suppress the LiPSs shuttle, enhance sulfur utilization, and accelerate interfacial reaction kinetics, but also modulate lithium deposition behavior, thereby improving the overall capacity and longevity of Li-S batteries. Herein, drawing upon recent literature, this review systematically explores the multifunctional mechanisms, representative material systems, and application performance of various TMCs, ranging from earth-abundant, cost-effective base metals to highly catalytic noble and rare-earth metal compounds. Furthermore, the characteristics, advantages, and limitations of these materials are summarized. Finally, this review delineates the design principles of TMCs for separator modification and provides perspectives on their application prospects in overcoming the core technical bottlenecks of Li-S batteries.

KEYWORDS: lithium-sulfur batteries, transition metal compounds, functionalized separators, lithium polysulfide, catalytic conversion

1 Introduction

The development of high-performance energy storage systems is critical for realizing global carbon peak and neutrality objectives. Electrochemical energy storage technologies have garnered widespread application owing to their efficient energy conversion and storage capabilities[1, 2]. Currently, commercial lithium-ion batteries (LIBs) including those employing lithium iron phosphate, lithium manganese oxide, and ternary lithium cathodes, are extensively deployed across diverse sectors such as grid-scale energy storage and electric vehicles[3-5]. However, driven by the escalating demand for high-energy-density storage devices in wearable electronics, aerospace, electric mobility, military applications, and smart grid systems (Figure 1), the energy density of conventional LIBs is gradually approaching its theoretical limit[6-8]. Consequently, the development of innovative, next-generation energy storage systems has emerged as an urgent technological imperative.

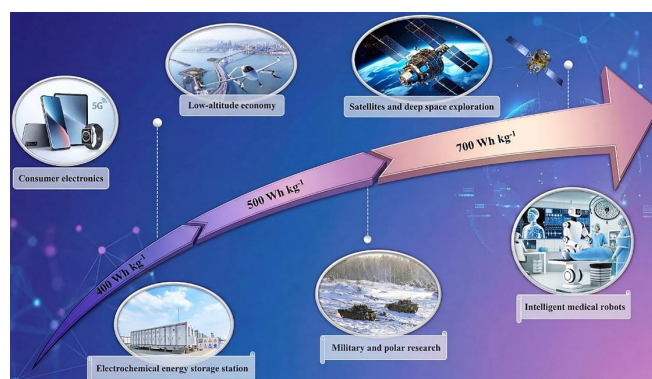


Figure 1 The demand and application fields for high-energy-density electrochemical energy storage systems.

Lithium-sulfur (Li-S) batteries are widely regarded as highly promising candidates for next-generation energy storage technologies, primarily owing to their exceptional electrochemical performance, particularly an ultrahigh theoretical specific capacity (1675 mAh·g⁻¹) and energy

density ($2600 \text{ Wh}\cdot\text{kg}^{-1}$)[9, 10]. In contrast to traditional LIBs, Li-S batteries employ sulfur as the cathode active material, which offers intrinsic advantages such as natural abundance, environmental benignity, and cost-effectiveness[11, 12]. The underlying energy storage mechanism relies on a reversible multi-electron conversion reaction, which not only endows these systems with a significantly higher energy output compared to intercalation-based batteries but also substantially minimizes material costs[13, 14]. Nevertheless, the large-scale commercialization of Li-S batteries remains impeded by a series of critical scientific and technical challenges: (i) the intrinsically poor electronic and ionic conductivity of sulfur and its solid discharge end-products ($\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$), which severely hinders reaction kinetics[15, 16]; (ii) the massive volume fluctuation ($\sim 80\%$) of the sulfur cathode during repeated charge/discharge cycling, which induces structural degradation of the electrode[17]; (iii) the shuttle effect of soluble lithium polysulfide (LiPSs) intermediates across in the electrolyte, which precipitates active material loss, diminished Coulombic efficiency, rapid capacity decay, and limited rate capability[18, 19]; (iv) the uncontrolled proliferation of lithium dendrites on the metal anode, posing severe safety hazards[20]. Furthermore, advancing the practical commercialization of Li-S batteries, requires satisfying stringent electrode and electrolyte parameters namely, a high areal sulfur loading ($> 4 \text{ mg cm}^{-2}$), an elevated sulfur mass fraction ($> 70 \text{ wt}\%$), and a lean electrolyte condition (electrolyte/sulfur (E/S) ratio $< 5 \mu\text{L mg}^{-1}$), while concurrently optimizing the comprehensive electrochemical performance under these rigorous constraints[21-23]. These multifaceted and often competing prerequisites present formidable barriers to the large-scale deployment of Li-S battery.

To address the aforementioned challenges, extensive research efforts have been dedicated to developing the following strategies: (i) designing advanced cathode architectures that integrate physical confinement, chemical adsorption, and catalytic conversion to effectively mitigate the LiPSs shuttle effect[24-26]; (ii) developing novel electrolyte systems (e.g., high-concentration electrolytes[27], room-temperature ionic liquids[28], and solid-state electrolytes[29]) or employing functional additives to restrict LiPSs dissolution, and enhance interfacial stability[30]; (iii) fabricating functional interlayers or modifying separators to improve sulfur utilization and accelerate reaction kinetics[31-33]; (iv) constructing stable artificial solid-electrolyte interphases (SEI) on the lithium metal anode or employing alloying strategies (e.g., Li-Al, Li-Si alloys) to suppress dendrite proliferation and bolster safety[34-37]; (v) optimizing cathode binder systems to preserve electrode structural integrity and maintain continuous electrical contact[38]; (vi) implementing integrated strategies, such as synergistic cathode/electrolyte designs, to achieve the coordinated regulation of multiple interfaces and comprehensively elevate overall electrochemical performance[39].

Among these diverse approaches, separator modification represents a uniquely practical solution due to its multifunctionality and scalability. Fundamentally, it decouples LiPSs confinement from electrode design,

avoiding the introduction of inactive weight into the cathode while allowing simultaneous anode protection via Li-ion flux regulation. Moreover, separator modifications do not introduce severe interfacial resistance, nor do they deplete during prolonged cycling. Furthermore, their seamless compatibility with commercial roll-to-roll fabrication lines renders them a practical strategy for the scalable manufacturing of Li-S batteries[40, 41]. This concept was originally pioneered by Manthiram and co-workers, who first introduced a free-standing microporous carbon paper as a bifunctional interlayer to physically intercept migrating LiPSs and provide an auxiliary conductive network[42]. Building upon this foundational concept, the strategy rapidly evolved towards more integrated and lightweight customized separator coatings to enhance energy density and cycle life[43]. Subsequently, to overcome the saturation limits of simple physical confinement, researchers introduced various polar and active materials into separators to enable strong chemical chemisorption and accelerated redox kinetics[44]. Concurrently, cutting-edge spatial confinement strategies, such as metal-organic framework (MOF)-based separators, were pioneered to achieve precise sub-nanometer ion sieving effectively blocking large LiPSs[45].

Recently, driven by their unique electronic structures, transition metal compounds (TMCs) have emerged as pivotal materials for Li-S batteries, exhibiting robust LiPSs anchoring capabilities coupled with exceptional catalytic activities. Such catalytic proficiency significantly accelerates the kinetic conversion of soluble long-chain LiPSs into insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, thereby enhancing the overall redox kinetics and reaction efficiency of the Li-S batteries[46-48]. Furthermore, the application of an ultrathin TMCs-based modification layer on the separator effectively minimizes the mass and volume fraction of inactive components. This architectural optimization leads to a substantial improvement in both gravimetric and volumetric energy densities, ensuring superior comprehensive performance even under the rigorous constraints of high sulfur loading and lean electrolytes[49]. Consequently, modifying separators with TMCs is widely regarded as a highly viable and promising strategy to expedite the practical implementation of Li-S batteries.

To systematically navigate this expansive and complex material library, this review categorizes TMCs into four distinct groups by integrating industrial classification standards with their intrinsic electronic properties: mainstream non-ferrous metal compounds (e.g., Co, Ni, and Ti), low-cost ferrous metal compounds (e.g., Fe, Mn, and Cr), rare-earth metal compounds, and noble metal compounds (Figure 2). Notably, although rare-earth and noble metal compounds inherently fall under the broad metallurgical classification of non-ferrous metal compounds [50-52], they are deliberately delineated as independent categories in this review. This structural separation accounts for the unique 4f-orbital-driven catalytic paradigms characteristic of rare-earth elements, as well as the juxtaposition of benchmark catalytic activities and prohibitive costs intrinsic to noble metals. Through this multidimensional framework, this review aims to comprehensively elucidate the structure-

property relationships of diverse metal systems within Li-S

Figure 2 shows a periodic table where elements are color-coded based on their classification. The legend indicates: Ferrous metals (red), Non-ferrous metals (blue), Rare-earth metals (green), and Noble metals (yellow). The table includes elements from H to Uub, with the lanthanide and actinide series shown separately at the bottom.

batteries, thereby providing pragmatic guidance and strategic insights for their future industrialization.

Figure 2 Classification map of metal elements in the periodic table, highlighting the four distinct categories discussed in this review. Based on a combination of industrial classification standards and electronic configurations, the elements are strategically grouped into: Ferrous metals (red); Rare-earth metals (green); Noble metals (yellow); and Non-ferrous metals (blue).

In light of the rapid advancements in Li-S battery technologies, this review systematically summarizes recent progress in separator modification strategies based on TMCs, with a particular emphasis on synthesis methodologies, electrochemical performance optimization, and underlying physicochemical mechanisms. The primary objective is to offer robust theoretical guidance for the design of high-performance separator materials, thereby facilitating their practical application. As illustrated in Figure 3, this review encompasses a broad spectrum of TMCs-based materials and comprehensively examines the mechanisms by which they suppress LiPSs shuttle, catalyze sulfur conversion reactions, and enhance interfacial stability. Furthermore, critical challenges associated with current separator modification materials are highlighted, and future development paths are delineated to accelerate the commercialization of high-performance Li-S batteries.

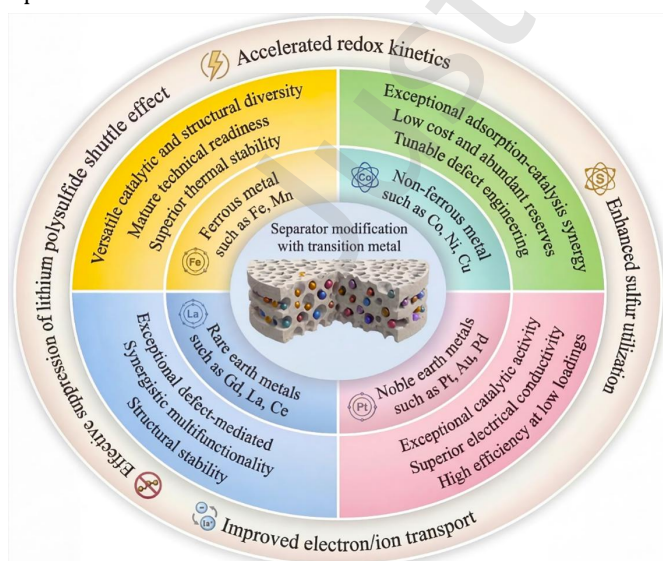


Figure 3 Various TMCs employed in modifying separators for Li-S batteries.

2 The role of TMCs in separator modification for Li-S batteries

Renowned as the vitamins of modern industry, TMCs are extensively utilized across a diverse array of fields

including energy storage and conversion, heterogeneous catalysis, environmental remediation, and electronic/magnetic materials to activate reactant molecules and substantially lower activation energy barriers[53-55]. In the context of Li-S batteries, the introduction of TMCs can effectively mitigate the LiPSs shuttle effect, accelerate the multiphase conversion kinetics of sulfur species, and improve the electronic and ionic conductivities of the reaction interfaces. Synergistically, these effects comprehensively elevate the overall electrochemical performance of the battery[56]. Accordingly, this section systematically delineates the multifunctional roles of various TMCs in the modification of separators for high-performance Li-S batteries.

2.1 LiPSs confinement and trapping

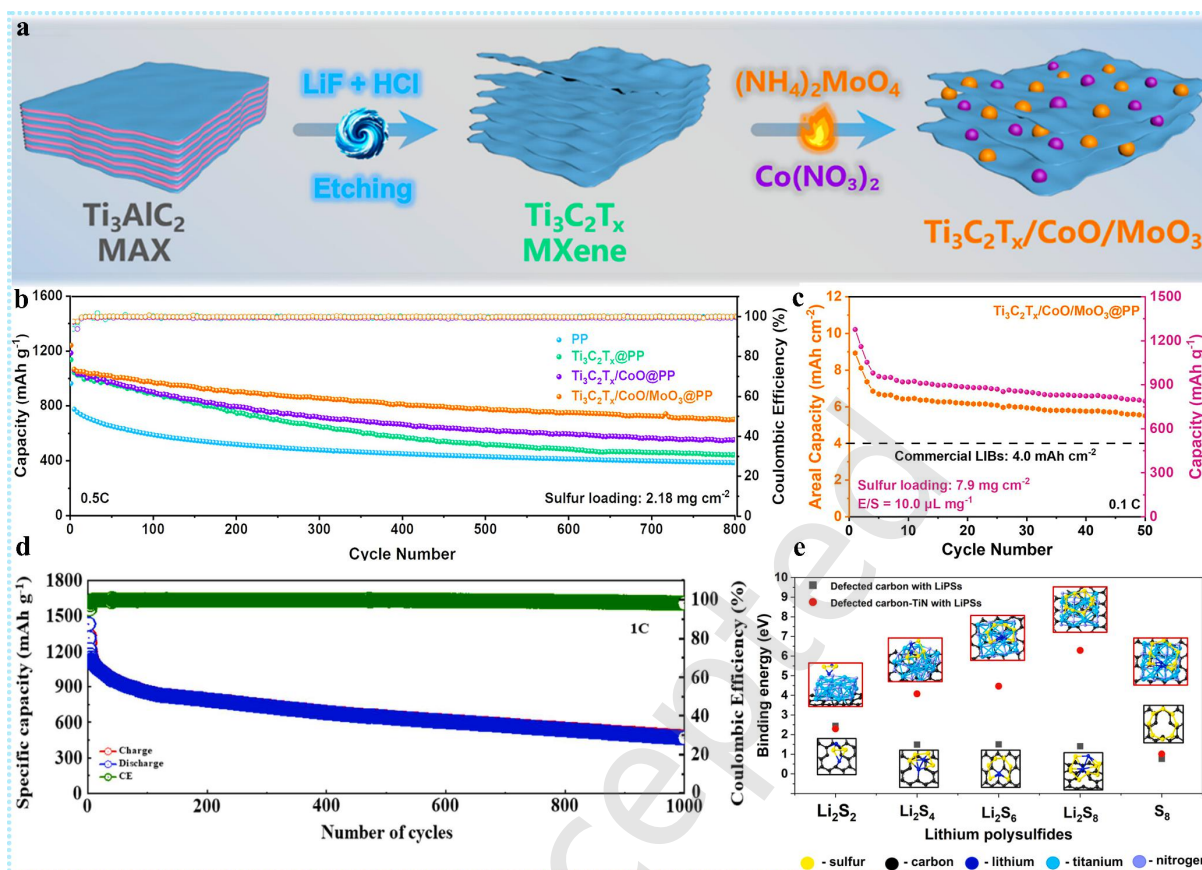
During the discharge process, the sulfur cathode generates long-chain LiPSs that are highly soluble in conventional ether-based electrolytes. Driven by concentration gradients and the internal electric field, these soluble intermediate species migrate continuously between the cathode and the anode. This shuttling effect precipitates irreversible active material loss, continuous corrosion of the lithium metal anode, and accelerated electrolyte depletion, ultimately resulting in severely truncated cycle life of Li-S batteries[57, 58]. The integration of a TMCs-based modification layer onto the separator establishes a robust functional barrier. This barrier leverages the intrinsic polarity and abundant active sites of the TMCs to synergistically achieve the physical confinement and chemical entrapment of LiPSs, thereby effectively mitigating the shuttle phenomenon.

For example, Fan et al. designed a composite separator coating comprising a multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene a support decorated with transition metal oxide nanoparticles (CoO and MoO_3), denoted as $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{MoO}_3$ [59]. Within this architecture, the lamellar $\text{Ti}_3\text{C}_2\text{T}_x$ functions as an intricate physical shield to impede LiPSs migration, while the highly polar CoO and MoO_3 nanoparticles further enhance the anchoring efficacy via robust chemisorption (Figure 4(a)). When applied to a commercial polypropylene (PP) separator, this functionalized layer significantly inhibited LiPSs shuttling and enhanced the cycling stability of the Li-S battery. As illustrated in Figure 4(b), the Li-S battery assembled with the $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{MoO}_3/\text{PP}$ separator demonstrated a low capacity decay rate of 0.042% per cycle after 800 cycles at 0.5 C. Moreover, even under stringent conditions of high areal sulfur loading (7.9 mg cm^{-2}) and a lean electrolyte ratio ($E/S = 10 \text{ } \mu\text{L mg}^{-1}$), the Li-S battery delivered an impressive areal capacity of 6.85 mAh cm^{-2} , demonstrating excellent potential for practical applications (Figure 4(c)).

Similarly, Sultanov et al. proposed a synergistic strategy combining physical confinement and chemical anchoring to effectively suppress LiPSs migration[60]. They fabricated a composite separator coating (GPC-TiN) integrating biomass-derived TiN nanoparticles with highly porous graphene-like carbon (GPC). The resulting GPC-TiN modified separator bolstered the rate capability, cycling stability, and capacity retention of the Li-S batteries (Figure 4(d)). Subsequent density functional theory (DFT) calculations revealed that

the binding energy between the GPC-TiN composite and LiPSs is higher than that of pristine carbon materials. This

composite, thereby providing rigorous mechanistic insight into the observed improvements in electrochemical



confirms the enhanced chemical adsorption capability of the

Figure 4 (a) Illustration of $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{MoO}_3$ composite preparation. (b) Cycling performance of PP, $\text{Ti}_3\text{C}_2\text{T}_x/\text{PP}$, $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{PP}$ and $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{MoO}_3/\text{PP}$ at 0.5 C. (c) Cycling performance of $\text{Ti}_3\text{C}_2\text{T}_x/\text{CoO}/\text{MoO}_3/\text{PP}$ with a sulfur loading of 7.9 mg cm^{-2} at 0.1 C [59]. (d) Cycling performance at 1.0 C of the batteries with GPC@S cathode and GPC-TiN-10 modified separator. (e) DFT-calculated binding energies of sulfur species on the carbon and carbon-TiN composite. Reproduced with permission [60]. Copyright 2025, Elsevier.

2.2 Accelerating sulfur conversion kinetics

While robust adsorption is essential for trapping LiPSs, relying exclusively on adsorption to suppress the shuttle effect is fundamentally insufficient [61]. The redox electrochemistry of Li-S batteries is inherently constrained by inadequate electronic conductivity and the sluggish kinetics associated with its complex multiphase transitions [62, 63]. The absence of rapid subsequent conversion dictates the severe interfacial agglomeration of confined LiPSs. This stagnation precipitates rapid active-site passivation and severe electrochemical polarization, while simultaneously sustaining a high local concentration of LiPSs that aggravates the shuttling phenomenon [64, 65]. Consequently, coupling robust adsorption with accelerated electrocatalytic conversion to dissipate the concentration gradient emerges as a crucial strategy for mitigating the LiPSs shuttle effect. Benefiting from TMCs unique electronic configurations, particularly the presence of unfilled d -orbitals, their function not just as passive trapping sites but as highly active electrocatalytic promoters. By propelling the sluggish bidirectional sulfur redox kinetics, TMCs facilitate the sustained and highly reversible operation of the sulfur cathode.

For instance, Ma et al. designed a bifunctional separator coating (SSZ-13/ ZnS/PP) comprising an SSZ-13 zeolite base layer and a ZnS surface layer (Figure 5(a)), capitalizing on

performance of Li-S batteries (Figure 4(e)).

the highly ordered nanoporous structure of the SSZ-13 zeolite and alongside the pronounced electronegativity and superior thiophilicity of ZnS [66]. Through a synergistic mechanism integrating physical confinement, chemical adsorption, and catalytic conversion, this modified separator effectively intercepts the LiPSs shuttle and accelerates the overall electrochemical reaction kinetics. Consequently, the assembled Li-S battery delivers exceptional cycling stability and rate performance even under the stringent conditions of high sulfur loading and lean electrolyte formulations (Figure 5(b-d)). Similarly, through sequential hydrothermal synthesis, ion exchange, and sulfurization processes (Figure 5(e)), Song et al. successfully engineered an island-like p-n heterojunction composite consisting of FeS_2 nanoparticles and TiO_2 nanobelts ($\text{FeS}_2/\text{TiO}_2$). This functional material was employed for separator modification to facilitate the highly efficient trapping and catalytic conversion of LiPSs [67]. Within this tailored heterostructure, TiO_2 provides robust adsorption sites that effectively arrest LiPSs migration, whereas FeS_2 functions as a highly active electrocatalytic center that significantly accelerates LiPSs conversion kinetics (Figure 5(f)). As depicted in Figure 5(g-j), experimental and theoretical calculations corroborate that Li-S batteries utilizing the $\text{FeS}_2/\text{TiO}_2$ -modified separator achieve outstanding electrochemical performance.

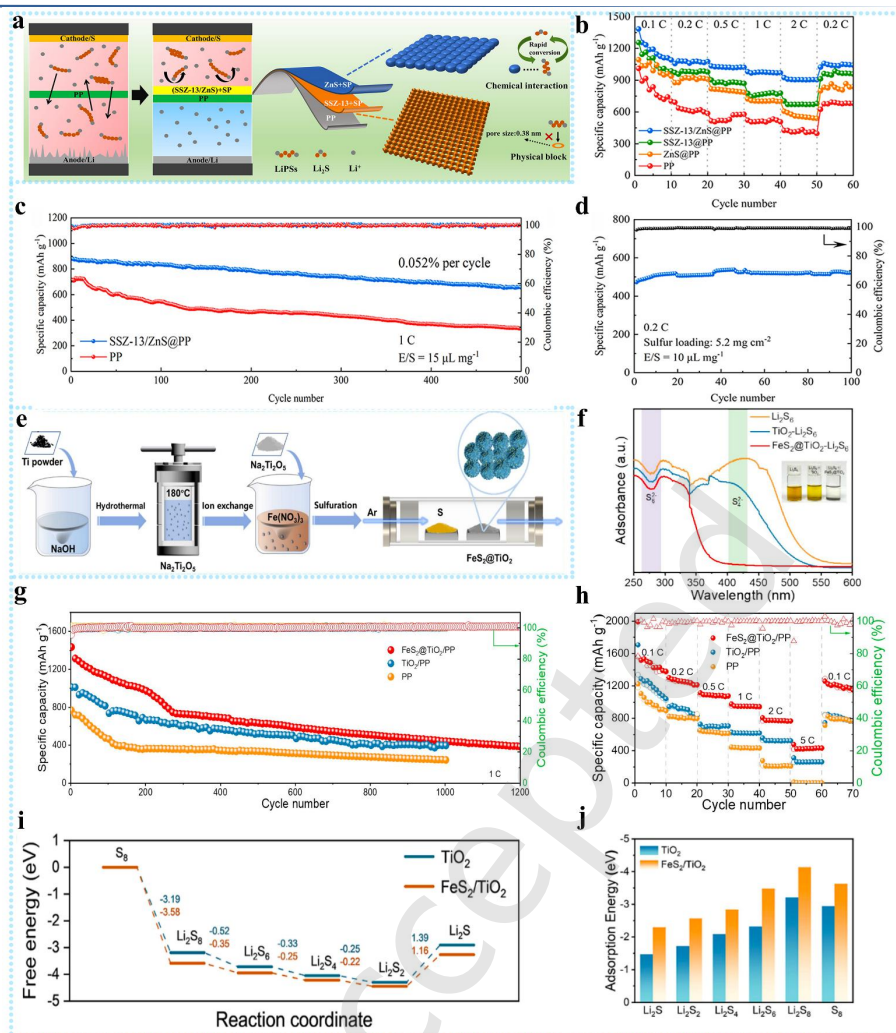


Figure 5 (a) Structure and function illustration of the SSZ-13/ZnS modified separator. (b) The rate performance of the Li-S batteries. (c) Long-term cycling performance of the Li-S batteries at 1.0 C. (d) Cycle performance of the Li-S battery with SSZ-13/ZnS@PP separator at high sulfur loading at 0.2 C[66]. (e) Schematic depiction of the synthesis of $\text{FeS}_2@\text{TiO}_2$. (f) The UV-vis absorbance curves of Li_2S_6 adsorption test following a 10 h adsorption by different samples. (g) Cycling performance at 1.0 C for batteries with $\text{FeS}_2@\text{TiO}_2/\text{PP}$, TiO_2/PP and PP separators. (h) Rate performance for batteries with $\text{FeS}_2@\text{TiO}_2/\text{PP}$, TiO_2/PP and PP separator. (i) Gibbs free energy profiles for the reduction of S_8 to Li_2S on the surface of TiO_2 and $\text{FeS}_2/\text{TiO}_2$. (j) The adsorption energies of the LiPSs and S_8 cluster with the TiO_2 and $\text{FeS}_2/\text{TiO}_2$ heterojunction. Reproduced with permission[67]. Copyright 2025, Elsevier.

Additionally, by virtue of their intrinsic electronic conductivity, certain TMCs are capable of constructing continuous electron pathways, thereby lowering interfacial impedance and accelerating the catalytic conversion processes. Feng et al. utilized defect-rich MnO_2 (D- MnO_2) as a functional separator coating, leveraging its intrinsic polarity to achieve the highly efficient adsorption of LiPSs[68]. Simultaneously, the MnO_2 matrix serves as a potent redox mediator to catalyze the rapid conversion of LiPSs. Notably, the integration of oxygen vacancies substantially enhances the intrinsic electrical conductivity of the material, synergistically boosting both electrode reaction kinetics and sulfur utilization efficiency. As a result, the Li-S battery incorporating the D- MnO_2 -modified separator exhibited exceptional rate capability, delivering an initial specific capacity of $1074 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C, retaining 55% of this capacity after 500 cycles, and maintaining a low capacity decay rate of 0.089% per cycle.

2.3 Lithium anode protection

Beyond mitigating LiPSs shuttling, the uncontrolled proliferation of lithium dendrites at the anode presents

another formidable barrier to the commercial viability of Li-S batteries. The spatially non-uniform Li^+ flux across conventional porous separators exacerbates local current density fluctuations, ultimately triggering dendritic growth, internal short circuits, and severe safety hazards. The separator modification strategies employing TMCs can regulate Li^+ flux distribution and homogenize the local electric field. This effectively induces uniform lithium deposition and suppresses dendrite proliferation[69, 70]. Furthermore, the enhanced mechanical integrity and improved electrolyte wettability of the functional modification layer contribute to the superior thermal stability and operational safety of the Li-S battery[71, 72].

Deng et al. constructed a binder-free, $\text{SnO}_2@\text{MXene}$ heterojunction-based functional separator coating with a thickness of merely several hundred nanometers, leveraging the laminated architecture of stacked two-dimensional MXene nanosheets[73]. This tailored heterostructure exhibits both strong chemical adsorption capabilities and high catalytic activity toward LiPSs (Figure 6(a)). The integration of this modification layer onto the separator

enables multiple synergistic effects, including the effective suppression of LiPSs shuttling, accelerated sulfur conversion kinetics at the cathode, and the induction of uniform lithium deposition at the anode (Figure 6(b) and 6(c)). Leveraging these synergistic advantages, the Li-S batteries equipped with the SnO_2 @MXene-modified separator demonstrated enhanced sulfur utilization, superior rate performance, reduced internal resistance, and significantly improved capacity retention over prolonged cycling (Figure 6(d)).

Similarly, Xie et al. engineered a two-dimensional nanosheet-like trimetallic metal-organic framework (2DT-MOF) derived from an Fe-doped NiCo-MOF precursor. This structure was subsequently hybridized with aminated carbon nanotubes (CNT-NH₂) to formulate a functional modification coating (FMC) for Li-S battery separators[74]. The resultant FMC not only facilitates the efficient chemisorption and rapid catalytic conversion of LiPSs but

also provides highly ordered sub-nanometer channels that selectively sieve and homogenize the Li^+ flux, suppressing dendrite formation (Figure 6(e) and 6(f)). Consequently, the Li-S battery equipped with the FMC@PP separator delivered an initial discharge capacity of 948 $\text{mAh}\cdot\text{g}^{-1}$ at 1.0 C, representing a 50% enhancement over the PP separator. After 1500 cycles, it maintained a reversible specific capacity of 649 $\text{mAh}\cdot\text{g}^{-1}$, demonstrating exceptional long-term cycling stability (Figure 6(h)). Even under the rigorous conditions of high areal sulfur loading (6.32 mg cm^{-2}) and a lean electrolyte formulation ($\text{E/S} = 10 \text{ }\mu\text{L mg}^{-1}$), the Li-S battery delivered an impressive initial specific capacity of 1300 mAh g^{-1} at 0.1 C (Figure 6(g)). These findings validate the robust electrochemical reliability of the FMC@PP modified separator under practically relevant parameters, underscoring its immense potential for commercialization.

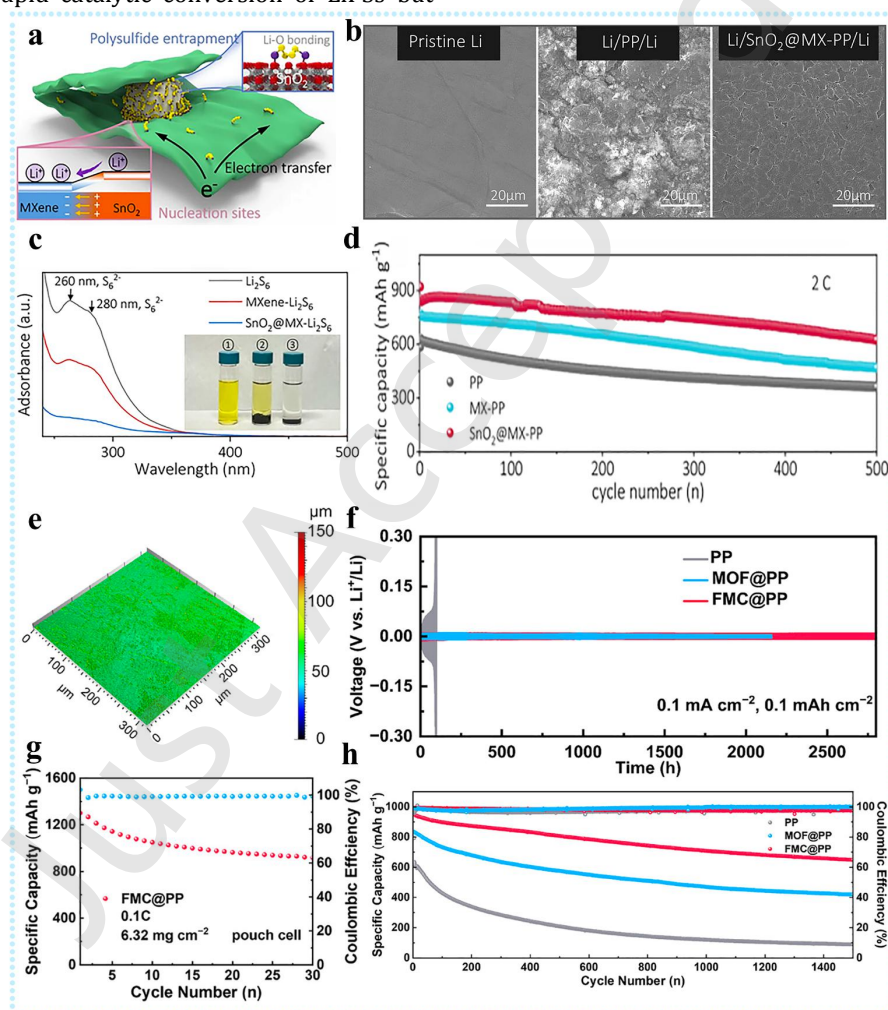


Figure 6 (a) Illustration of the efficient LiPSs adsorption and catalytic conversion process in SnO_2 @MX heterostructure. (b) SEM of pristine Li and Li electrode surface with various separators after 400 cycles. (c) UV-vis spectra of Li_2S_6 after adsorption by MXene and SnO_2 @MX powder for 24 h. (d) Cyclic performances of Li-S batteries with various separators at 2.0 C[73]. (e) 3D LSCM images of cycled Li metal anode with symmetric lithium cells using FMC@PP. (f) Cycle stability of the Li||Li symmetric batteries based on different membrane at a current density of 0.1 mA cm^{-2} with an areal capacity of 0.1 mAh cm^{-2} . (g) Cycling performance of pouch battery at 0.1 C. (h) Long-life cycling tests of different separator-based Li-S batteries at 1 C[74]. Copyright 2025, Wiley.

3 Diverse TMCs for separator modification: mechanisms and progress

TMCs are fundamentally characterized by their high melting and boiling points, exceptional mechanical hardness, and high density, coupled with excellent ductility, electrical

conductivity, and thermal conductivity. More importantly, owing to their partially filled *d*-orbital valence electron shells, TMCs can donate multiple valence electrons for chemical bonding, thereby manifesting a rich array of variable oxidation states[75]. In recent years, polar TMCs

encompassing pure metals, oxides, sulfides, nitrides, and carbides have garnered intensive research interest across the domains of electrochemical energy storage (e.g., lithium-ion batteries, supercapacitors) and electrocatalysis (e.g., oxygen evolution, hydrogen evolution, and oxygen reduction reactions)[76-79]. Accordingly, this section systematically reviews the application of polar TMCs including non-ferrous, ferrous, rare-earth, and noble metal compounds as functional separator modification layers in Li-S batteries. The discussion primarily centers on their LiPSs anchoring efficacy, the modulation of multiphase sulfur conversion kinetics, and the corresponding strategies for optimizing the cycling stability and rate performance of Li-S batteries.

3.1 Non-ferrous metal compounds

Non-ferrous metal compounds (incorporating elements such as Ti, Co, Ni, Cu, Zn, V, Mo, and W) have emerged as pivotal materials for mitigating the LiPSs shuttle effect and accelerating sulfur conversion kinetics, primarily owing to their exceptional electrocatalytic activities and highly tunable electronic structures[80, 81]. A diverse array of these materials encompassing oxides, sulfides, selenides, nitrides, carbides, and phosphides, as well as single-atom catalysts, nanoparticles, and alloyed architectures has been extensively utilized for separator modification to improve the overall electrochemical performance of Li-S batteries[82, 83]. Given that non-ferrous metal compounds represent the most comprehensively investigated and structurally diverse category of materials in this domain, and recognizing that their electrochemical efficacies are profoundly governed by their specific anionic coordination environments (e.g., O, S, N, C, and P), this section provides a systematic discussion categorized by their respective compound classes.

(1) Non-ferrous metal oxides

Non-ferrous metal oxides offer three fundamental advantages for application in Li-S batteries. First, their highly polar surfaces facilitate the robust chemisorption of LiPSs, significantly mitigating the shuttle effect[84]. Second, their inherent electrocatalytic activity accelerates the multiphase conversion of LiPSs[85]. Third, compared with precious metal-based materials, these compounds are abundant and cost-effective, rendering them highly viable for large-scale practical deployment. Nonetheless, the intrinsically low electrical conductivity of non-ferrous metal oxides critically impedes rapid electron transport, resulting in sluggish electrode reaction kinetics and elevated internal battery resistance. To circumvent this fundamental limitation, researchers conventionally hybridize these metal oxides with highly conductive carbonaceous scaffolds (e.g., graphene, carbon nanotubes, or acetylene black) to construct continuous three-dimensional conductive

networks. This strategy markedly improves charge transfer pathways and comprehensively enhances the overall electrochemical performance[86, 87]. For instance, Zhou et al. successfully synthesized a nitrogen-doped mesoporous carbon-supported defect-rich titanium dioxide composite ($\text{TiO}_{2-x}\text{@NMC}$) via an in-situ growth strategy (Figure 7(a)), which was subsequently employed as a functional separator coating for Li-S batteries[88]. The $\text{TiO}_{2-x}\text{@NMC}$ modification layer featuring defective nano-catalytic units anchored within a mesoporous carbon matrix demonstrates superior LiPSs adsorption capability coupled with highly efficient catalytic conversion activity (Figure 7(b)). Concurrently, its high specific surface area substantially improves the electrolyte wettability of the separator, effectively minimizing interfacial resistance and promoting Li^+ transport kinetics, thereby curtailing the deleterious self-discharge. As shown in Figure 7(c) and 7(d), the Li-S battery equipped with this modified separator exhibited exceptional cycling stability, demonstrating a capacity decay rate of 0.067% per cycle over 500 cycles at 2.0 C.

In an alternative approach, Yang et al. successfully synthesized two-dimensional nitrogen-doped vanadium dioxide (SVO) nanosheets via the controlled calcination of a vanadium-based zeolitic imidazolate framework (V-ZIF) precursor. This SVO was subsequently hybridized with acetylene black (AB) to serve as a functional separator modification layer in Li-S batteries[89]. Cyclic voltammetry (CV) assessments revealed that compared to batteries employing only AB or a pristine PP separator, the Li-S battery equipped with the SVO/AB-modified separator exhibited the lowest electrochemical polarization and highest peak currents, thereby corroborating significantly enhanced interfacial reaction kinetics for LiPSs conversion. Meanwhile, the SVO/AB coating functions as an auxiliary current collector to facilitate rapid electron transport. Capitalizing on its two-dimensional architecture and homogeneously distributed metallic active sites, the SVO layer effectively anchors LiPSs via a robust adsorption-catalysis synergy, substantially mitigating the shuttle effect. As shown in Figure 7(f), the Li-S battery utilizing the SVO/AB modified separator demonstrated an exceptionally low capacity decay rate of 0.081% per cycle over 500 cycles at 1.0 C. Notably, even under the rigorous constraints of high areal sulfur loading (6.3 mg cm^{-2}) and lean electrolyte conditions ($E/S = 5 \text{ } \mu\text{L mg}^{-1}$), the battery delivered an impressive areal capacity of 4.16 mAh cm^{-2} , underscoring its profound potential for practical commercial deployment (Figure 7(e)).

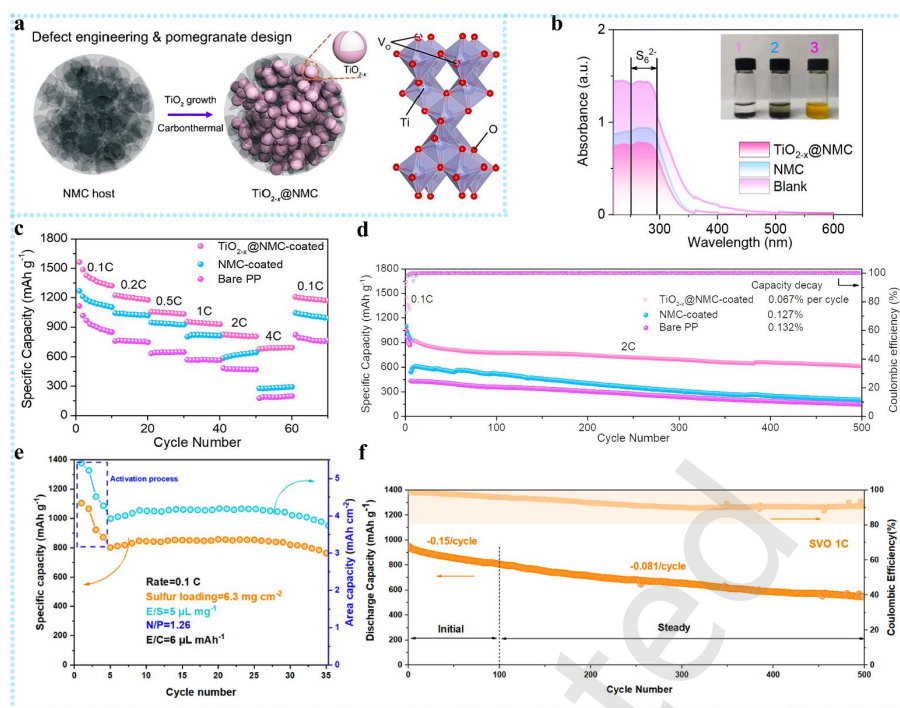


Figure 7 (a) Schematics of the fabrication process of TiO_{2-x}@NMC composite. (b) UV-vis spectra of treated Li₂S₆ solution supernatants. Inset shows the photograph of Li₂S₆ solutions after adsorption. (c) Rate performance of the Li-S batteries with different separators, respectively. (d) Cycling performance of the batteries with different separators at 2.0 C. Reproduced with permission[88]. Copyright 2024, Elsevier. (e) Cycle performance of the Li-S batteries with SVO/AB separator under harsh conditions. (f) Cycling performance of Li-S battery with SVO/AB separator at 1.0 C. Reproduced with permission[89]. Copyright 2021, Elsevier.

(2) Non-ferrous metal sulfides

Benefiting from their exceptional electrocatalytic activities and strong chemical adsorption capacities, non-ferrous metal sulfides can effectively catalyze the multiphase conversion of LiPSs and suppress the shuttle effect in Li-S batteries[90, 91]. Simultaneously, their intrinsic electrical conductivity is superior to that of their oxide counterparts, facilitating more efficient charge transfer kinetics and accelerating redox reactions[90-92]. As demonstrated in Figure 8(a), Fan et al. designed a multifunctional transition metal sulfide composite characterized by high adsorption capacity and catalytic activity to anchor LiPSs and accelerate their conversion kinetics[72]. By systematically integrating amorphous carbon and MoS₂ onto graphene oxide nanosheets, the researchers engineered a unique rGO/MoS₂/C composite as a functional separator modification layer to comprehensively mitigate LiPSs shuttling (Figure 8(b)). The rGO/MoS₂/C architecture provides abundant LiPSs adsorption sites owing to its superior electrolyte wettability and high specific surface area. Meanwhile, the highly active sites on the MoS₂ basal and edge surfaces strongly bind and catalyze the conversion of LiPSs, systematically preempting their cross-electrolyte migration toward the anode. Consequently, the Li-S battery incorporating this modified separator exhibited outstanding electrochemical performance and cycling stability (Figure 8(c-e)), achieving a remarkably low capacity decay rate

of merely 0.022% per cycle after 1000 cycles at a high rate of 2.0 C.

Furthermore, integrating transition metal sulfides into carbonaceous matrices to construct functional separator coatings can synergistically leverage the high conductivity of the carbon scaffold alongside the superior electrocatalytic properties of the sulfides, collectively enhancing the overall electrochemical performance of Li-S batteries. For instance, Chen et al. synthesized a CoS@NC/NCNT composite for separator modification by embedding in-situ grown CoS nanoparticles into polypyrrole-derived N-doped carbon nanotubes via a sequential strategy encompassing oxidative polymerization, surface modification, and chemical vapor deposition sulfurization[93]. The unique three-dimensional structure of this composite facilitates the formation of a highly robust conductive network. When deployed as a separator coating, it ensures the homogenous distribution of active catalytic sites, prevents their aggregation, significantly suppresses the LiPSs shuttle effect, and dramatically enhances interfacial charge transfer kinetics (Figure 8(f)). As demonstrated in Figure 8(g), the Li-S battery utilizing the CoS@NC/NCNT-modified separator achieved a formidable initial specific capacity of 1537 mAh g⁻¹ at 0.1 C, underscoring its exceptional electrochemical efficacy.

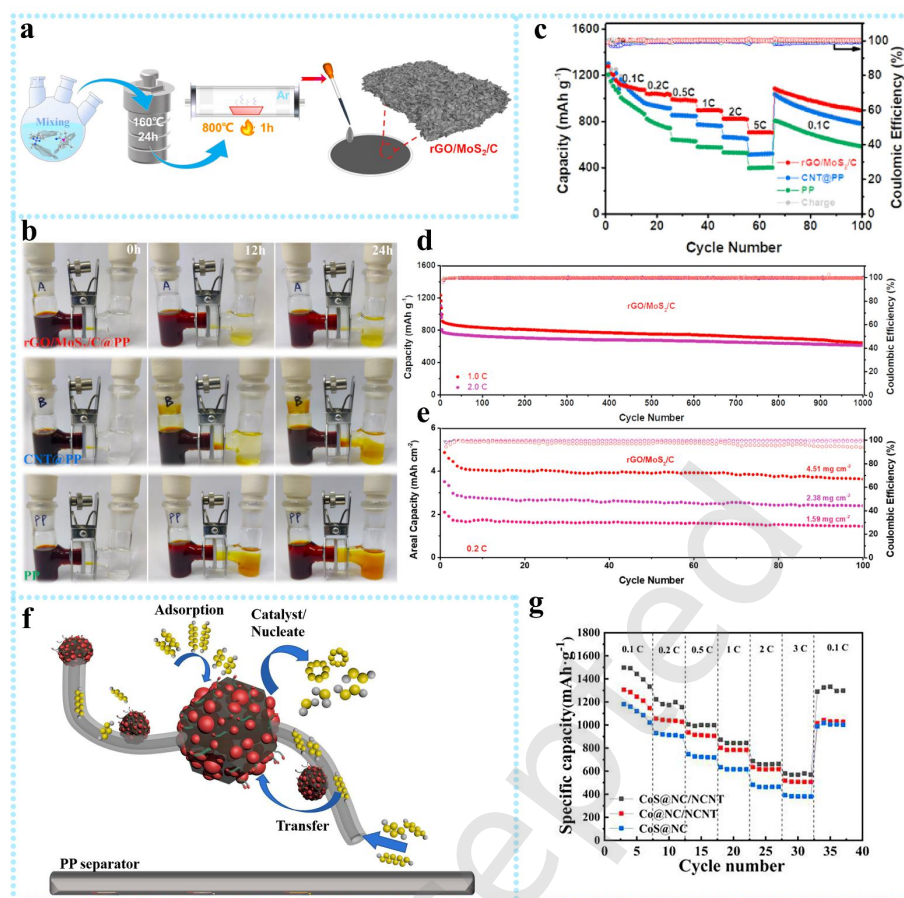


Figure 8 (a) Illustration of the synthesis process of rGO/MoS₂/C@PP separator. (b) Optical images of H-type batteries of different separator are used to isolate LiPSs electrolyte. (c) Rate performance of Li-S batteries with different separators. (d) Cycling performance of the Li-S batteries with rGO/MoS₂/C@PP separator at 1.0 and 2.0 C. (e) Specific areal capacities of the Li-S batteries with rGO/MoS₂/C@PP separator and different sulfur loadings at 0.2 C. Reproduced with permission[72]. Copyright 2023, Elsevier. (f) Mechanism demonstration for reducing shuttle of LiPSs by CoS@NC/NCNT separator. (g) Rate capability of Li-S batteries with different separators. Reproduced with permission[93]. Copyright 2025, Elsevier.

(3) Non-ferrous metal selenides

Non-ferrous metal selenides (e.g., MoSe₂, WSe₂, and CoSe₂) represent highly promising candidates for functional separator modification in Li-S batteries. These materials feature a synergistic combination of unique layered structure, superior electronic conductivity, and abundant intrinsic catalytically active sites, which collectively facilitate the highly efficient chemisorption of LiPSs and the acceleration of sulfur conversion kinetics[94, 95]. Compared to their oxide and sulfide counterparts, non-ferrous metal selenides generally exhibit enhanced electrical conductivity, optimized metal-selenium bond energetics, and more pronounced electrocatalytic activity, thereby establishing a robust physicochemical foundation for the development of high-efficiency Li-S batteries[96]. For instance, to simultaneously mitigate the LiPSs shuttle effect and overcome sluggish multiphase conversion kinetic, Zhang et al. engineered a zinc selenide/carbon (ZnSe/C) composite as a functional separator coating[97]. Comprehensive experimental evaluations revealed that the ZnSe/C matrix not only curtails shuttling via the robust entrapment of LiPSs but also systematically accelerates bidirectional redox kinetics throughout the charge and discharge processes. Consequently, Li-S batteries equipped with the ZnSe/C-modified PP separator demonstrated exceptional electrochemical performance, delivering a formidable initial specific discharge capacity of 1458 mAh g⁻¹ at 0.1 C and maintaining a robust rate capability of 605 mAh g⁻¹ at 5.0 C. Furthermore, the Li-S battery exhibited remarkable long-

term operational stability, retaining a reversible specific capacity of 608 mAh g⁻¹ after 1000 cycles at 1.0 C, which corresponds to an ultra-low average capacity decay rate of merely 0.04% per cycle.

To synergistically resolve the bottlenecks of LiPSs shuttling and sluggish reaction kinetics in Li-S batteries, Li et al. constructed a multifunctional separator modification material (PMo12/CoSe₂@NC/CNTs) that integrates highly catalytically active polyoxometalate (POM) nanoclusters with strongly polar cobalt selenide (CoSe₂)[98]. Through a comprehensive suite of adsorption assays, electrochemical evaluations, in situ characterizations, and density functional theory (DFT) calculations, the intricate synergy and distinct functional roles of the PMo12 and CoSe₂ components during the charge/discharge processes were elucidated. Specifically, the highly polar CoSe₂ phase predominantly facilitates the efficient chemisorption of LiPS, whereas the PMo12 nanoclusters govern the rapid bidirectional catalytic conversion of the sulfur species (Figure 9 (a-e)). This synergistic interplay not only profoundly suppresses the LiPSs and accelerates multiphase conversion kinetics but also homogenizes the Li⁺ flux, thereby inducing uniform lithium nucleation and deposition to effectively preclude dendrite proliferation (Figure 9 (f)). Additionally, the hierarchically porous and highly conductive framework composed of a nitrogen-doped carbon (NC) matrix interspersed with carbon nanotubes (CNTs) ensures robust electron transport and unhindered Li⁺ migration pathways. Consequently,

electrochemical evaluations revealed that the Li-S batteries with the $\text{PMo}_{12}/\text{CoSe}_2/\text{NC}/\text{CNTs}/\text{PP}$ separator delivered an impressive initial specific capacity of $1263.79 \text{ mAh g}^{-1}$ at 0.1 C and maintained a robust reversible capacity of $635.77 \text{ mAh g}^{-1}$ even under a rate of 3.0 C . Furthermore, the battery exhibited exceptional long-term cycling stability, demonstrating an ultra-low capacity decay rate of merely 0.06% per cycle over 500 cycles.

(4) Non-ferrous metal nitrides

Endowed with intrinsic metallic conductivity and exceptional electrocatalytic activity, non-ferrous metal nitrides significantly accelerate the multiphase conversion reactions of LiPSs and effectively mitigate the shuttle effect. Consequently, they represent a highly promising material platform to simultaneously resolve the pivotal challenges of poor electrical conductivity and sluggish redox kinetics in Li-S batteries[99-101]. As a paradigm of applying bifunctional transition metal nitrides to enhance electrochemical performance, Jing et al. reported a facile synthesis of vanadium nitride nanoparticles anchored on nitrogen-doped graphene (VN/NG) via direct calcination[102]. Serving as a robust bifunctional redox electrocatalyst, the VN/NG composite profoundly modulates sulfur electrochemistry. Comprehensive kinetic analyses and activation energy calculations demonstrated that the VN/NG matrix effectively entraps soluble LiPSs, facilitates the rapid nucleation and deposition of insoluble Li_2S during the discharge process, and substantially lowers the energy barrier for Li_2S decomposition during the subsequent charging phase (Figure 9 (g-j)). Benefiting from this adsorption-catalysis synergy, the Li-S batteries with the VN/NG modified separator exhibited remarkable rate capability, delivering a specific capacity of 791 mAh g^{-1} at 5.0 C . Furthermore, the battery demonstrated

exceptional long-term cycling stability, retaining a reversible capacity of 863 mAh g^{-1} after 300 cycles at 1.0 C , which corresponds to an ultra-low capacity decay rate of only 0.068% per cycle.

Beyond single-component transition metal nitrides, the rational design of two-dimensional/two-dimensional heterostructures represents a highly promising paradigm to overcome the practical challenges of Li-S batteries. For example, Yin et al. reported a two-dimensional TiN/MoN heterojunction (M-TiN/MoN) synthesized via the structural transformation of a Ti_3C_2 MXene/ MoS_2 precursor[103]. This heterostructure effectively mitigates LiPSs diffusion and accelerates electron/ion transport kinetics through the synergistic interplay of robust chemical anchoring and two-dimensional spatial confinement. Comprehensive *in situ* and ex-situ characterizations, coupled with theoretical calculations, corroborate that the M-TiN/MoN heterointerface exhibits a robust binding affinity for LiPSs and accelerates the bidirectional redox kinetics of sulfur species. Consequently, this unique structure minimizes the thermodynamic activation barriers for both Li_2S nucleation and its subsequent dissolution, ultimately enhancing the electrochemical performance of the battery (Figure 9 (k-n)). As a result, Li-S battery incorporating the M-TiN/MoN-modified separator delivered an impressive initial specific capacity of 1328 mAh g^{-1} at 0.2 C and exhibited an ultra-low capacity decay rate of only 0.09% per cycle after 500 cycles at 1.0 C . Notably, even under an elevated areal sulfur loading of 5.12 mg cm^{-2} , the Li-S batteries still achieved a considerable area capacity of 5.91 mAh cm^{-2} at 0.1 C , unequivocally underscoring its exceptional viability for practical commercial deployment.

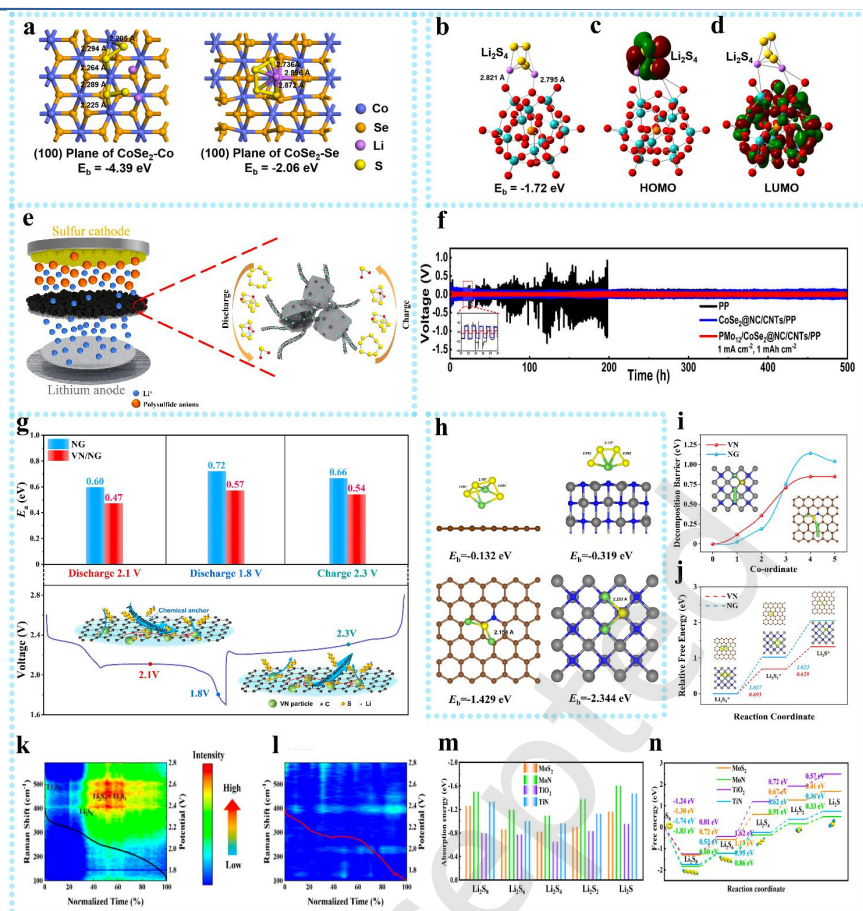


Figure 9 (a) Optimized geometric structures of the CoSe₂-Co-Li₂S₄ and CoSe₂-Se-Li₂S₄ interaction systems from the top view. (b) Optimized structure of PMo₁₂-Li₂S₄ complex with the corresponding binding energy (Color code: P, orange; Mo, blue; O, red; Li, pink; S, yellow). (c-d) Frontier molecular orbital diagrams of PMo₁₂-Li₂S₄. (e) Catalytic scheme of PMo₁₂/CoSe₂@NC/CNTs/PP separator in Li-S battery. (f) Galvanostatic cycling of Li||Li symmetric batteries assembled with different separators at 1 mA cm⁻². Reproduced with permission[98]. Copyright 2025, Elsevier. (g) Activation energies at different voltages and the corresponding voltage profile. (h) Side view for the Li₂S₄ molecule and top view for the Li₂S molecule adsorption configurations on NG (001) and VN (200) surface. (i) Energy barrier profiles of Li₂S decomposition on the surface of VN and NG. (j) Energy profiles for the reversible reactions from Li₂S₄ to Li₂S on VN and NG. Reproduced with permission [102]. Copyright 2022, Elsevier. The *in situ* Raman spectra of Li-S battery with (k) PP and (l) M-TiN/MoN separators at 0.5 C. (m) Adsorption of LiPSs on various samples. (n) Gibbs free energy of transformation of S₈ into Li₂S. Reproduced with permission [103]. Copyright 2025, Elsevier.

(5) Non-ferrous metal carbides

Non-ferrous metal carbides such as molybdenum carbide, tungsten carbide, and MXenes exhibit promising potential for functional separator modification in Li-S batteries[104, 105]. Their primary advantages stem from intrinsic metallic conductivity, robust structural stability, and highly tunable surface chemistry. These attributes synergistically facilitate the efficient chemisorption and catalytic conversion of LiPSs, profoundly suppressing the shuttle effect and elevating overall battery performance[106, 107]. In 2011, Gogotsi first reported a class of MXene materials consisting of novel transition metal carbides or nitrides/carbonitrides[108]. Since then, MXene has exerted considerable influence and found widespread application in the field of energy storage and conversion. Its unique intrinsic structural properties confer multiple functional advantages. First, the distinctive two-dimensional layered architecture and tailorable interlayer spacing effectively accommodate the severe volumetric fluctuations of sulfur cathode during repeated redox cycles[109]. Second, the highly polar surface of MXenes, which are densely populated with electronegative terminal functional groups (e.g., -O, -OH, and -F), exhibit a remarkably strong adsorption affinity

toward LiPSs. This enables the effective suppression of the shuttle effect via robust Lewis acid-base interactions while concurrently catalyzing the multiphase conversion of soluble LiPSs into insoluble solid Li₂S[110].

As illustrated in Figure 10(a), Feng et al. prepared a nitrogen/sulfur co-doped Ti₃C₂T_x MXene (NSMX) with a unique wrinkled morphology via a thiourea-induced pyrolysis method and employed it as a bifunctional separator modification layer for Li-S batteries[111]. The wrinkled MXene nanosheets construct a continuously interconnected conductive network that facilitates the rapid transport of both electrons and ions. Furthermore, the expanded interlayer spacing sterically restricts LiPSs diffusion without compromising rapid Li⁺ transport kinetics. DFT calculations revealed that the dual-heteroatom doping of N and S shifts the d -band center of the Ti active sites in NSMX closer to the Fermi level, thereby substantially enhancing the electron-donating capability of Ti to the LiPSs (Figure 10(b)). This precise electronic modulation significantly amplifies both the chemisorption affinity and catalytic conversion activity toward LiPSs, optimizing the complex sulfur redox processes from both thermodynamic and kinetic perspectives. Comprehensive experimental

characterizations further corroborated that the NSMX promotes the rapid reduction of Li_2S_6 to Li_2S_4 at high potentials and accelerates the nucleation and deposition of Li_2S , culminating in a markedly enhanced utilization of the active sulfur species (Figure 10(c) and 10(d)). Consequently, the Li-S battery with the NSMX-modified separator delivered outstanding electrochemical performance (Figure 10(e)). It achieved an initial specific capacity of $1249.0 \text{ mAh g}^{-1}$ at 0.2 C and demonstrated exceptional rate capability, delivering reversible capacities of 1315.1, 1041.4, 922.6, 795.6, 712.0, 649.0, and 595.0 mA g^{-1} across escalating current densities ranging from 0.2 to 5.0 C. Most notably, even under the stringent operational parameters of a high areal sulfur loading (7.2 mg cm^{-2}) and a lean electrolyte formulation ($\text{E/S} = 7.0 \text{ }\mu\text{L mg}^{-1}$), the Li-S battery maintained a reversible capacity of 729.9 mAh g^{-1} after 100 cycles at 0.2 C, alongside an exceptional average Coulombic efficiency of 99.7%. These results underscore the enhanced sulfur reaction kinetics enabled by the NSMX architecture and highlight its viability for practical application.

Compared with monometallic non-ferrous carbides, bimetallic carbides provide a higher density of catalytically active sites, facilitating the highly efficient chemisorption and multiphase catalytic conversion of LiPSs. This architectural advantage significantly accelerates the redox kinetics of sulfur species and substantially enhances overall cycling stability. For example, Zhang et al. modified the PP

separator with a cobalt-molybdenum bimetallic carbide ($\text{Co}_3\text{Mo}_3\text{C}$) [112]. Relative to single-metal carbides, the $\text{Co}_3\text{Mo}_3\text{C}$ delivered superior LiPSs adsorption affinity and robust bidirectional electrocatalytic activity toward both the sulfur reduction and Li_2S oxidation reactions, which is attributed to its optimized electronic structure and the synergistic densification of active sites. Experimental results demonstrated that the $\text{Co}_3\text{Mo}_3\text{C}$ modification layer not only facilitates rapid ion migration but also mitigates LiPSs shuttling, thereby simultaneously preserving the interfacial stability of both the sulfur cathode and the lithium metal anode. Under harsh conditions including a high areal sulfur loading (8 mg cm^{-2}) and a lean electrolyte regime ($\text{E/S} = 6 \text{ }\mu\text{L mg}^{-1}$), the Li-S battery with the $\text{Co}_3\text{Mo}_3\text{C}/\text{PP}$ separator achieved an areal capacity of 6.8 mAh cm^{-2} . Furthermore, the $\text{Co}_3\text{Mo}_3\text{C}$ modified layer exhibited exceptional structural integrity, providing compelling evidence for its viability in practical applications. Nevertheless, the widespread implementation of non-ferrous metal carbides still confronts several challenges. These encompass complex synthetic routes, energy-intensive high-temperature processing requirements, the inherent propensity of layered structures to restack and agglomerate, and a high susceptibility to surface oxidation, all of which critically impede their large-scale commercial scalability.

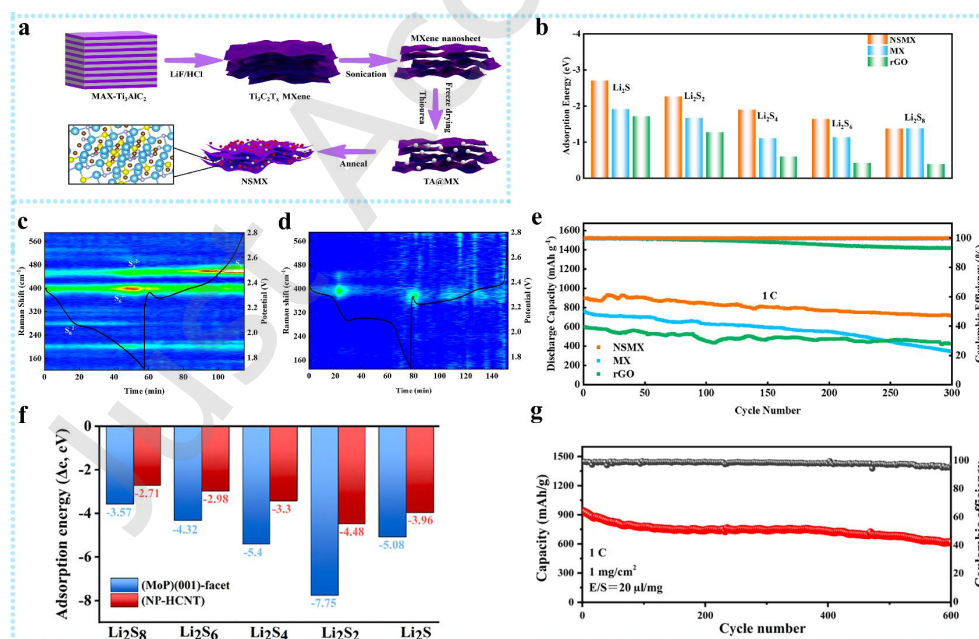


Figure 10 (a) Schematic diagram of the synthesis of NSMX. (b) Adsorption energy of different samples to LiPSs. The in-situ Raman spectra of Li-S batteries with PP (c) and NSMX (d) separators at 0.5 C. (e) Cycling performance of batteries with different separators at 1.0 C. Reproduced with permission [111]. Copyright 2024, Elsevier. (f) Comparison of adsorption energies between intermediate LiPSs and NP-HCNT or the MoP (001) face. (g) Long cycle performance of the Li-S battery with the MPQ@NP-HCNT-modified separator at 1.0 C. Reproduced with permission [113]. Copyright 2022, American Chemical Society.

(6) Non-ferrous metal phosphides

Non-ferrous metal phosphides including monometallic, bimetallic, and polycrystalline, alongside their composite structures exhibit exceptional electrocatalytic activities and unique physicochemical properties [114–116]. When deployed as functional separator modifiers in Li-S batteries,

these materials effectively mitigate the LiPSs shuttle effect and accelerate the multiphase conversion kinetics of sulfur redox reactions, thereby elevating overall battery performance. For instance, Zhang et al. demonstrated that the immobilization of MoP quantum dots onto N, P co-doped hollow carbon nanotubes (MPQ@NP-HCNT) to serve as a

separator modifier profoundly enhanced the electrochemical performance of Li-S batteries[113]. The N, P co-doped hollow carbon framework not only serves as a robust structural scaffold for the MoP quantum dots bolstering the mechanical integrity of the separator, but also provides interconnected conduits for rapid Li^+ transport kinetics. Furthermore, the uniformly dispersed MoP quantum dots acted as highly polar catalytic centers, enabling the efficient chemisorption and continuous catalytic conversion of LiPSs.

As illustrated in Figure 10(f), the DFT calculations revealed that the MoP phase exhibits a strong adsorption affinity toward both S_8 and diverse Li_2S_n intermediate species. This interaction fundamentally lowers the thermodynamic activation barrier for Li_2S nucleation and accelerates the subsequent kinetics of Li_2S deposition and dissolution. Consequently, Li-S battery with the MPQ@NP-HCNT-modified separator delivered an impressive initial specific capacity of 1293 mAh g^{-1} at 0.1 C and sustained a robust rate capability of 747 mAh g^{-1} at 3.0 C. Moreover, the battery demonstrated remarkable long-term cycling stability, retaining a reversible capacity of 600 mAh g^{-1} after 600 cycles at 1.0 C (Figure 10(g)). Even under an elevated areal sulfur loading of 3.68 mg cm^{-2} , the Li-S battery achieved an initial areal capacity of 3.58 mAh cm^{-2} at 0.1 C and maintained an 80% capacity retention over 110 cycles, underscoring its immense potential for practical commercial implementation.

Bimetallic phosphides (e.g., NiCoP, FeCoP, and CoMoP) exhibit superior electrocatalytic activity, enhanced electronic conductivity, and greater structural stability compared to their monometallic counterparts, primarily owing to the synergistic electronic modulation between the distinct metal centers[117, 118]. Consequently, these bimetallic architectures have emerged as promising functional materials for mitigating the LiPSs shuttle effect and accelerating multiphase redox reaction kinetics in Li-S batteries. For instance, Zhu et al. successfully fabricated a composite material for separator modification via the thermal annealing and subsequent phosphorization of a Ni-ZIF-67 precursor (Figure 11(a)), embedding bimetallic NiCoP nanoparticles within a nitrogen-doped dual-carbon conductive network (NiCoP@NC) [119]. Within this NiCoP@NC architecture, the dual-carbon scaffold not only acted as a physical barrier that effectively hinders LiPSs

shuttling but also provides highly efficient and interconnected pathways for Li^+ transport (Figure 11(b)). Simultaneously, the highly dispersed and strongly polar NiCoP nanoparticles serve as dense catalytically active sites, accelerating the bidirectional the redox kinetics of the sulfur species (Figure 11(c)). Capitalizing on the synergistic integration of the conductive dual-carbon network, robust chemisorption capabilities, and exceptional catalytic activity, the Li-S battery with the NiCoP@NC modified separator demonstrated outstanding electrochemical performance. As shown in Figure 11(d) and 11(e), the battery delivered an initial specific capacity of $1083.4 \text{ mAh g}^{-1}$ at 0.5 and exhibited a minimal capacity decay rate of only 0.09% per cycle after 300 cycles, indicating superior cycling stability and rate capability. Even under high sulfur loading conditions, the Li-S battery maintained a high capacity alongside excellent long-term cycling durability.

In addition, Co-Fe bimetallic phosphides have been systematically explored as highly effective separator modifiers to elevate the comprehensive electrochemical performance of Li-S batteries. Yoo et al. developed a composite comprising FeCoP nanoparticles anchored on graphitic carbon nitride nanosheets (CFP@CN) prepared via an electrostatic self-assembly strategy, which was applied as a functional coating for separator modification in Li-S batteries[120]. The high specific surface area and abundant active sites of the CFP@CN-PP modified separator foster strong chemical interactions toward LiPSs, thereby effectively suppressing their transmembrane diffusion (Figure 11(f) and 11(g)). Moreover, this tailored composite synergistically integrates high electrical conductivity with the pronounced bimetallic electrocatalytic effects of the Co and Fe sites, enhancing both the multiphase conversion kinetics and the overall utilization of the sulfur active material. Electrochemical tests revealed that the Li-S battery with the CFP@CN-PP separator delivered an initial specific capacity of 786.4 mAh g^{-1} at 1.0 C and retained a reversible capacity of 528.3 mAh g^{-1} after 650 cycles. This performance corresponds to an ultra-low capacity decay rate of only 0.084% per cycle and a stable Coulombic efficiency consistently exceeding 99%, demonstrating exceptional long-term cycling stability and electrochemical reversibility (Figure 11(h)).

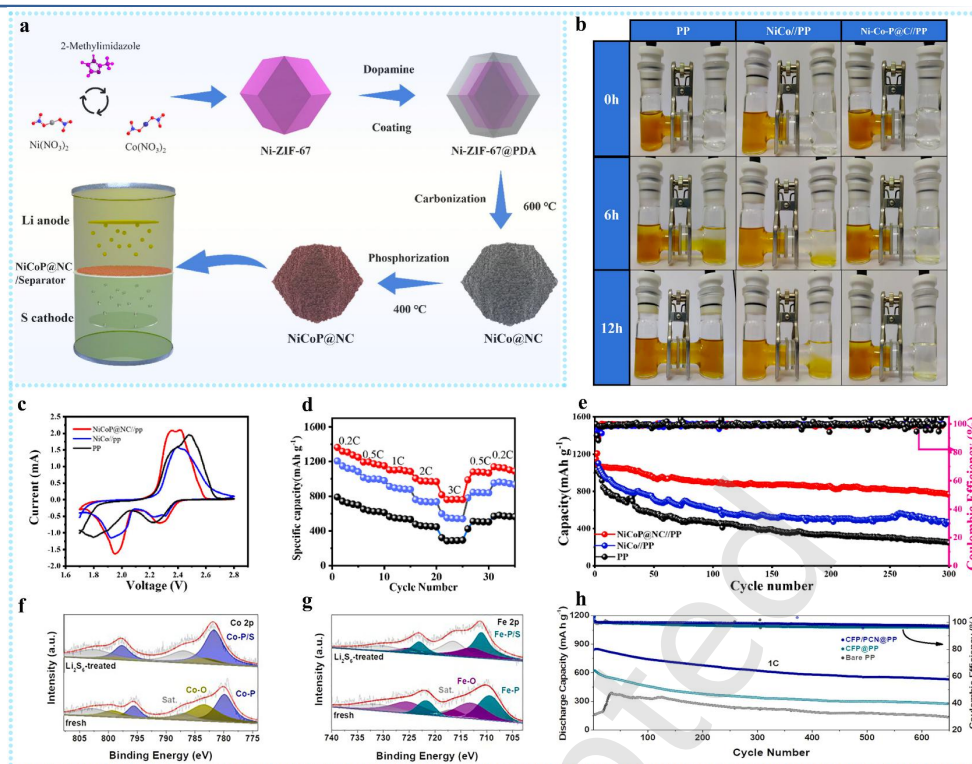


Figure 11 (a) Illustration for the preparation procedure of NiCoP@NC modified separator. (b) Li_2S_6 permeation measurements with different separators. (c) CV curves of different batteries at 0.1 mV s^{-1} . (d) Rate performance of different batteries at various rates. (e) Cycling performance of different batteries at 0.5 C. Reproduced with permission[119]. Copyright 2023, Elsevier. High-resolution XPS spectra of (f) Co 2p, (g) Fe 2p. (h) Cycling performances of Li-S batteries with CFP@CN-PP, CFP-PP, and PP separators, respectively, for 650 cycles at 1.0 C. Reproduced with permission[120]. Copyright 2023, Elsevier.

(7) Non-ferrous metal single atom

Single-atom catalysts (SACs) exhibit immense potential for enhancing the electrochemical performance of Li-S batteries, owing to their maximized atomic utilization efficiency and highly tunable local electronic structures[121-123]. Consequently, non-ferrous transition metal-based SACs (incorporating active centers such as Co, Cu, Zn, and Ni) have garnered extensive research focus. These advanced materials effectively mitigate the shuttle effect and accelerate multiphase reaction kinetics by enhancing the chemisorption and catalytic conversion of LiPSs[124, 125], thereby delineating a critical pathway toward the realization of high-performance Li-S batteries. To elucidate the modulatory effects of functionalized separators on LiPSs conversion behavior, He et al. prepared a Ni single-atom-anchored graphene membrane (Ni-SA-G) via an *in situ* electrochemical doping and self-assembly strategy (Figure 12(a-c)), systematically evaluating its advantages in promoting sulfur redox kinetics[20]. The Ni-SA-G architecture integrates intrinsic electrocatalytic activity with precise nanochannel sieving, effectively enhancing the dissociation kinetics of Li^+ -solvent complexes. As corroborated by theoretical simulations and *in situ* Raman spectroscopy (Figure 12(d-g)), the unique Ni- O_5 coordination microenvironment within the Ni-SA-G significantly lowers the thermodynamic dissociation energy barrier for Li^+ -solvent complexes. This precisely engineered structural feature expedites Li^+ migration and consequentially facilitates highly efficient sulfur conversion. Meanwhile, the precisely tailored nanoscale transport channels enforce the effective steric sieving and stringent spatial confinement of bulky solvent molecules and LiPSs.

Consequently, Li-S battery with the Ni-SA-G-modified separator demonstrated outstanding rate capability and long-term cycling stability. The reversible specific capacities of 1169, 977, 798, 680, and 565 mAh g^{-1} were achieved at escalating current densities of 0.1, 0.2, 0.5, 1.0, and 2.0 C, respectively. After 700 cycles at 1.0 C, the battery exhibited an ultra-low capacity decay rate of merely 0.024% per cycle (Figure 12(h)). Furthermore, even under a high sulfur loading of 4.78 mg cm^{-2} , the battery achieved a high areal capacity of 4.0 mAh cm^{-2} at 0.2 C, demonstrating promising potential for practical application.

To date, the majority of reported SACs for Li-S battery have predominantly centered on traditional M-N-C configurations supported by carbonaceous matrices. However, the nonpolar nature of the M-N₄ coordination microenvironment frequently results in an insufficient chemical affinity for highly polar LiPSs. To transcend this limitation, Dong et al. rationally immobilized single Ni atoms onto MoS_2 nanosheets (Ni-MoS_2) to serve as a separator modifier, corroborating the precise atomic dispersion of Ni via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 12(i-k))[126]. The Ni-MoS_2 @PP separator demonstrated multiple advantages including high electrolyte wettability, robust mechanical properties, and excellent thermal stability, contributing to improved safety of Li-S batteries. Furthermore, the electronic synergy between Ni single atoms and the polar MoS_2 substrate generated a high density of dual-functional active sites. This tailored architecture drastically amplified the chemisorption affinity toward soluble long-chain LiPSs and accelerated their multiphase redox kinetics (Figure 12(l)). Consequently, Li-S battery

with this engineered separator exhibited exceptional electrochemical performance. As depicted in Figure 12(m), the battery maintained excellent long-term stability after 400 cycles at a high current density of 2.0 C. Most notably, even under a commercially relevant, ultrahigh areal sulfur loading of 7.5 mg cm⁻², the battery delivered an impressive

retained areal capacity of 5.9 mAh cm⁻² after 50 cycles. This study establishes an innovative and highly efficient materials design paradigm, elegantly coupling single-atom catalysis with polar host substrates to synergistically optimize the entrapment and catalytic conversion of LiPSs in high-performance Li-S batteries.

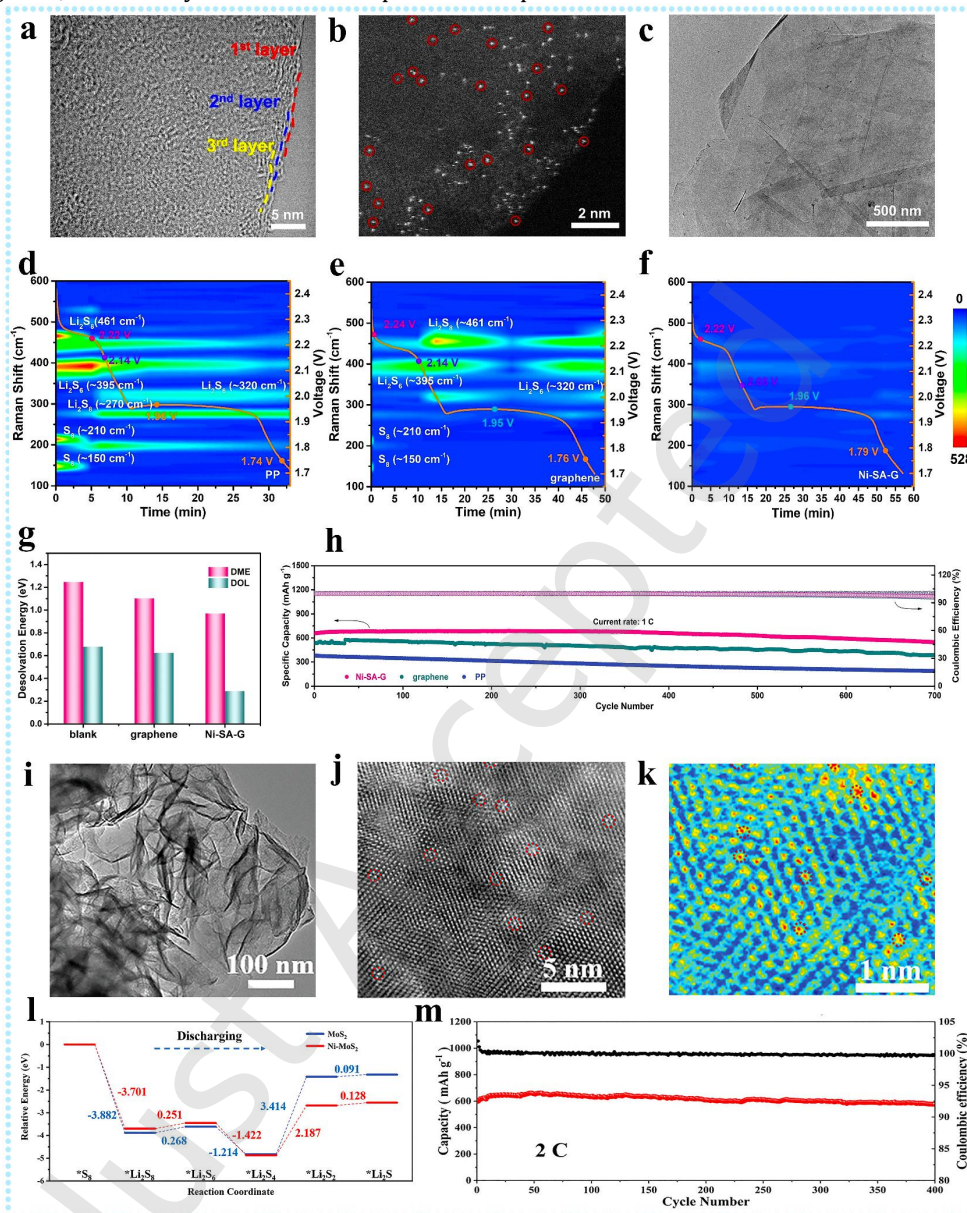


Figure12 (a) HR-TEM image of Ni-SA-G. (b) AC-HAADF-STEM image of Ni-SA-G. (c) TEM image of Ni-SA-G. *In situ* Raman contour plots with different separators: (d) PP, (e) graphene, and (f) Ni-SA-G separators. (g) Li⁺ desolvation energy on different substrates. (h) Cycling performance for Li-S batteries with different separators at 1 C. Reproduced with permission[20]. Copyright 2025, Wiley. (i) TEM images of Ni-MoS₂ nanosheets. (j) Atomic resolution picture of the Ni-MoS₂ nanosheets. (k) FFT-filtered atomic resolution image of the Ni-MoS₂ nanosheets. (l) Energy profiles for the reduction of lithium polysulfides on MoS₂ and Ni-MoS₂ substrates. (m) Cycling performance of the Li-S battery with Ni-MoS₂@PP separator at 2.0 C. Reproduced with permission[126]. Copyright 2022, Wiley.

Non-ferrous metal compounds play a crucial role in modifying separators for Li-S batteries by effectively suppressing LiPSs shuttling, enhancing redox kinetics, and improving overall electrochemical performance (Table 1). However, the practical industrial application still faces multiple challenges[96, 127, 128]. First, the intrinsically poor electrical conductivity, especially metal oxides, results in sluggish electrode reaction kinetics. Second, insufficient structural stability during long-term cycling often results in the loss of active components and particle agglomeration.

Moreover, existing synthesis methods often rely on harsh conditions such as high temperature and high pressure, suffering from high energy consumption, complex processes, and poor reproducibility. Therefore, realizing breakthroughs in advanced microstructural engineering and the development of scalable, energy-efficient synthetic methodologies is imperative to propel the commercial viability and practical implementation of next-generation Li-S batteries.

Table 1 Electrochemical performance of nonferrous metal-based compounds as separator modifiers in Li-S batteries

Type of Metals	Coating materials	Coating loading (mg cm ⁻²)	Cathodes	S loading (mg cm ⁻²)	Rate (C)	Initial capacity (mAh g ⁻¹)	Decay rate (%) & Cycles	Ref.
Nonferrous metal oxides	(TiO ₂ + Super P) ST	0.5-1.0	INPC/S	1.5	1.0	910	0.037 (500)	[129]
	MoO ₃	0.1-0.8	S-EG	1.5	5.0	696	0.014 (5000)	[130]
	ZnO/Graphene	0.4	Carbon black/S	1.1-1.5	1.0	895	0.093 (500)	[131]
	CoS@NC/NCNT	0.8	Li ₂ S ₆ /CC	1.0	1.0	1046	0.083 (500)	[132]
Nonferrous metal sulfides	MoS ₂ @CNT	0.8	super P/S	1.5	0.5	1291	0.089 (500)	[133]
	CoS ₂ /NC@1T MoS ₂	-	S/MWCNT	0.8	1.0	953	0.070 (500)	[134]
	TiN NSs	0.4	MWCNTs/S	1.2	1.0	854	0.046 (1000)	[135]
Nonferrous metal nitrides	Mo ₂ N	0.2	CNT/S	1.5-1.8	2.0	967	0.039 (800)	[100]
	VN	1.5	S/CNT	1.4-1.6	1.0	895	0.077 (800)	[136]
	V ₂ C MXene	-	S/super P	2.4-3.0	1.0	821	0.04 (600)	[137]
Nonferrous metal carbides	Ti ₃ C ₂ Tx-CNT	-	S/KB	0.9	1.0	823	0.07 (500)	[138]
	Co ₃ Mo ₃ C	0.8	S/Super P	1.6	1.0	840	0.034 (1000)	[112]
	Ni-Co-P	0.4	S/CNT	1.8	0.5	961	0.056 (1000)	[139]
Nonferrous metal phosphides	CoP/C	0.3	KB/S	1.4	1.0	938	0.08 (500)	[140]
	Ni ₁₂ P ₅ @rGO	0.4	Carbon black/S	1.1-1.5	1.0	809	0.074 (500)	[141]
	ZnSe/C	0.3	CB/S	1.3	1.0	923	0.04 (1000)	[97]
Nonferrous metal selenides	CoSe/NCC	0.8	MWCNTs/S	0.8	1.0	874	0.051 (500)	[142]
	Sb ₂ Se _{3-x} /rGO	0.5	S/CNT	1.8	1.0	961	0.027 (500)	[96]
	NiSA-N-PGC	-	Carbon black/S	-	0.5	801	0.069 (600)	[143]
Nonferrous metal single atom	VN _{1-x} @V-NC	0.25	acetylene black/S	1.5	1.0	1075	0.047 (500)	[144]
	SAZ-AF Janus	-	Ketjen Black/S	1.5	2.0	920	0.05 (1000)	[145]
	NiS ₂ -MnS/MoS ₂ -3DNGr	2.16	S/3DGr	2.5	3.0	353	0.0265 (1000)	[146]
Nonferrous metal heterojunction	NiS ₂ -CoS ₂	-	Carbon black/S	0.9-1.1	1.0	901	0.121 (300)	[147]
	CoO-Co ₃ O ₄	-	KB/S	0.9-1.2	5.0	693	0.065 (1000)	[148]

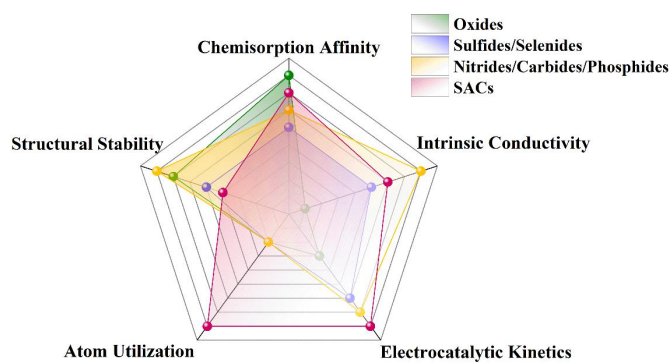
To systematically elucidate the structure-property relationships among diverse non-ferrous metal compounds, their intrinsic physicochemical metrics are comparatively synthesized in a radar chart (Figure 13). Overall, the performance of these materials is rooted in their anionic coordination chemistry, encompassing a spectrum from strong chemisorption to highly efficient electrocatalysis. Fundamentally, metal oxides provide robust polar sites for LiPs anchoring, yet their inherently poor electronic conductivity severely impedes conversion kinetics. To bridge this gap, substituting oxygen with less electronegative chalcogens (S, Se) yields metal sulfides and

selenides, establishing a vital equilibrium between chemical affinity and accelerated charge transfer. Furthermore, driven by the imperative for rapid bidirectional redox kinetics, interstitial compounds (metal nitrides, carbides, and phosphides) featuring near-metallic conductivity have been explored to effectively lower thermodynamic activation barriers. Additionally, by transitioning from bulk lattices to atomically dispersed active centers, SACs achieve near 100% atom utilization and permit precise microenvironment tailoring. This atomic-level structural precision resolves the intrinsic trade-off between separator coating mass and catalytic efficiency, establishing a promising frontier for advanced Li-S battery engineering.

Figure13 Radar chart comparing the intrinsic properties of various non-ferrous metal compounds.

3.2 Ferrous metal compounds

Ferrous metals (Fe, Mn, Cr, and their alloys) are abundantly available in the Earth's crust and exhibit significantly lower raw material costs compared to non-



ferrous metals such as Co and Ni, as well as noble metals[149, 150]. When applied as separator modifiers in Li-S batteries, ferrous metal compounds can effectively mitigate the LiPSs shuttle effect and reduce the reaction energy barriers of sulfur species conversion via the excellent adsorption and catalytic properties, significantly enhancing sulfur utilization and rate performance[151, 152]. Accordingly, this subsection systematically reviews the application of ferrous metals and the compounds in separator modification for Li-S batteries, with a focus on the mechanisms of action and electrochemical performance.

(1) Fe

Fe-based compounds have emerged as highly compelling materials for functional separator modification in Li-S batteries, driven by their natural terrestrial abundance, tunable electronic structures, and abundant active sites. These intrinsic attributes empower them to synergistically mitigate the LiPSs shuttle effect while simultaneously accelerating multiphase sulfur conversion kinetics[153]. The mechanistic underpinnings of these enhancements are predominantly twofold. On the one hand, the strategic of defect engineering specifically the precise modulation of oxygen vacancy concentrations generates highly polar interfaces. These interfaces not only foster the robust chemisorption of soluble long-chain LiPSs but also facilitate their selective screening[154]. On the other hand, the rational optimization of the local electronic structure, achieved through sophisticated compositional design or the regulation of the coordination microenvironment (e.g., targeted Fe-doping strategies), drastically augments intrinsic electrical conductivity. This electronic modulation diminishes the thermodynamic activation energy barriers for LiPSs conversion, propelling the bidirectional kinetics of both the sulfur reduction and evolution reactions[155]. The synergistic orchestration of these interfacial and electronic mechanisms culminates in enhancement of the overall electrochemical performance of the Li-S battery.

As illustrated in Figure 14(a), Qiao et al. designed an iron-based compound/carbon composite (FeCFeOC) with a three-dimensional vesicular porous structure, which was simultaneously used as the cathode host and separator modification layer for Li-S batteries to enhance the electrochemical performance[156]. Both theoretical computations and empirical characterizations corroborated that the FeCFeOC composite exhibits robust chemisorption affinity coupled with exceptional electrocatalytic activity toward LiPSs (Figure 14(b-d)). Mechanistic investigations revealed that Fe^{3+} within the FeCFeOC matrix spontaneously react with migrating LiPSs to precipitate bulky ferromagnetic FeS_x specie. The spatial confinement of these macromolecular derivatives within the cathodic region systematically obstructs the LiPSs shuttle effect (Figure 14(e) and 14(f)). Leveraging this synergistic adsorption-catalysis paradigm, the FeCFeOC architecture facilitates the efficient

anchoring and rapid multiphase conversion of LiPSs, thereby profoundly maximizing the utilization of sulfur. Consequently, as depicted in Figure 14(g) and 14(h), the Li-S battery with FeCFeOC/S as the cathode material and FeCFeOC as the separator modification layer demonstrated excellent electrochemical performance. The system delivered a high specific capacity of 947 mAh g^{-1} after 200 cycles at 0.2 C, maintained a capacity retention rate of 77.6% following 500 cycles at 1.0 C, and exhibited an ultralow average capacity decay rate of only 0.036% per cycle after 1000 cycles at 3.0 C. Remarkably, even under a stringent current density of 5.0 C, the battery still achieved a specific capacity of 659 mAh g^{-1} , underscoring its superior high-rate capability.

Optimization of dopant species and concentrations represents a potent strategy for addressing the inherent limitations of Li-S batteries, specifically low active material utilization, sluggish redox kinetics, and lithium anode corrosion caused by LiPSs dissolution. Du et al. successfully synthesized an oxygen vacancy (OV)-rich $\text{rGO}/\text{H}_2\text{TiO}_{3-x}\text{-Fe}$ composite via a one-step hydrothermal method for application as a multifunctional separator modification layer[71]. A selective sieving mechanism based on the chain-length disparity of LiPSs species was proposed to systematically circumvent the technical bottlenecks associated with LiPSs dissolution (Figure 14(i)). In this architecture, Fe doping not only optimizes the electronic configuration and diminishes the activation energy barrier for LiPSs redox reactions, but also induces the generation of Lewis acidic oxygen vacancies by balancing the charge difference between Fe^{3+} and Ti^{4+} . This functional layer effectively immobilizes long-chain LiPSs through robust Lewis acid-base interactions. Meanwhile, as Li^+ concentration rises during discharge, the Lewis acid-base interactions between Li^+ and the material intensify, leading to a regulated reduction in the adsorption affinity of the $\text{rGO}/\text{H}_2\text{TiO}_{3-x}\text{-Fe}$ for short-chain LiPSs species. This transition permits the controlled permeation of trace Li_2S_4 across the separator to facilitate the construction of a stable SEI on the surface of the lithium metal anode. This SEI effectively passivates the anode surface against LiPSs corrosion while suppressing deleterious dendrite proliferation (Figure 14(j-l)). Consequently, the $\text{rGO}/\text{H}_2\text{TiO}_{3-x}\text{-Fe}$ modification layer serves as a trifunctional barrier, sieving, and catalytic medium that synergistically inhibits the LiPSs shuttle effect, protects the lithium anode, and accelerates reaction kinetic. The resulting Li-S battery demonstrated exceptional performance, exhibiting a lower capacity decay rate of only 0.035% per cycle after 1000 cycles at a high rate of 5 C (Figure 14(m)) and maintaining a reversible capacity of 642 mAh g^{-1} at 10 C. Furthermore, the system retained remarkable cycling stability and high capacity even under harsh conditions of high sulfur loading (7.9 mg cm^{-2}) and lean electrolyte ($\text{E/S ratio} = 4.5 \text{ }\mu\text{L mg}^{-1}$).

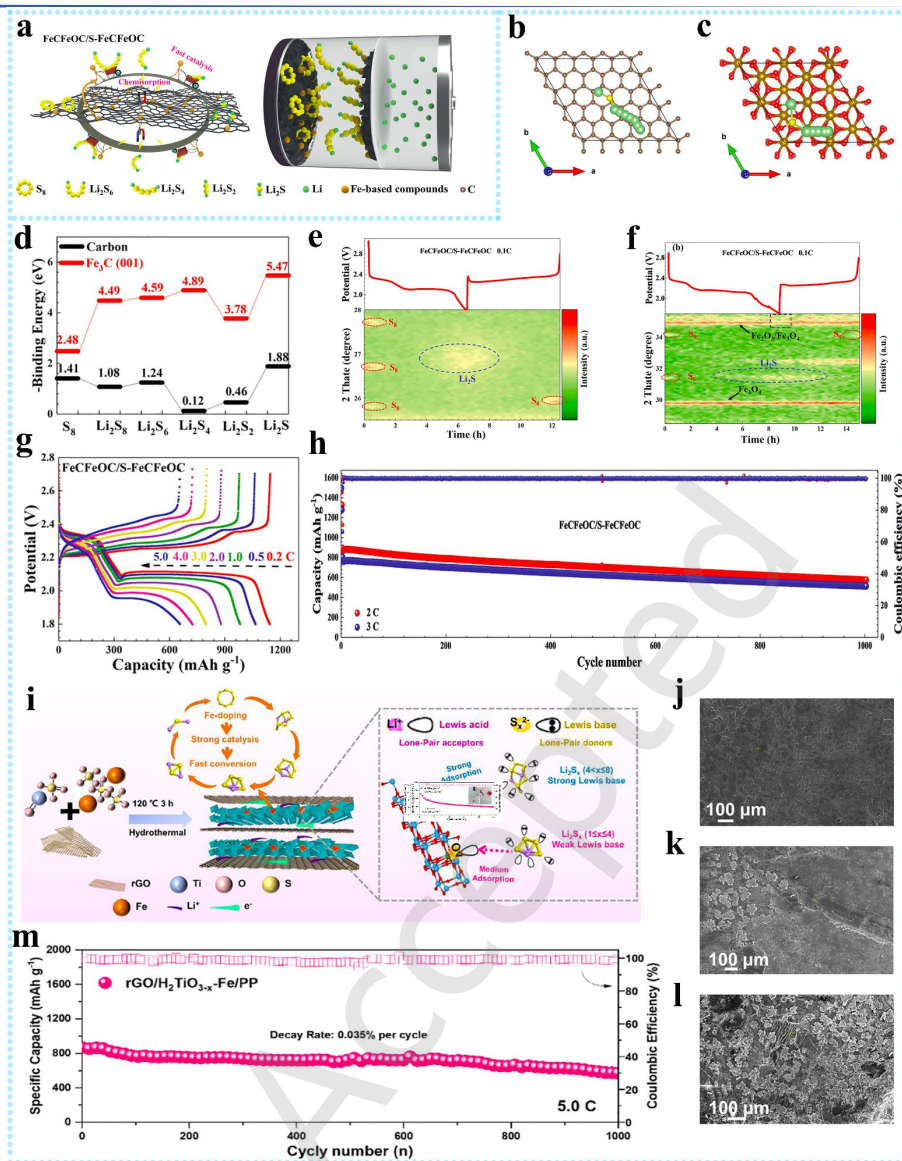


Figure 14 (a) Illustrations of the conversion process of sulfur on the surfaces of FeCFEOC composite and corresponding illustrations of discharge-charge processes. Top view schematic representations of the corresponding decomposition pathways for (b) C and (c) Fe₂O₃, (d) Binding energies of LiPSs with C, and the (001) plane of Fe₃C. (e-f) In situ XRD patterns in contour plots of the Li-S batteries with FeCFEOC/S cathode and FeCFEOC modified separator as a function of discharge/charge during the first cycle. (g) The charging-discharging curves of the Li-S batteries with FeCFEOC/S cathode and FeCFEOC modified separator at different rates. (h) Cycling performance of the Li-S batteries with FeCFEOC/S cathode and FeCFEOC modified separator at 2.0 and 3.0 C. Reproduced with permission[156]. Copyright 2021, Wiley. (i) Fabrication scheme and working mechanism of rGO/H₂TiO_{3-x}-Fe. SEM images of Li anodes after cycling in Li-S batteries with (j) rGO/H₂TiO_{3-x}-Fe/PP, (k) rGO/H₂TiO₃/PP, and (l) rGO/PP as separator. (m) Long cycle stability of the rGO/H₂TiO_{3-x}-Fe-based battery at 5.0 C. Reproduced with permission[71]. Copyright 2025, Wiley.

Fe-based oxides have garnered widespread attention in the field of Li-S batteries due to their pronounced capability to enhance active sulfur utilization and prolong cycling stability. For instance, Zhang et al. precisely constructed Fe₃O₄ nanospheres with a hollow hierarchical porous structure (p-Fe₃O₄-NSs) via a solvothermal self-assembly strategy[157]. By modifying these nanospheres as a functional coating on the surface of PP separators, they successfully developed a novel multifunctional composite separator. This modified separator not only effectively obstructed the migration of LiPSs, but also significantly accelerated the bidirectional conversion between soluble LiPSs and insoluble Li₂S₂/Li₂S. Concurrently, the unique hollow porous structure of the p-Fe₃O₄-NSs established highly efficient pathways for rapid ion transport, thereby boosting ion diffusion kinetics and synergistically elevating

the overall electrochemical reaction efficiency. Consequently, the Li-S battery based on this multifunctional separator achieved high sulfur utilization, excellent rate capability, ultra-long cycle life, and high areal capacity.

Additionally, Fe-based heterojunctions represent a pivotal materials engineering strategy to synergistically circumvent the dual bottlenecks of Li-S batteries namely, the LiPSs shuttle effect and sluggish redox kinetics through the construction of heterointerfaces endowed with robust built-in electric fields. On the one hand, the different components form a complementary catalytic mechanism. The polar components establish high-density adsorption sites through polar-polar interactions, enabling precise anchoring LiPSs. While catalytically active components form a closed adsorption-conversion-desorption loop via the division of labor among bifunctional sites. On the other hand, the

spontaneous formation of a built-in electric field at the heterointerface induces directional charge redistribution, regulating the d-band center of Fe toward the Fermi level to optimize binding energies. Collectively, these integrated structural and electronic attributes lay a critical materials foundation for the performance optimization and subsequent large-scale application of Li-S battery.

As illustrated in Figure 15(a), Song et al. successfully constructed an island-like p-n heterojunction comprising FeS₂ nanoparticles anchored on TiO₂ nanobelts (FeS₂@TiO₂) via a sequential hydrothermal, ion exchange, and sulfurization process[67]. When deployed as a functional separator coating in Li-S batteries, this tailored architecture enables the highly efficient capture and catalytic conversion of LiPSs. DFT calculations revealed that within this heterostructure, the TiO₂ phase functions as a robust adsorption domain, effectively immobilizing LiPSs via strong chemisorption to mitigate shuttle diffusion (Figure 15(b) and 15(c)). Concurrently, the FeS₂ domains serve as highly active electrocatalytic centers that accelerate LiPSs conversion kinetics. This synergistic interplay suppresses the accumulation of free LiPSs in the electrolyte. Furthermore, band structure analysis demonstrated that the energy level difference between FeS₂ and TiO₂ induced the formation of a built-in electric field at the heterointerface. This built-in electric field drives rapid and directional charge transfer, thereby remarkably accelerating the multiphase conversion of LiPSs, particularly the sluggish reduction of Li₂S₂ to solid Li₂S (Figure 15(d)). Moreover, the island-like architecture provided abundant heterogeneous interfaces, ensuring a continuous and dynamic cycle of localized adsorption and catalysis. Electrochemical evaluations demonstrated that Li-S battery with FeS₂@TiO₂-modified separator exhibit outstanding comprehensive performance (Figure 15(e)). The system delivered a high initial specific capacity of 1318 mAh g⁻¹ at 0.1 C and demonstrated exceptional long-term cycling stability, registering a capacity decay rate of only 0.061% per cycle at 1.0 C. Ultimately, this study not only elucidates the critical role of p-n heterojunctions in synergistically regulating the adsorption-diffusion-conversion dynamics of LiPSs, but also establishes a robust theoretical framework and empirical foundation for the rational design of advanced functional separators for high-performance Li-S battery.

Bridging the gap between laboratory-scale research and

the commercialization of Li-S battery hinges on effectively mitigating the LiPSs shuttle effect and accelerating sluggish multiphase conversion kinetics. A critical strategy to resolve these bottlenecks lies in the rational design of bifunctional electrocatalysts that simultaneously integrate robust chemisorption capabilities with superior catalytic activity. To this end, Zhou et al. successfully fabricated a novel Fe₃Se₄/FeSe@MXene heterojunction catalyst via in-situ growth of Fe-based metal-organic frameworks (Fe-MOFs) followed by a gas-phase selenization process[33]. The Fe₃Se₄/FeSe heterointerface not only furnished a high density of active sites but also optimized the activation barriers of surface reactions through interfacial electronic reconfiguration. Furthermore, leveraging its large specific surface area and robust chemical affinity, the two-dimensional MXene scaffold exerted a synergistic dual effect of physical confinement and robust chemical entrapment toward migrating LiPSs (Figure 15(f)). Driven by strong interfacial coupling, these integrated components established a synergistic tripartite regulatory paradigm, encompassing LiPSs capture, selective adsorption, and highly efficient catalytic conversion, which effectively suppressed the LiPSs shuttle effect and accelerated the reaction kinetics.

When the synthesized Fe₃Se₄/FeSe@MXene heterojunction was deployed as a functional coating on PP separator, the assembled Li-S battery delivered a high cycle stability at a current rate of 1.0 C (Figure 15(g)). Even at an elevated rate of 4.0 C, the battery sustained a substantial reversible capacity of 758.8 mAh g⁻¹, demonstrating the excellent rate performance. Furthermore, under a stringent high sulfur loading of 5.8 mg cm⁻², the Li-S battery still achieved a specific capacity of 862.6 mAh g⁻¹ at 0.2 C, alongside outstanding cycling stability, retaining 92.3% of its initial capacity after 120 charge-discharge cycles. DFT calculations and in situ Raman spectroscopy revealed that the Fe₃Se₄/FeSe heterointerface augments the density of states (DOS) near the Fermi level, reducing the activation energy barrier for Li₂S decomposition (Figure 15(h) and 15(i)). Moreover, the spontaneous formation of a built-in electric field across the interface accelerates localized charge-transfer kinetics. Collectively, this work delineates a highly efficacious material engineering paradigm for the rational design and optimization of advanced functional architectures in next-generation Li-S battery.

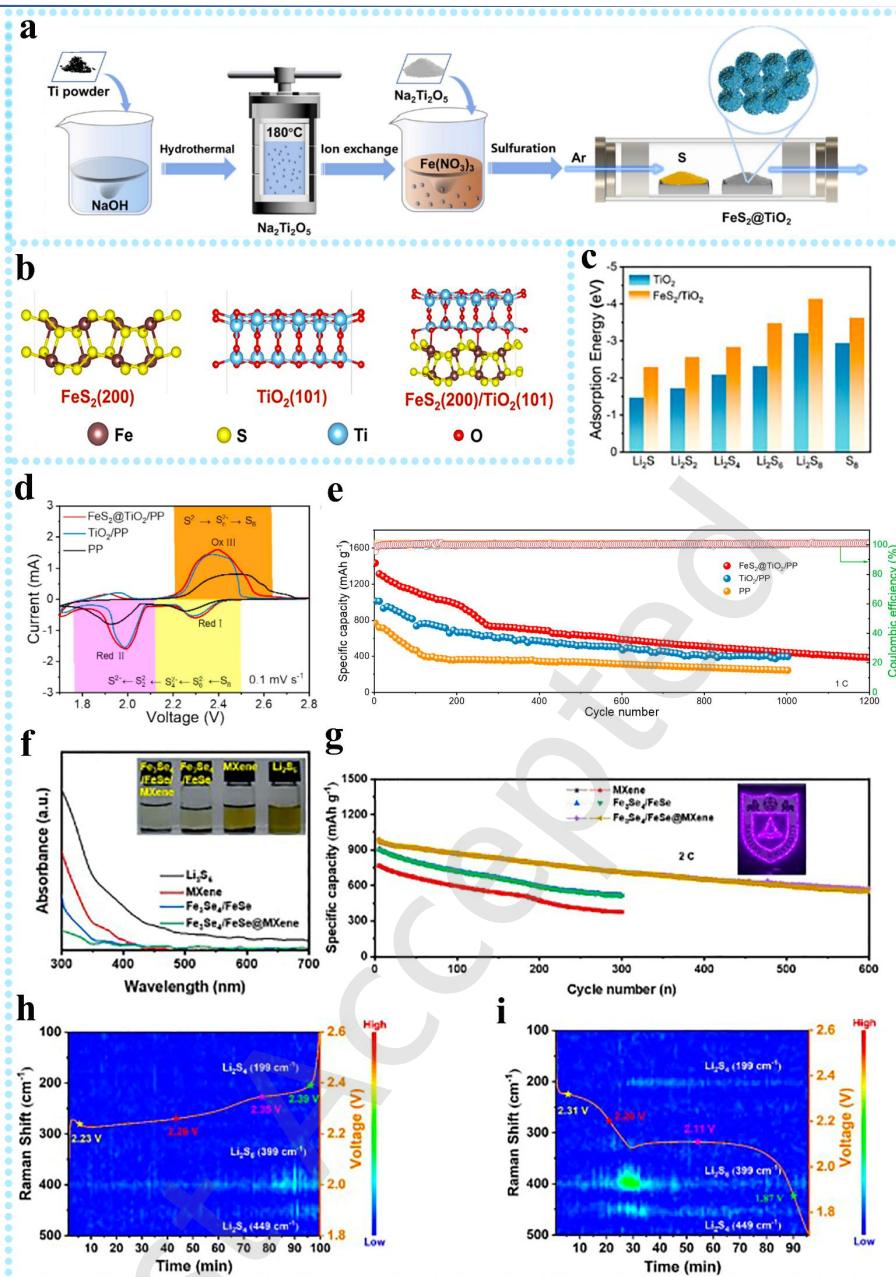


Figure 15 (a) Schematic depiction of the synthesis of FeS₂@TiO₂. (b) Calculation model of front views of FeS₂ (200), TiO₂ (101) and schematic illustration of FeS₂/TiO₂ heterostructure. (c) The adsorption energies of LiPSs and S₈ cluster with the TiO₂ and FeS₂/TiO₂ heterojunction. (d) The CV curves of Li-S batteries with different separators at 0.1 mV s⁻¹. (e) Cycling performance at 1.0 C for Li-S batteries with different separators. Reproduced with permission[67]. Copyright 2025, Elsevier. (f) UV-vis adsorption spectra, the inset is the corresponding digital photographs of Li₂S₆ adsorption experiment. (g) cycling life of the batteries at 2.0 C, the inset is a photograph showing a LED. (h-i) *In situ* Raman spectra of Li-S batteries with Fe₃Se₄/FeSe/MXene-PP separator during discharge and charge at 0.5 C. Reproduced with permission[33]. Copyright 2023, Elsevier.

(2) Mn

Mn, the fourth most abundant transition metal in the Earth's crust, is distinguished by its low toxicity and exceptional cost-effectiveness[158]. Combined with the inherently low cost of sulfur cathodes, Mn-based materials are expected to break the cost constraints of current energy storage systems and enable the development of highly cost-competitive battery systems. Furthermore, Mn and its compounds effectively mitigate the LiPSs shuttle effect and accelerate multiphase sulfur conversion kinetics, comprehensively augmenting overall battery performance and underscoring their profound fundamental and industrial potential for advancing the practical application of Li-S battery[159, 160].

As shown in Figure 16(a), Raza et al. introduced a Mn²⁺-containing single-phase high-entropy oxide (MS-HEO) as a functional separator modifier for Li-S batteries via MOF-template-assisted low-temperature calcination strategy[161]. Leveraging the synergistic electrocatalytic effects of multi-metallic active sites and robust chemisorption affinities toward sulfur species, the MS-HEO enhanced LiPSs conversion efficiency and effectively suppressed the shuttle phenomenon (Figure 16(b)). In addition, the ultralow-loading MS-HEO coating (0.23 mg cm⁻²; Figure 16(c)) provided a compact catalytic interface that dynamically propelled LiPSs redox kinetics and Li⁺ transport. Crucially, this strategy minimizes the weight of the separator, thereby elegantly bridging the gap between high practical

energy density and prolonged cycling stability. Electrochemical test results revealed that the Li-S battery with the MS-HEO-modified separator delivered an exceptional initial specific capacity of 1642 mAh g⁻¹ under a low sulfur loading (~1.5 mg cm⁻²), and exhibited a capacity decay rate of only 0.055% per cycle after 450 cycles at 1.0 C (Figure 16(d)). Cyclic voltammetry (CV) profiles exhibited augmented peak currents and minimized electrochemical polarization (Figure 16(e)), indicative of accelerated LiPSs conversion kinetic. The EIS further corroborated that the MS-HEO modifier effectively diminished interfacial charge transfer resistance and improves Li⁺ diffusion (Figure 16(f)). Under high sulfur loading (~7.0 mg cm⁻²), the Li-S battery delivered an initial capacity of 819 mAh g⁻¹ and sustained robust electrochemical stability over 30 cycles. Furthermore, the modified Li-S battery demonstrated superior rate capability, exhibiting excellent capacity retention across current densities from 0.1 C to 2.0 C. When the current density was restored to 0.1 C, the reversible capacity recovered to 1215 mAh g⁻¹, validating the efficient anchoring and catalytic conversion capabilities of the Mn-based high-entropy oxide separator, even under high-loading conditions.

Furthermore, the pronounced intrinsic polarity and a suitable redox window of defective MnO₂ (D-MnO₂) confer compelling attributes for its application as a functional separator modifier in Li-S batteries. Upon integration, D-MnO₂ not only enhanced the adsorption capacity for LiPSs but also significantly improved the multiphase redox kinetics of sulfur species. For example, Feng et al. applied defect-rich MnO₂ as a separator coating, exploiting its inherent strong polarity to achieve highly efficient LiPSs capture[162]. Simultaneously, D-MnO₂ scaffold functioned as a robust redox mediator to promote the catalytic conversion of LiPSs, while the presence of oxygen vacancies further enhanced the intrinsic conductivity of the material, synergistically boosting interfacial charge-transfer kinetics and maximizing active sulfur utilization. Electrochemical

evaluations demonstrated that Li-S batteries with D-MnO₂-modified separator exhibited exceptional high-rate capability and prolonged cyclic longevity. The enhanced reaction kinetics effectively minimized electrochemical polarization and yielded superior capacity retention. Consequently, the modified system delivered an initial discharge specific capacity of 1074 mAh g⁻¹ at 0.2 C, retaining 55% of its capacity over 500 cycles with an ultralow decay rate of merely 0.089% per cycle.

Mn-based heterojunctions have also emerged as highly efficacious architectures for augmenting the electrochemical performance of Li-S batteries. For instance, Ma et al. constructed an α -MnO₂/RuO₂ heterostructure on PP separator, which effectively promoted the conversion efficiency of LiPSs during both the sulfur reduction and oxidation processes, concurrently optimizing the activation barriers of the rate-determining steps[163]. Corroborated by in-situ Raman spectroscopy and DFT calculations, this tailored heterointerface was shown to systematically regulate the critical transition states within the LiPSs conversion pathway. Furthermore, the strategic integration of RuO₂ significantly enhanced the electron conduction capability of the composite separator (Figure 16(g-i)). Consequently, this functionalized architecture mitigated the dissolution and subsequent shuttling of soluble LiPSs. Electrochemical test results demonstrated that the Li-S battery with the α -MnO₂/RuO₂-modified separator maintained a high areal capacity exceeding 5.0 mAh cm⁻² after 55 cycles at 0.2 C, achieving an exceptional capacity retention rate of 91.7%. Notably, a scaled-up pouch battery based on this modified separator retained 78.2% of its initial capacity after 200 cycles at 0.1 C, demonstrating promising potential for commercial application (Figure 16(j)). This study provides new insights and establishes a robust interfacial engineering paradigm for precisely regulating multiphase reaction pathways in next-generation Li-S batteries.

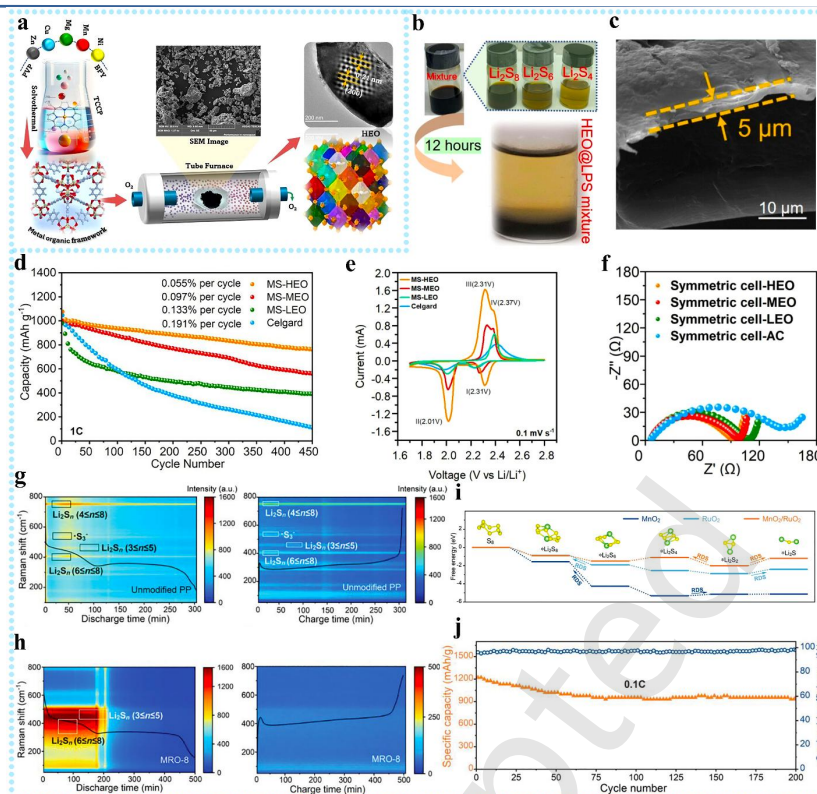


Figure 16 (a) Schematic illustration of entropy depends on oxides fabrication and separator modification. (b) Visual test of adsorption of LPSs in HEO after 12 h. (c) Cross-sectional SEM image of modified separator (MS-HEO). (d) Cycling stability comparison of MS-HEO, MS-MEO, MS-LEO, and Celgard at 1.0 C. (e) CV curves comparison MS-HEO, MS-MEO, MS-LEO, and bare Celgard separator at scan rate of 0.1 mV s⁻¹. (f) Nyquist plots of symmetric batteries of HEO, MEO, LEO, and AC as working and counter electrodes[161]. (g) *In situ* Raman spectra of electrolyte and unmodified PP. (h) *In situ* Raman spectra of electrolyte and MRO-8 modified separator. (i) Free energy profiles of transformation from S₈ to Li₂S on α -MnO₂, RuO₂, and α -MnO₂/RuO₂. (j) Cycling performance of Li-S pouch battery with modified separator. Reproduced with permission[163]. Copyright 2024, Wiley.

(3) Cr

In the field of separator modification for Li-S batteries, Cr-based materials have yet to emerge as a mainstream research focus, with systematic investigations remaining markedly limited. Addressing this gap, Li et al. developed a single-atom catalyst featuring a uniquely under-coordinated CrN₃ structure[164]. This tailored electronic configuration induces a moderate enrichment of electron density within the Cr 3*d* orbitals and activates favorable in-plane orbital orientations, thereby optimizing *d-p* orbital hybridization with sulfur species. Consequently, this structural design preserves sufficient adsorption strength toward LiPSs and significantly reduces the energy barrier of sulfur conversion reactions. Synergistically coupled with the high density of electrochemically active interfaces provided by a two-dimensional porous framework, Li-S battery equipped with the CrN₃-modified separator demonstrated superior electrochemical performance.

At present, the research on ferrous metal-based separator modifiers has predominantly focused on Fe and Mn elements and their corresponding compounds. However, the development of Cr-based materials remains nascent and faces multiple challenges for further advancement. From a materials engineering perspective, ensuring robust structural stability during prolonged electrochemical cycling, alongside mitigating the procedural complexity and stringent conditions (e.g., elevated temperatures and pressures) inherent to current synthetic protocols, necessitates significant refinement. Furthermore, from environmental and safety standpoints, the severe biotoxicity

and ecological risks associated with potential hexavalent chromium (Cr⁶⁺) generation impose rigorous demands for stringent safety oversight throughout both the synthesis and practical deployment phases.

As summarized in Table 2, ferrous metal compounds exhibit remarkable electrocatalytic efficacy when utilized as separator modification materials in Li-S batteries, demonstrating significant potential for accelerating LiPSs conversion. However, their transition to practical application continues to be impeded by multiple performance limitations and implementation barriers. Specifically, although Fe-based compounds possess an abundance of active sites, their overall electrochemical performance is constrained by the inherent conflict between insufficient electrical conductivity and the complexities of synergistic functional regulation[156, 165]. Similarly, while Mn-based compounds deliver high catalytic activity, their long-term cycling stability is severely compromised by lattice degradation originating from the Jahn-Teller effect, coupled with deleterious Mn dissolution during repetitive charge-discharge processes[166-169]. Furthermore, despite the robust LiPSs chemisorption capabilities exhibited by Cr-based materials, their commercial viability is fundamentally constrained by the combined challenges of hexavalent Cr toxicity, elevated material costs, and poor interfacial compatibility with liquid electrolytes[170]. To overcome these contemporary performance bottlenecks, future research endeavors must prioritize integrated engineering paradigms. The synergistic implementation of microstructural design, interfacial optimization, and

targeted defect chemistry modulation is poised to accelerate electron/ion transport kinetics and fortify structural integrity. By maximizing catalytic conversion efficiency

through these multifaceted strategies, the practical deployment of such advanced functional materials in next-generation Li-S battery can be effectively realized.

Table 2 Electrochemical performance of ferrous metal-based compounds as separator modifiers in Li-S battery

Type of Metals	Coating materials	Coating loading (mg cm ⁻²)	Cathodes	S loading (mg cm ⁻²)	Rate (C)	Initial capacity (mAh g ⁻¹)	Decay rate (%) & Cycles	Ref.
Fe-based compounds	Fe-N ₄ /CNPO	-	KB/S	1.0	1.0	1176	0.080 (500)	[171]
	Fe ₃ C/Fe@NC/G	0.2	S/KB	1.0-1.2	1.0	850	0.062 (500)	[82]
	Fe ₃ C-N-rGO	0.26-0.33	Super/S	0.7-1.0	0.5	774	0.068 (100)	[106]
	rGO/H ₂ TiO _{3-x} Fe	0.3	CNT/S	1.2-1.5	5.0	876	0.035 (1000)	[172]
	Fe/Fe ₃ C@GNC	0.6	SP/S	1.3	1.0	912	0.077 (250)	[173]
Mn-based compounds	Mn ₃ O _{4-x}	0.19	CB/S	1.5	2.5	572	0.028 (2000)	[168]
	D-MnO ₂	-	CMK3/S	1.0	0.2	1074	0.089 (500)	[162]
	treated MnO ₂	0.83	S-CNT	1.1-1.5	1.0	1179	0.082 (500)	[174]
	SMO	-	S/KB	1.0-1.2	0.5	707	0.058 (500)	[175]
	G/M@CNT	0.05	S-CNT	1.1-2.3	1.0	1065	0.029 (2500)	[176]

3.3 Rare-earth metal compounds

Rare-earth metals possess unique 4*f* electronic configurations and incompletely filled electron orbits, endowing them with exceptional optical, electronic, and magnetic properties as well as high chemical reactivity. Consequently, they demonstrate significant application potential in the fields of catalysis, energy storage, and advanced functional materials[177-179]. Recently, rare-earth metal compounds have emerged as pivotal functional materials for addressing the core challenges of the LiPSs shuttle effect and sluggish redox kinetics in Li-S batteries. These architectures facilitate the highly efficient chemical anchoring of LiPSs via strong Lewis acid sites and significantly accelerate multiphase conversion kinetics through flexible valence state transitions, thereby establishing a distinctive synergistic adsorption-catalysis paradigm. Furthermore, their inherent structural designability (e.g., MOF-derived materials, single-atom catalysts and heterojunction) facilitates the construction of multi-level active interfaces, which not only effectively suppress LiPSs shuttling but also enhance electrode interfacial stability and electrochemical reversibility[180-182]. This paradigm provides innovative material design strategies and theoretical foundation for advancing the performance of Li-S batteries. This section systematically reviews the application of rare-earth metal compounds and their derived architectures in separator modification for Li-S battery, with a primary focus on the influence of the microstructural characteristics on LiPSs anchoring-catalysis behavior, and the elucidation of the corresponding structure-property relationships and reaction mechanisms.

As illustrated in Figure 17(a), Hong et al. developed a novel composite for separator modification by hybridizing a cerium-based MOF with CNT (Ce-MOF/CNT) to enhance the electrochemical performance of Li-S batteries[183]. This rationally designed architecture harnesses the synergistic effects of physical confinement and robust chemisorption to

effectively immobilize LiPSs. Moreover, the superior intrinsic electrocatalytic activity of the composite accelerates the multiphase conversion of LiPSs, effectively mitigating the shuttle effect (Figure 17(b) and 17(c)). Consequently, Li-S battery with Ce-MOF/CNT modified separator demonstrated exceptional electrochemical performance and cycling stability even under high sulfur loading conditions. At a sulfur loading of 2.5 mg cm⁻², the battery delivered an initial specific capacity of 1021.8 mAh g⁻¹ at 1.0 C and retained 838.8 mAh g⁻¹ after 800 cycles with a Coulombic efficiency approaching 100%. Remarkably, even when subjected to an elevated sulfur loading of 6.0 mg cm⁻², the Li-S battery achieved an initial specific capacity of 993.5 mAh g⁻¹ at 0.1 C and retained 886.4 mAh g⁻¹ after 200 cycles (Figure 17(d) and 17(e)), demonstrating outstanding potential for practical application.

Although the unique 4*f* orbital configurations of rare-earth metals theoretically provide a versatile range of electronic states and coordination environments, these deep-seated orbitals are characteristically shielded by outer-shell 5*d* and 6*s* electrons. This shield effect often impedes their effective activation within conventional catalytic frameworks[184, 185]. Consequently, despite the significant potential for electronic modulation in theory, the practical electrocatalytic activity of rare-earth-based materials in redox reactions frequently remains suboptimal. Recent investigations have demonstrated that the rational design of single-atom local coordination structures can effectively activate spin-orbit coupling in rare-earth metals, thereby enhancing the electrocatalytic performance. As shown in Figure 16(f), Zhou et al. synthesized a samarium (Sm)-based single-atom catalyst featuring a unique Sm-N₃C₃ coordination motif for deployment in Li-S battery[186]. Comprehensive theoretical simulations and experimental characterizations revealed that the Mott transition between the 4*f* and 5*d* orbitals at the Sm-N₃C₃ sites induces *f-d-p* orbital hybridization with LiPSs, which markedly accelerates

LiPSs conversion kinetics and lowers the decomposition energy barrier for Li_2S (Figure 17(g)). The Li-S battery with $\text{Sm-N}_3\text{C}_3$ modified separator exhibited exceptional durability, maintaining 84.3% capacity retention after 2000 cycles at a high rate of 4.0 C, while sustaining a reversible capacity exceeding 600 mAh g^{-1} . Additionally, the $\text{Sm-N}_3\text{C}_3$ layer functioned as a lithiophilic interface that facilitates uniform lithium deposition and effectively suppresses dendrite growth (Figure 17(h)). Notably, the $\text{S/CNTs}[\text{Sm-N}_3\text{C}_3@\text{PP}]/\text{Sm-N}_3\text{C}_3\text{-Li}$ battery achieved a high capacity retention of 80.6% after 100 cycles at 0.2 C, demonstrating excellent practical potential (Figure 17(i)). This research not only realizes the efficient utilization of rare-earth single atoms in Li-S battery but also provides important insights for the development of advanced electrocatalysts for next-generation energy storage technologies.

In the rational design of separator modifiers for Li-S battery, the efficient management of LiPSs requires overcoming the critical challenge of synergistically enhancing activity and stability. While non-ferrous and ferrous transition metal compounds (e.g., Co, Fe and Ni) exhibit superior electrocatalytic activity that effectively propels LiPSs adsorption and conversion, their high surface energies frequently induce irreversible bonding with sulfur species, inevitably leading to active site poisoning and catalyst deactivation[187]. Conversely, rare-earth oxides possess exceptional chemical stability but suffer from insufficient intrinsic catalytic activity, rendering them incapable of satisfying the kinetic requirements for rapid LiPSs conversion. Therefore, integrating the advantages of both material types to construct a novel separator modification system with both high catalytic activity and long-term stability has become a key scientific challenge in this field.

To circumvent this limitation, Wang et al. constructed a rationally designed non-ferrous transition metal/rare-earth oxide heterostructure comprising ultrafine gadolinium oxide and cobalt nanocrystals confined within a nitrogen-doped carbon shell ($\text{Gd}_2\text{O}_3/\text{Co}@\text{NC}$)[188]. This heterostructure design provides an innovative paradigm to resolve the classical activity-stability trade-off inherent to Li-S battery separator materials. As elucidated by both experimental characterizations and theoretical computations (Figures 17(j-m)), the strong electronic coupling established between Co and Gd_2O_3 at the heterointerface synergistically

modulates the local electronic structure and binding energetics. This interfacial effect profoundly accelerates LiPSs conversion kinetics while effectively forestalling transition metal sulfidation. Electrochemical test results showed that the Li-S battery with the $\text{Gd}_2\text{O}_3/\text{Co}@\text{NC}$ modified separator achieved a specific capacity of 628.0 mAh g^{-1} at a high current density of 4.0 C, retaining 504.2 mAh g^{-1} after 500 cycles, demonstrating excellent cycling stability (Figure 17(o)). Even under harsh conditions including high sulfur loading (5.1 mg cm^{-2}) and lean electrolyte ($\text{E/S} = 7.5 \text{ }\mu\text{L mg}^{-1}$), the Li-S battery delivered a high areal capacity of 4.8 mAh cm^{-2} , indicating promising practical potential. This study provided a new design strategy for developing high-performance separator modification materials for Li-S battery.

The multi-step sulfur redox reactions, characterized by complex reaction pathways and differentiated energy requirements, lead to sluggish overall kinetics and have become a critical bottleneck limiting the performance enhancement of Li-S battery. The integration of high-efficiency electrocatalysts is widely acknowledged as a paramount strategy to propel LiPSs conversion and mitigate their dissolution and shuttling within the electrolyte. However, traditional single-component catalysts possess only unidirectional electron donation or acceptance capabilities, making it difficult to simultaneously optimize the reaction energy barriers of all steps in the sulfur reduction reaction[189]. Although previous investigations have explored heterojunction architectures to facilitate synergistic multi-step catalysis, weak interfacial electronic coupling and constrained interfacial charge transfer restrict the enhancement of electrode reaction kinetics[190-192]. Therefore, developing a single catalyst material with dynamic electron regulation capability has become an important research direction. Such advanced architectures function as active electron donors to sulfur species during the cathodic discharge process, while reversibly transitioning into electron acceptors during the anodic charge phase, thereby establishing a continuous, reversible electron-buffering cycle. These materials achieve a reduction in activation energy barriers across all reaction stages by concurrently activating both kinetically favorable and sluggish steps in the reaction pathway. This capability enables sustained efficient electrocatalysis and pioneers a new material paradigm for advanced Li-S battery.

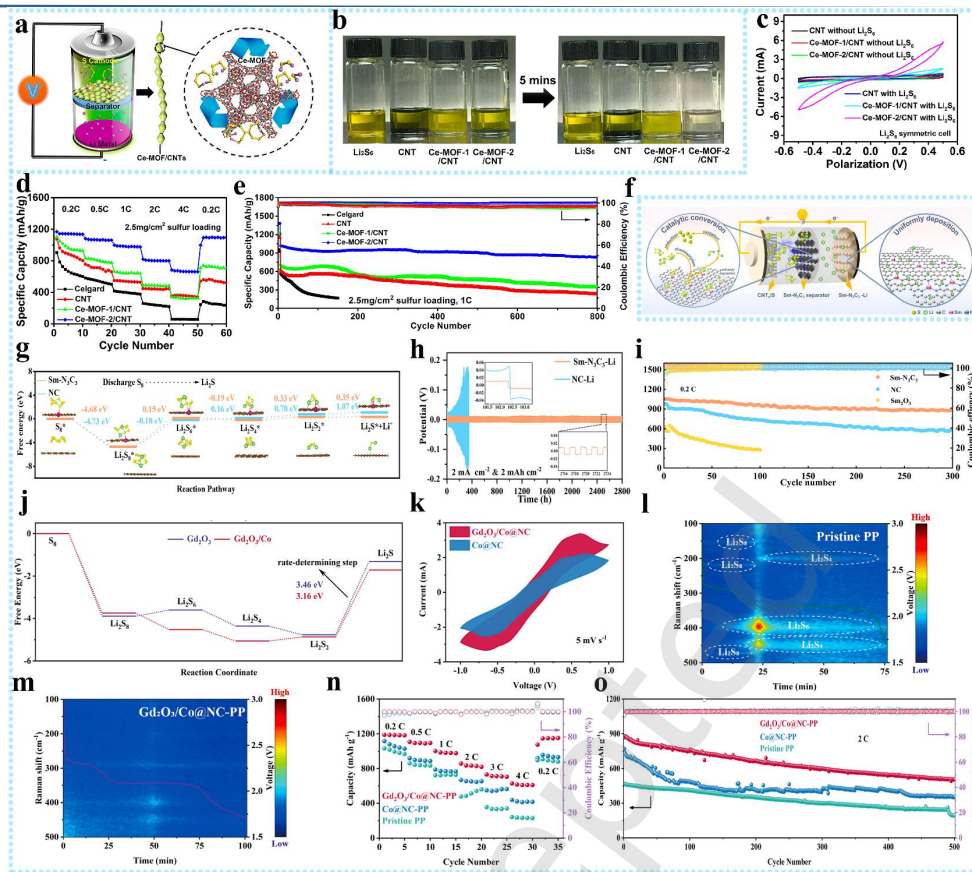


Figure 17 (a) Scheme of MOFs/CNT composites with catalysis of the conversion of LiPSs as the separator coating materials for Li-S battery. (b) Visual test of adsorption of LiPSs in CNT, Ce-MOF-1/CNT, and Ce-MOF-2/CNT. (c) CV curves of symmetrical batteries using different coating materials with and without Li_2S_6 at a scan rate of 50 mV s^{-1} . (d) Rate performance at various rates for the batteries with different separator. (e) Cyclic performance of batteries with different separator at 1.0 C for 800 cycles. Reproduced with permission[183]. Copyright 2019, American Chemical Society. (f) Illustration of the $\text{Sm-N}_3\text{C}_3\text{-Li}/\text{Sm-N}_3\text{C}_3/\text{PPIS}/\text{CNTs}$ batteries. (g) Relative Gibbs free energies of conversion reactions from S_8 to Li_2S catalyzed by $\text{Sm-N}_3\text{C}_3$ and NC. (h) Cycling performance of symmetric battery with $\text{Sm-N}_3\text{C}_3\text{-Li}$ and NC-Li electrodes. (i) Cycling performance of $\text{Sm-N}_3\text{C}_3\text{-Li}/\text{Sm-N}_3\text{C}_3/\text{PPIS}/\text{CNTs}$ battery at 0.2 C . Reproduced with permission[186]. Copyright 2024, Wiley. (j) Gibbs free energies for the reduction of LiPSs on Gd_2O_3 and $\text{Gd}_2\text{O}_3/\text{Co}$. (k) CV curves of $\text{Gd}_2\text{O}_3/\text{Co}@/\text{NC}$ and $\text{Co}@/\text{NC}$ symmetrical batteries. In situ Raman results for batteries with (l) PP and (m) $\text{Gd}_2\text{O}_3/\text{Co}@/\text{NC-PP}$. (n) Rate performance of the batteries with different separators. (o) Cycle performance of the battery with different separators at 2.0 C . Reproduced with permission[188]. Copyright 2025, American Chemical Society.

As illustrated in Figure 18(a), Yu et al. constructed an electron structure with $\text{Tb}^{3+}/^{4+}$ dynamic valence states on a nitrogen-doped graphene (Gh) conductive substrate ($\text{Gh-Tb}^{3+}/^{4+}$) and employed it as a separator modifier in Li-S batteries to activate continuous and efficient sulfur reduction reactions[193]. This structure optimized LiPSs adsorption behavior by the synergistic effects of Tb-S and N-Li bonds, significantly reducing reaction activation barriers while accelerating Li^+ transport, achieving selective catalytic conversion of both long and short-chain LiPSs during charge-discharge cycling. By integrating theoretical computations, in-situ spectroscopic characterizations, and systematic electrochemical analyses (Figure 18(b)), the intrinsic kinetic and underlying reaction mechanisms were comprehensively elucidated. The results revealed that Tb^{3+} preferentially catalyzed the conversion of long-chain LiPSs, while Tb^{4+} predominantly promoted short-chain LiPSs conversion. Leveraging its moderately unfilled f-orbital electronic configuration, the Li-S battery with $\text{Gh-Tb}^{3+}/^{4+}$ modified separator delivered a high discharge specific capacity of 1522 mAh g^{-1} at 0.2 C and exhibited exceptional cycling stability with a capacity decay rate of only 0.087% per cycle after 500 cycles at 1.0 C (Figure 18(c)). Even under

harsh conditions including high sulfur loading (5.2 mg cm^{-2}) and lean electrolyte ($E/S = 7.5 \text{ } \mu\text{L mg}^{-1}$), the Li-S battery maintained remarkable electrochemical performance. Ultimately, this pioneering work validates the considerable potential of f-orbital engineering in advancing high-energy-density Li-S battery.

Furthermore, layered rare-earth hydroxides (LREHs) have recently garnered escalating attention as emerging functional materials in the field of energy storage. Their generalized crystallographic composition is formulated as $\text{Ln}_8(\text{OH})_{20}\text{A} \cdot n\text{H}_2\text{O}$, where Ln denotes a rare-earth metal (e.g., Nd, Sm, Eu, and Gd), and A represents an intercalated anion (e.g., NO_3^- , Cl^- , and SO_4^{2-}). This structure is constructed with rare-earth metal hydroxides as the host layers, wherein the structural dimensions and chemical environment of the two-dimensional interlayer channels can be precisely tailored by the modulation of host layer architecture and interlayer anion species. As shown in Figure 18(d), Wang et al. prepared layered gadolinium hydroxide $[\text{Gd}_2(\text{OH})_5(\text{H}_2\text{O})_n]\text{Cl}$ nanosheets (LGdH) with a hydrocalcite-like structure via a hydrothermal method and constructed a two-dimensional rare-earth-based functional material (LGdH@GO) by compounding with graphene oxide (GO)[194]. The

LGdH@GO composite was then employed to construct a functional coating on the separator for Li-S battery. Comprehensive experimental evaluations revealed that the LGdH nanosheets not only possess a chemisorption affinity toward migrating LiPSs but also exhibit exceptional electrocatalytic activity, significantly promoting the liquid-solid conversion process of LiPSs (Figure 18(e-g)). Meanwhile, the highly conductive GO matrix establishes an interconnected network that facilitates rapid and continuous electron and ion transport. This synergistic effect between these components substantially enhanced the redox kinetics of the battery. Benefiting from the cooperative advantages of

the LGdH@GO modification layer, the Li-S battery with LGdH@GO modified separator demonstrated outstanding rate capabilities, registering reversible specific discharge capacities of 1163.26, 968.32, 872.52, 779.33, 703.77, and 605.34 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 C, respectively (Figure 18(h)). Moreover, after 500 cycles at a high rate of 2.0 C, the capacity decay rate per cycle was only 0.087% (Figure 18(i)). This study provided new insights for designing highly electrocatalytic separator modification layers for Li-S battery and highlighted the broad application prospects of layered rare-earth hydroxides in high-efficiency energy storage systems.

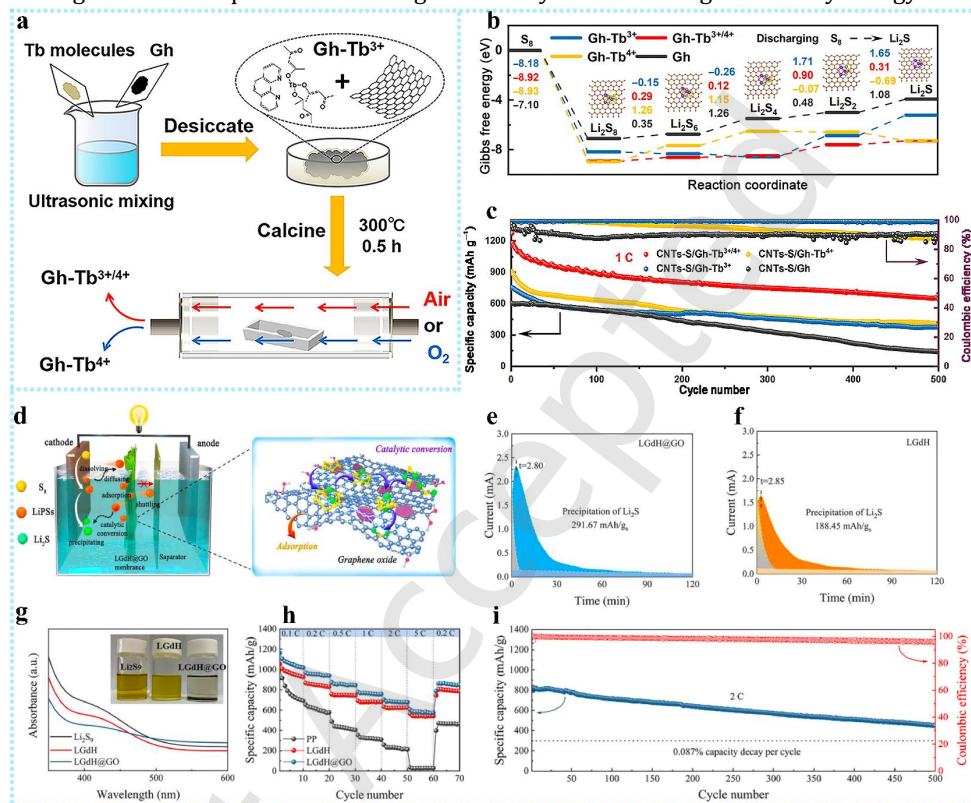


Figure 18 (a) Illustration of the synthetic procedures for Gh-Tb^{x+} (x = 3, 4) composites. (b) The changes of Gibbs free energy during sulfur reduction reactions on four catalyst surfaces. (c) Cycling performance of Li-S battery at 1.0 C with different cathode interlayer[193]. (d) Illustration of the catalytic conversion mechanism of LiPSs on LGdH@GO surface. Potentiostatic discharge profiles of Li₂S₈ solution on (e) LGdH@GO and (f) LGdH at 2.05 V. (g) UV-vis spectra of Li₂S₉ solution mixed with various samples. The inset is a digital image of LiPSs adsorption test after 24 h. (h) Rate performances of Li-S battery at various current density from 0.1 C to 5.0 C for different separators. (i) Cycling performance of Li-S batteries with LGdH@GO modified separator at a current density of 2.0 C for 500 cycles. Reproduced with permission[194]. Copyright 2024, Elsevier.

As summarized in Table 3, rare-earth metals and their derivative compounds exhibit substantial potential for addressing the critical challenges of Li-S battery, an attribute fundamentally rooted in their unique electronic configurations. Nevertheless, the practical deployment of these advanced material systems remains impeded by several challenges. First, the relatively low crustal abundance of specific rare-earth elements leads to high raw material costs, thereby restricting large-scale commercial viability. Second, the development of green, scalable, and sustainable synthetic protocols demands substantial

refinement to align with contemporary ecological and industrial standards[195]. Third, from a materials engineering perspective, achieving precise atomic-level control over lattice matching and interfacial defect chemistry during the fabrication of rare-earth-based heterojunctions remains technically challenging[196]. Systematically addressing these multidimensional challenges is imperative to unlock the full catalytic potential of rare-earth-based materials in high-performance Li-S battery.

Table 3 Electrochemical performance of rare-earth metals-based compounds as separator modifiers in Li-S batteries

Type of Metals	Coating materials	Coating loading (mg cm ⁻²)	Cathodes	S loading (mg cm ⁻²)	Rate (C)	Initial capacity (mAh g ⁻¹)	Decay rate (%) & Cycles	Ref.
Rare-earth metals-based compounds	Nd ₂ O ₃ /RGO	-	acetylene black/S	-	2.0	879	0.052 (1000)	[197]
	Gd ₂ O ₃ /Co@NC	0.19	S@HPC	1.5	2.0	878.6	0.085 (500)	[188]

Gh-Tb	-	CNTs-S	1.0	1.0	1157	0.087 (500)	[193]
Eu ₂ O ₃ /KB	0.22	Pure S	1.3	2.0	633	0.068 (1000)	[198]
YHS@C	-	YHS@C/S	2.1	1.0	809.65	0.710 (500)	[184]
MWCNTs/CeO ₂	0.15	Super P/S	1.8-2.0	0.2	898.3	0.140 (300)	[199]
CeO ₂ @G	0.38	S/ketjen black	1.2	1.8	861	0.044 (300)	[200]
Sc ₂ O ₃ @CNT	-	CMK8-S	1.5	1.0	1.37	0.480 (500)	[201]
Y ₂ O ₃ -KB	-	KB/S	1.2	1.0	1054	0.112 (816)	[202]
CeO ₂ /KB	0.25	Pure S	1.3	2.0	832	0.060 (1000)	[203]

3.4 Noble metal compounds

Noble metals (e.g., Pt, Ir, Pd, and Ru) have garnered significant attention as highly efficient electrocatalysts for Li-S battery owing to their unique electronic structures and exceptional catalytic activities that accelerate LiPSs conversion kinetics and maximize sulfur species utilization[204, 205]. However, their widespread practical application is severely hampered by prohibitive costs and natural scarcity. To circumvent these limitations, a common strategy involves integrating trace amounts of noble metals with cost-effective transition metals or high-surface-area carbon matrices. This synergistic design effectively minimizes noble metal loading, thereby reducing overall material costs without compromising electrochemical performance. For instance, Arava et al. engineered a composite modifier by uniformly depositing Pt nanoparticles onto a graphene (GO) substrates, systematically evaluating its electrochemical impact relative to Ni/GO, and pristine GO architectures[206]. As depicted in Figure 19(a), the Li-S battery with Pt/GO modified separator delivered the highest specific capacity, significantly surpassing the Ni/GO-based counterpart. Notably, this configuration exhibited a capacity improvement of approximate 40% over the battery with pristine GO-modified separator, with a Coulombic efficiency consistently above 99.3%. Comprehensive studies demonstrated that the highly dispersed Pt nanoparticles on the GO effectively accelerated the reversible conversion kinetics of LiPSs, substantially improving the reaction efficiency and cycling stability of sulfur species (Figure 19(b) and 19(c)). Inspired by these foundational insights, the targeted application of noble metals as functional separator modifiers has emerged

as a compelling frontier in the optimization of advanced Li-S batteries[207].

Similarly, Zuo et al. developed a composite modifier by anchoring iridium nanoparticles onto a highly conductive Ketjen black matrix (KB@Ir) to serve as a functional separator coating for Li-S batteries (Figure 19(d))[205]. Comprehensive visual adsorption assays combined with XPS characterizations confirmed robust chemisorption between the Ir nanoparticles and LiPSs, effectively mitigating the shuttle effect (Figure 19(e)). CV and EIS evaluations revealed that Li-S battery with KB@Ir modified separator exhibited a lower Tafel slopes, higher current responses, and reduced interfacial charge-transfer resistances. These findings substantiate that the incorporation of Ir depresses thermodynamic activation barriers and accelerates multiphase sulfur redox kinetics (Figure 19(f) and 19(g)). As shown in Figures 19(h) and 19(i), electrochemical assessments further confirmed that the Li-S battery with the KB@Ir modified separator demonstrated significant enhancements in both rate capability and cycling stability compared to the control battery. At 0.2 C, the Li-S battery with the KB@Ir modified separator delivered a high initial specific capacity of 1508 mAh g⁻¹, corresponding to a remarkable active sulfur utilization of 90.0%. After 500 cycles at 1.0 C, the battery sustained an ultralow capacity decay rate of merely 0.105% per cycle alongside a persistently high Coulombic efficiency. Ultimately, this investigation provides compelling experimental validation and innovative design principles for integrating noble metal-based functional architectures into high-efficiency Li-S battery separator modifications.

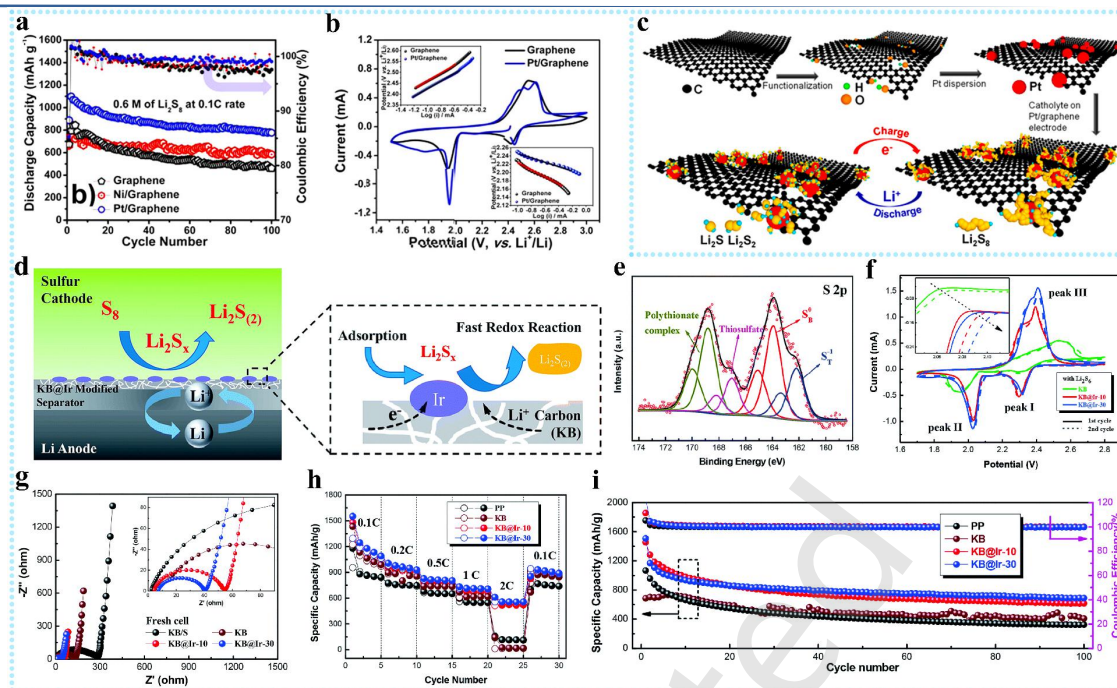
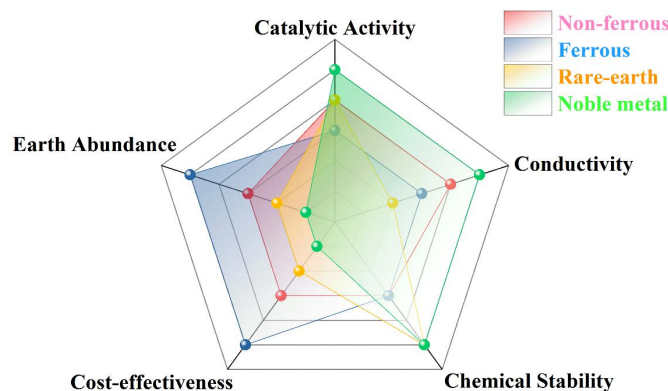


Figure 19 (a) Galvanostatic charge/discharge behavior and Coulombic efficiency of pristine and electrocatalyst anchored graphene electrodes at 0.1 C. (b) CV curves of graphene and Pt/graphene electrodes at a scan rate of 0.05 mV s^{-1} (inset: Tafel plots for corresponding oxidation and reduction reactions). (c) Illustration of electrocatalyst anchored graphene nanocomposite preparation and its interaction with LiPSs during charge/discharge process of the Li-S battery. Reproduced with permission[206]. Copyright 2015, American Chemical Society. (d) Schematic of a Li-S battery configuration with a KB@Ir modified separator. (e) S 2p XPS spectra of KB@Ir catalytic layer after cycling. (f) CV profiles of Li-S batteries with Li_2S_6 as the active material at the scan rate of 0.1 mV s^{-1} . (g) Nyquist plots of the batteries with or without the KB@Ir catalytic layer before cycling. (h) Rate performance of Li-S battery with different separators. (i) Cycle performance of Li-S battery with different separators at 0.2 C. Reproduced with permission[205]. Copyright 2017, Royal Society of Chemistry.

Despite the extraordinary electrocatalytic proficiency of noble metals, their prohibitive costs and elemental scarcity severely impede their large-scale application in practical energy storage systems. Consequently, the direct implementation of noble metal-based functional modifiers in Li-S battery separators remains an ancillary research direction, due to the considerable gap between the economic viability and practical application requirements. To benchmark the practical viability of various metal-based modifiers for Li-S battery, Figure 20 presents a semi-quantitative radar chart comparing non-ferrous, ferrous, rare-earth, and noble metal-based materials across five pivotal metrics: catalytic activity, electrical conductivity, chemical stability, cost-effectiveness, and elemental abundance. As elucidated by the radar chart, no single category of metal compounds exhibits a universally optimal properties, revealing an inherent trade-off among the evaluated metrics. Specifically, while noble metals materials deliver exceptional catalytic activity and electronic conductivity, their commercial feasibility is severely hindered by economic constraints and resource limitations. Conversely, earth-abundant ferrous metals (e.g., Fe, Mn, and Cr) offer unparalleled cost-effectiveness, however, their constrained intrinsic conductivity and susceptibility to structural degradation (e.g., Mn dissolution) often compromise the requisite kinetics for rapid and durable LiPSs conversion. Rare-earth compounds demonstrate robust chemical stability and unique $4f$ -orbital-driven catalytic kinetics, but their inherently low electrical conductivity and substantial raw-material costs preclude their deployment as isolated functional layers. Meanwhile,

other non-ferrous transition metals exhibit a comparatively balanced multiparameter profile, although their broader application remains encumbered by structural instabilities and the high economic premiums associated with critical elements such as Co and Ni.

Figure 20 Radar chart of the comprehensive properties of non-iron, iron, rare earth, and noble metal compounds used for separator modification



in Li-S battery.

Across the aforementioned non-ferrous, ferrous, rare-earth, and noble metal compounds, their practical must be evaluated under harsh commercial parameters such as high areal sulfur loading and lean electrolyte. As shown in Table 4, the current literature addressing such stringent conditions is predominantly concentrated on non-ferrous and ferrous metals, reflecting the inherent practical trade-offs among these four categories. Non-ferrous and ferrous metal compounds currently represent the most pragmatic and widely investigated choices for scale-up. Their relatively low

atomic mass and robust conductive architectures (e.g., nitrides, carbides, SACs) ensure continuous electron/ion transport, routinely sustaining impressive capacities under high sulfur loading and lean electrolyte conditions. In contrast, while rare-earth metal compounds deliver superior chemisorption affinity via oxygen vacancies under practical operating conditions, their high atomic mass compromises

the energy density of the battery. Moreover, while noble metals boast unparalleled intrinsic catalytic, their exorbitant costs fundamentally preclude widespread commercialization. Consequently, the prevailing dominance of ferrous and non-ferrous materials in Li-S battery evaluations underscores that selecting the optimal TMCs separator modifier necessitates a multidimensional balance.

Table 4 Performance comparison of TMC-modified separators under practical operating conditions (high sulfur loading and lean electrolyte)

Separator	Cathode	Sulfur loading (mg cm ⁻²)	E/S ratio (μL mg ⁻¹)	Current rate (C)	Initial capacity (mAh g ⁻¹)	Capacity retention (cycles)	Ref.
Co/Co _{0.85} Se@NC-PP	Super P/S	10.7	6	0.05	935	77.0% (40)	[208]
NC@CoNiFe/CNTs-PP	CNT/S	8.9	11	0.1	999	81.4% (100)	[209]
NbB ₂ /rGO/PP	CNT/S	7.1	10	0.1	600	98.5% (40)	[210]
Co ₃ Fe ₇ -MXene-PP	KB/S	3.2	4	0.2	580	91.4% (45)	[211]
MoSe ₂ -NSHC-PP	MoSe ₂ -NSHC/S	3.2	10	0.1	1212	66.6% (50)	[212]
Fe-ZIF-8/PP	CNT/GO/S	5.0	5	0.05	517	96.7% (4)	[213]
H-TiN-Cu-CNFs/PP	CNT/S	3.8	10	0.1	1144	58.3% (100)	[214]
DC/A O-CoVSe NPs/PP	CNT/S	5.6	8	0.2	1027	64.1% (100)	[215]
CoFe/NC@NC-PP	Super P/S	5.3	-	0.1	1000	76.4% (100)	[216]
PP@Pt	Super P/S	4	8	0.05	1365	80.0% (50)	[207]
Gd ₂ O ₃ /Co@NC-PP	S/HPC	5.1	7.5	0.1	941	-(25)	[217]
CeO ₂ /KB/PP	acetylene black/S	3.8	-	0.2	860	99.3% (100)	[203]

4 Design strategies of TMCs-based separator modifiers for overcoming critical challenges

Overall, TMCs serve as versatile modifiers for separators in high-performance Li-S battery, playing a critical role in suppressing LiPSs shuttling, accelerating redox kinetics, and improving electrochemical performance. Therefore, rational material design, precise structural regulation, and scalable synthesis are imperative to synergize robust catalytic and

adsorption properties with optimal cost-effectiveness. Achieving this delicate balance is crucial for bridging the gap between laboratory-scale research and the large-scale commercialization of Li-S battery. The Figure 21 summarizes the fundamental design principles for TMCs as advanced separator modification layers in Li-S battery. Specifically, the design strategies are delineated as follows:

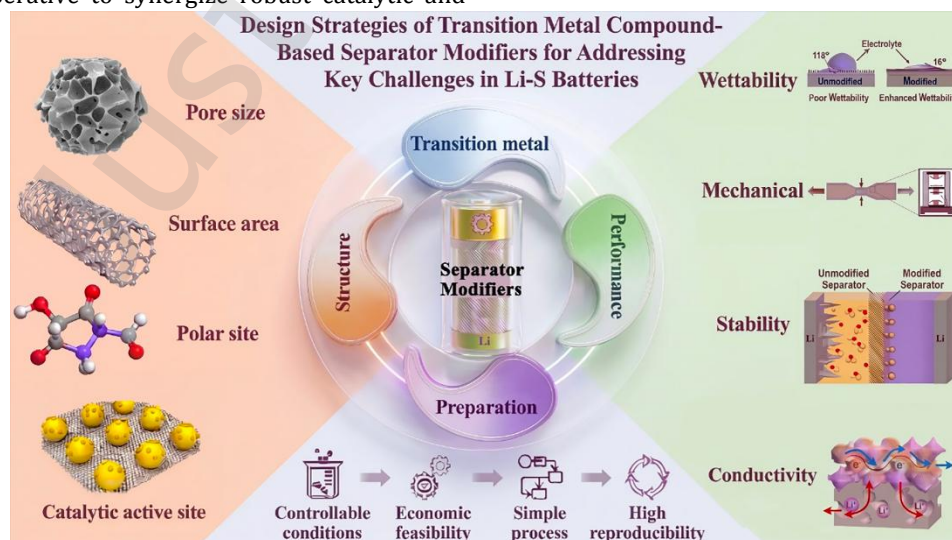


Figure 21 Rational design strategies of TMCs-based separator modifiers for high-performance Li-S battery.

(I) Controllable synthesis and scalability: the synthetic methods for modifier materials should feature simple processes, controllable conditions, and high reproducibility to meet future commercial-scale production requirements. Figure 22 systematically summarizes the mainstream

synthesis strategies for TMCs utilized as separator modification materials for Li-S battery, providing a comparative assessment of the respective advantages and limitations. Consequently, the development of sustainable synthetic routes that synergistically integrate environmental

benignity, cost-effectiveness, and facile processing is paramount for enabling scalable production and industrial translation.

(II) Structure and performance tunability: achieving precise control over the multi-scale microstructure including particle size, pore architecture, and surface morphology is imperative. Specifically, rational nanostructuring maximizes the density of accessible catalytic sites, while targeted doping strategies meticulously modulate the intrinsic electronic environment and surface chemistry. These regulations significantly boost both the chemisorption affinity and catalytic conversion kinetics of LiPSs.

(III) Electrochemical and structural stability: it is imperative for modification materials to preserve their structural integrity and chemical stability throughout extended cycling to mitigate performance decay triggered by material degradation. To ensure sustained efficacy, these functional layers must possess high electronic conductivity to facilitate charge transfer, alongside superior electrolyte wettability and mechanical to withstand the mechanical

stresses of Li-S battery.

(IV) Techno-economic viability and lifecycle sustainability: the design of separator modification materials must be guided by comprehensive lifecycle assessments, holistically evaluating raw material abundance, manufacturing energy footprints, operational longevity, and end-of-life recyclability. Reconciling economic feasibility with superior electrochemical performance necessitates a paradigm shift towards integrated innovations in scalable synthesis, intrinsic property enhancement, and closed-loop recycling architectures.

(V) Lightweight design and practical viability: to optimize the loading amount of the separator modification layer and advance the lightweight structural design of TMCs is a critical strategy for synergistically enhancing LiPSs conversion kinetics, improving cycling stability, and boosting battery energy density. This holds vital significance for advancing Li-S battery from laboratory research toward industrialized applications.

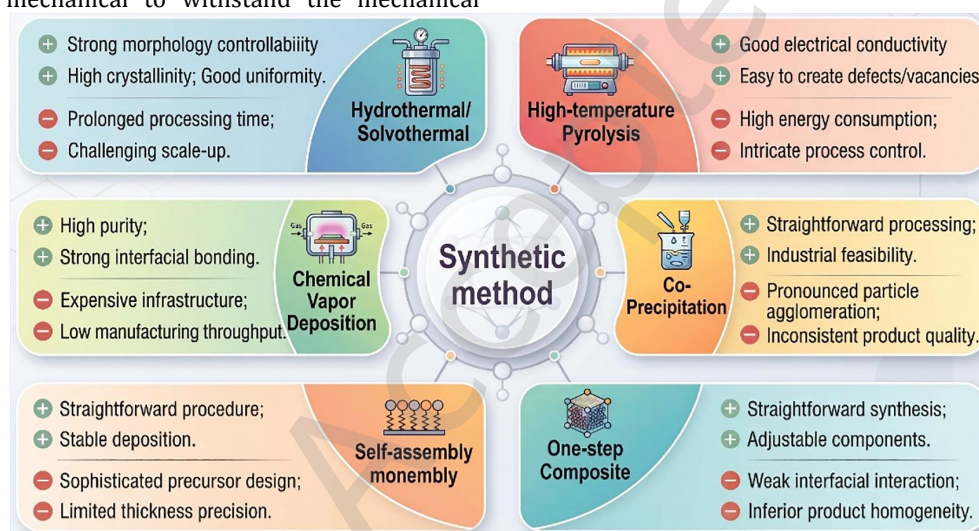


Figure 22 Synthesis strategies for TMCs used as separator modification materials for Li-S battery.

5 Conclusions and perspectives

In this review, we have comprehensively summarized the recent advancements in utilizing TMCs spanning non-ferrous, ferrous, rare-earth, and noble metals as functional separator modifiers for Li-S battery. Special emphasis was placed on elucidating the intrinsic structure-activity relationships that govern LiPSs anchoring, bidirectional catalytic conversion, and overall redox kinetics. Furthermore, the synergistic mechanisms within multi-component TMCs were systematically delineated as a robust strategy to amplify these electrochemical benefits. By effectively suppressing the shuttle effect and accelerating sulfur conversion, TMCs-engineered separators offer a highly promising pathway toward Li-S battery with exceptional sulfur utilization, cycling longevity, and energy density. However, to ultimately translate these impressive laboratory-scale triumphs into practical and industrialized Li-S battery technologies, several pivotal challenges and forward-looking opportunities still remain to be conquered:

First, a significant portion of the TMCs reviewed herein rely on intricate, multi-step synthetic protocols that are often incompatible with the rigorous demands of commercial-scale production and cost-efficiency. For

instance, while solvothermal methods yield highly active catalytic phases, their prolonged reaction durations and substantial solvent-recovery overheads impede high-throughput manufacturing. Similarly, thermal gradients inherent in large-scale pyrolysis frequently leads to heterogeneous particle size distributions, compromising both structural homogeneity and material purity. Consequently, it is paramount to pioneer green, streamlined synthesis routes characterized by mild operating conditions and intrinsic scalability, thereby facilitating a smooth transition from lab-scale preparation to industrial-scale fabrication.

Second, a paradigm shift toward evaluation under realistic operating conditions is urgently required. While TMC-based modifiers demonstrate exceptional efficacy in idealized coin-battery configurations, their electrochemical performance is frequently compromised under stringent practical parameters. To propel the development of viable high-energy-density Li-S batteries, future material design must focus on robust architectures that sustain superior cycling stability under high areal sulfur loadings ($\geq 4 \text{ mg cm}^{-2}$) and lean electrolyte ($E/S \leq 5 \text{ } \mu\text{l mg}^{-1}$) conditions. Moreover, the validation of these materials should advance

beyond standard coin batteries to the systematic assessment of practical pouch batteries under harsh real-world conditions, including wide-temperature operability. Ensuring the long-term structural integrity and sustained catalytic activity of the modification layers in such full-cell configurations stands as a critical prerequisite for successful commercialization.

Third, the integration of AI-assisted materials design represents an indispensable future direction. At present, the selection of TMCs modifiers relies heavily on resource-intensive trial-and-error approaches, which inherently limits the focus to well-documented elements. To transcend these bottlenecks, future endeavors should embrace a robust data-driven framework that tightly couples first-principles calculations with advanced artificial intelligence (AI) and machine learning (ML) algorithms. This sophisticated approach facilitates high-throughput computational screening across extensive material databases. By accurately deciphering complex structure-property correlations such as d -band center shifts and targeted adsorption energies ML models can uncover high-performance TMCs that traditional intuition might overlook. Ultimately, this AI-guided materials genome strategy will drastically accelerate the rational design and rapid deployment of optimal separator modifications.

Fourth, the extensive deployment of advanced operando characterization techniques is indispensable. To reconcile theoretical predictions with actual electrochemical behaviors, a dynamic, real-time understanding of the dynamic catalytic solid-liquid interface is required. Given that ex situ approaches provide only time-averaged, static snapshots, the field must pivot toward cutting-edge real-time probes, particularly *in situ* XRD, *in situ* Raman spectroscopy, and X-ray absorption fine structure (XAFS). These techniques are uniquely capable of dynamically tracking the transient multiphase liquid-solid conversions of LiPSs, while simultaneously elucidating the coordination environment and valence state fluctuations of TMCs active centers. This dynamic insight is critical for unraveling transient deactivation mechanisms and establishing concrete structure-activity relationships for next-generation TMCs modifiers.

Finally, the lack of standardized testing parameters severely impedes the objective evaluation of TMCs-based separator modifiers. Since battery performance is a collective result of the entire electrode-electrolyte architecture, the drastic variations in sulfur areal loadings ($1\text{--}10\text{ mg cm}^{-2}$), E/S ratios ($3\text{--}15\text{ }\mu\text{L mg}^{-1}$), and host material selections across current literature preclude reliable cross-comparisons. To accurately identify intrinsic catalytic functionalities, it is imperative to establish a universally accepted benchmarking system that unifies these critical baselines. The standardized system would lay a scientific foundation for the systematic structural design-performance optimization-industrial screening of Li-S battery materials, accelerating the translation of basic research into practical applications.

Data availability

This study did not generate new data and code.

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Declaration of competing interest

All the authors no conflict of interests in this work.

Author contribution statement

Ling Bai contributed to the overall conceptualization, literature organization, and initial draft preparation of the manuscript. Changgan Lai participated in the revision and editing of the manuscript. Binyang Du offered guidance, edited and revised the manuscript. Zhiliang Guo provided strong support in funding and research, and participated in the revision and editing of the manuscript.

Use of AI statement

None.

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