Recent Progress in Cathode Side for Lithium-Sulfur Batteries to Mitigate the Shuttle Effect

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Abstract. The great potential theoretical specific capacity (1675 mAh g^{-1}) and the energy density (2600 Wh kg^{-1}) of sulfur combined with the cost-effectiveness and environmental sustainability of this substance have catapulted lithium-sulfur (Li-S) batteries to become a leader in future energy storage. Irrespective of these merits, a ubiquitous "shuttle effect" caused by lithium polysulfides ($LiPS_x$) is still a tough obstacle to commercialization that induces rapid capacity decay and reduced Coulombic efficiency. This is a review of the Li-S electrochemical environment with special focus on the mechanistic bases of polysulfide shuttling. On the migration of the shuttle effect, this review paper has given the summation of the existing modification directions with emphasis on the modification strategies of cathodes and three discrete illustrations namely modification of carbon-based composite material, modification of transition metal catalyst, and modification of polymeric sulfur structure. Moreover, the chemical anchoring of the redox rate, physical sequestration, is broken down into the interplay between the two and synergistic strategies are revealed. The review ends with the determination of the long-term technical bottlenecks and the description of future directions of the achievement of high-performance and practical Li-S systems.

1 Introduction

Lithium-sulfur (Li-S) battery has attracted a lot of interest as the next-generation battery due to the increase in the global demand of high-capacity energy storage. They are attractive because of an enormous theoretical energy density (approximately 2600 Wh/kg) and the inherent benefits of sulfur which are its low cost, high abundance, and low environmental footprint. This potential rhymes however with a number of fundamental challenges to the practical utilization of Li-S systems: the sulfur volume increases dramatically, it is conductively insulating and, most infamously, the so-called shuttle effect [1].

The shuttle effect is connected to the dissolution and migration of long-chain lithium polysulfides ($LiPS_x$, x=4~8) at the cathode to the lithium anode. The existence of such intermediate polysulfides not only causes dissolution in the electrolyte, and therefore deactivation of active materials, but also closures between the cathode and anode. This would greatly diminish the Coulombic efficiency of the battery, corrode the anode and decrease the

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life of the battery in terms of service [2]. The existing research directions to solve this problem are built on the basis of structural design of concrete parts, such as the cathode (sulfur electrode), electrolyte, separator, and anode (lithium electrode) [3]. Being the source of the reaction, the cathode (sulfur electrode) has potential of reducing the shuttle effect through structural design alterations of the cathode side, and therefore, the cathode is the most interesting research.

This review summarizes the research developments of lithium-sulfur batteries in four categories, cathode, anode, electrolyte and separator, and particularly, the approaches to the cathode-side modification, namely, carbon-based composites, transition metal catalysts, polymeric sulfur modification. The purpose is to physically trap the shuttle effect away, chemically anchor the shuttle effect away, or catalytically convert lithium polysulfides ($LiPS_x$) at the source.

2 Fundamental mechanisms of shuttle effect

2.1 Working principle of lithium-sulfur batteries

The electrochemical performance of Li-S batteries is rooted in the complex, multi-step redox chemistry between sulfur (S_8) and lithium. Upon discharge, lithium metal at the anode is oxidized, releasing Li^+ into the electrolyte. Simultaneously, the S_8 molecules at the cathode undergo a stepwise lithiation process; this transition proceeds through a series of soluble, long-chain lithium polysulfides ($LiPS_x$, x=4~8) before culminating in the precipitation of insoluble Li_2S_2 and Li_2S. The net discharge process—S_8 +16 Li^+ +16 e^- →8Li_2 S—is reversed during charging [1, 4]. While this sophisticated reaction pathway underpins the system's high theoretical capacity, it also introduces the liquid-phase intermediates responsible for the notorious shuttle effect. The fundamental working principle and the parasitic shuttle mechanism are schematically depicted in Fig. 1.

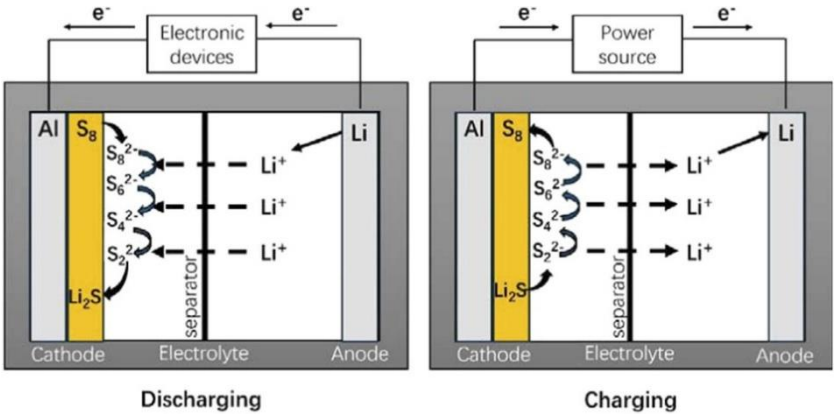

Fig. 1. Working principle diagram of lithium-sulfur battery [1].

2.2 Formation mechanism of shuttle effect

The formation of the shuttle effect arises from the redox reaction of elemental sulfur (Li_2 S_n, 4≤n≤8) at the cathode during discharge, which generates polysulfide intermediates soluble in the electrolyte (as Equation 1). These species migrate (shuttle) from the cathode to the lithium metal anode, where they undergo irreversible parasitic reactions with metallic lithium (as Equation 2). This process not only consumes the anode lithium but also produces

electrochemically inactive "dead" sulfur that cannot participate in the charge-discharge cycle, ultimately leading to the degradation of battery coulombic efficiency and the shortening of cycle life [5]. The detrimental effects of the shuttle effect during charge-discharge processes are illustrated in Fig. 2.

$$Li_2S_4+2S=Li_2S_6 \quad (1)$$
$$2Li_2S_6+2Li=3Li_2S_4 \quad (2)$$

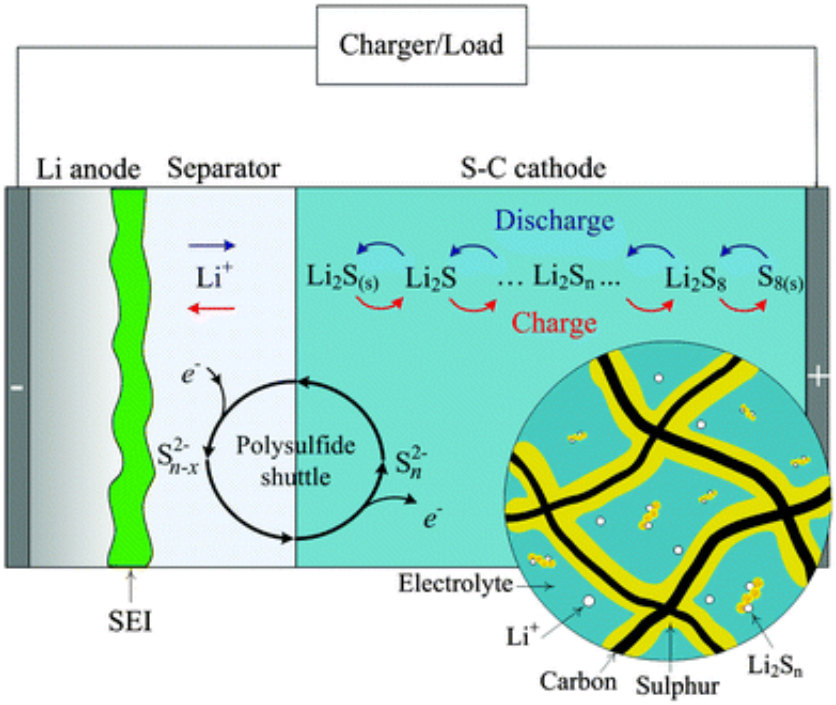

Fig. 2. Impacts of the Shuttle Effect on Charge-Discharge Behavior [2].

2.3 Mitigation strategies

For non-cathode modification directions, separator modifications include physical coating (carbon-based materials, MOFs, etc.) and chemical functionalization (plasma treatment, layer-by-layer assembly) to trap or repel polymeric sulfur [6, 7]. Electrolyte strategies involve optimizing solvent/salt systems, adding functional additives (e.g., $LiNO_3$) or redox mediators, and developing non-solvent electrolytes, though they face issues like high viscosity or poor stability [6, 8]. Anode improvements focus on SEI film optimization, surface functional coating (e.g., $Al_2 O_3$), and alloyed/composite structures to block polymeric sulfur-lithium reactions and stabilize interfaces [9].

Compared with non-cathode modification strategies, the sulfur cathode, acting as the primary host, is the frontline in managing redox kinetics and polysulfide confinement. Cathode architecture engineering has therefore become part of cornerstone strategy of mitigating the shuttle effect. Cathode Poorly suppressible are addressed largely on the cathode side and these three suppression mechanisms are namely physical confinement, chemical adsorption, and catalytic conversion [6]. There are three fundamental bills to counter mask the shuttle effect on lithium-sulfur batteries: physical confinement, the

chemical trapping, and catalytic conversion. In physical confinement, the porous materials employed have a small channel through which soluble polysulfides are prevented to diffuse physically. The mechanism of chemical trapping is based on the polar functional groups or metal site that captures the polysulfides through powerful chemical links that avoid the movement of the polysulfides. The redox transformation of soluble polysulfides to insoluble Li_2S_2, Li_2S is catalytically accelerated to get rid of soluble intermediates. The two make great efforts to reduce the shuttle effect and make cycling more stable [6]. Particular modification methods involve compounding the sulfur electrodes with carbon-based materials to confine and entrap lithium polysulfides; doping of transformation metal catalysts to catalyze long-chain lithium polysulfides; and polymeric sulfur; as opposed to the traditional sulfur electrodes.

3 Modification strategies

3.1 Physical confinement - carbon-based composite hosts

To address the shuttle effect, researchers have devoted themselves to the design and synthesis of sulfur cathode materials with unique compositions and structures. Among these strategies, the composite modification of sulfur with carbon-based materials (porous carbon nanotubes, carbon nanotubes, and graphene) is the most widely adopted. The carbon-based cathode composites inhibit the shuttle effect via physical confinement by virtue of their unique microstructures like 1D nanotubes and high specific surface areas. They form spatial steric hindrance to block the free diffusion and dissolution of lithium polysulfides, fix sulfur uniformly in the carbon matrix to reduce lithium polysulfides generation, and act as physical barriers to prevent lithium polysulfides from migrating to the anode, thus effectively suppressing the shuttle effect during charge-discharge cycles [10]. The specific modification strategies can refer to a special type of multifunctional polymeric phthalocyanine coated on carbon nanotubes

The modification strategy of coating triethylene glycol-functionalized polymeric cobalt phthalocyanine (TCP) on multi-walled carbon nanotubes (MC) via one-pot cyclization polymerization features innovative quadruple synergy of physical confinement, chemical adsorption, redox mediation and lithophilic transport, breaking the limitation of single physical confinement of traditional carbon-based hosts. With an optimal TCP: MC ratio of 1:3 and a 2~3 nm uniform amorphous TCP coating, the composite retains MC's high conductivity (charge transfer resistance 30 Ω vs. 60 Ω of pure MC) and disperses $Co\text{-}N_4$ active sites uniformly, reducing polarization (ΔE=150 mV vs. 201 mV of pure MC). TCP shows a strong Li_2S_6 adsorption energy of -1.0209 eV, and the $Co\text{-}N_4$ sites boost Li_2S precipitation capacity to 202.60 mA h g^{-1} (vs. 151.04 mA h g^{-1} of pure MC). The S@TCP/MC cathode achieves outstanding performance: 1392.8 mA h g^{-1} at 0.1 C, 667.9 mA h g^{-1} at 5.0 C, 81.5% capacity retention after 200 cycles at 0.2 C, and a high areal capacity of 6.83 mA h cm^{-2} at 6.6 mg cm^{-2} sulfur loading, far exceeding pure MC and commercial lithium batteries [11].

3.2 Catalytic conversion- transition metal catalyst

Catalytic conversion is crucial for inhibiting the shuttle effect because it rapidly transforms soluble long-chain lithium polysulfides into insoluble short-chain Li_2S_2 /Li_2S, minimizing LiPSs' dissolution and migration between the cathode and anode, which fundamentally eliminates the core cause of the shuttle effect. Transition metal catalysts (e.g., CoP, Co@N) inhibit the shuttle effect mainly through enhanced catalytic conversion of lithium

polysulfides [12, 13]. They lower reaction energy barriers (CoP reduces Li_2S diffusion barrier to 0.51 eV) and accelerate $LiPS_x$ transformation to insoluble Li_2S_2 /Li_2S. The catalysts' active sites (e.g., Co-N) facilitate electron transfer, promoting uniform Li_2S nucleation. This rapid conversion minimizes soluble $LiPS_x$ formation and migration, fundamentally suppressing the shuttle effect and improving battery cyclic stability [12].

The transition metal catalyst (CoP) structural design centered on enhancing catalytic conversion efficiency, which breaks through the limitations of traditional transition metal catalysts in lithium-sulfur batteries. Innovatively embedded in MOF-derived N-doped carbon nanoarrays (CC@CoP/C) via MOF derivation and in-situ phosphating, CoP forms a unique "carbon matrix-catalyst" composite structure that achieves uniform dispersion of active sites and ensures high conductivity, laying a foundation for efficient catalytic reactions. As a high-performance electrocatalyst, CoP significantly accelerates the catalytic conversion kinetics of lithium polysulfides: it reduces the Li_2S diffusion barrier to 0.51 eV (much lower than 0.63 eV of pure Co), effectively promoting the rapid conversion of soluble long-chain lithium polysulfides to insoluble short-chain Li_2S_2 /Li_2S and fundamentally alleviating the shuttle effect. These catalytic modification enable excellent battery performance: the initial discharge capacity reaches 1535 mAh g^{-1}at 0.1 C, and 833 mAh $g^{-1}$is retained after 600 cycles at 2C with a per-cycle decay rate of only 0.016%, while stable cycling is maintained even at a high sulfur loading of 4.17 mg cm^{-2}; fully verifying the superior catalytic performance of CoP [13].

3.3 Chemical trapping- polymeric sulfur hosts

Polymeric sulfur is regarded as a highly promising cathode material due to its ability to entrap lithium polysulfides via the formation of covalent bonds. Polymeric sulfur is a sulfur-rich polymer with sulfur chains covalently linked to organic groups, featuring controllable short sulfur chain lengths and high sulfur content [14]. It suppresses the shuttle effect fundamentally by restricting the redox reaction to only generate electrolyte-insoluble short-chain lithium polysulfides during cycling, completely avoiding the formation of soluble long-chain lithium polysulfides that cause shuttle. Its covalent structure ensures the sulfur species are firmly anchored, preventing dissolution and migration of polysulfides between cathode and anode, thus eliminating the core cause of the shuttle effect.

The modification innovatively synthesizes polyethylene hexasulfide (PEHS) via a mild condensation reaction, with 87 wt.% sulfur content yielding a theoretical specific capacity of 1217 mA h g^{-1}; a breakthrough over traditional sulfur polymers with uncontrollable chain lengths. PEHS is infiltrated into carbon nanotube (CNT) networks to form a binder-free PEHS-CNT composite cathode, which suppresses the shuttle effect fundamentally. Its covalently bonded short hexasulfide chains restrict redox reactions to only generate insoluble short-chain lithium polysulfides, avoiding soluble long-chain lithium polysulfides that dissolve and migrate. The organic backbone anchors sulfur firmly, preventing its detachment, while the CNT network reinforces physical confinement. Electrochemical tests confirm its stable performance: 1108 mA h g^{-1}at C/20, 71% capacity retention after 350 cycles at 1C, and good stability at 6.8 mg cm^{-2}sulfur loading, verifying its effectiveness in shuttle effect inhibition [15].

This approach exhibits excellent compatibility and practicality, as it does not require significant modifications to the existing battery system, can be synthesized via simple processes such as inverse vulcanization, and maintains effective suppression of the shuttle effect even under high sulfur loading conditions [14].

3.4 Synergistic modification

In Li-S batteries, synergistic modification refers to the collaborative work of multiple mechanisms (structural confinement, chemical adsorption, catalytic conversion) whose combined efficacy exceeds any single one. Structural confinement restricts lithium polysulfides ($LiPS_x$) migration; chemical adsorption anchors soluble $LiPS_x$ (e.g., Li_2S_6 adsorption energy -1.0209 eV); catalytic conversion accelerates their transformation into insoluble products. This cooperation minimizes $LiPS_x$ dissolution and shuttling between electrodes, efficiently suppressing the shuttle effect [6].

Combined with the three modification strategies mentioned above, the critical role of the synergistic effect in suppressing the shuttle effect can be further explored. The three modification strategies innovatively suppress the shuttle effect via well-designed multi-dimensional synergistic effects, which integrate structural confinement, chemical interaction, and catalytic conversion, overcoming the limitations of single inhibition mechanism and achieving efficient and stable regulation. For TCP/MC, it realizes quadruple synergistic effects with clear division of labor and mutual promotion: physical confinement from carbon nanotube networks restricts the spatial migration of $LiPS_x$; chemical adsorption (Li_2S_6 adsorption energy of -1.0209 eV) from polymeric phthalocyanine firmly anchors soluble $LiPS_x$ on the cathode surface; redox mediation accelerates the electron transfer during LiPS conversion; lithiophilic transport promotes rapid Li^+ diffusion to further facilitate reaction kinetics, collectively reducing polarization to 150 mV and inhibiting LiPS dissolution [13]. For Co(Zn)@N-C, the synergistic effect lies in the combination of structural optimization and catalytic enhancement: Zn-induced micropores (BET specific surface area of 279.7 $m^2 g^{-1}$) not only strengthen physical confinement but also enhance mass transfer efficiency, while Co-N active sites provide strong catalytic activity to accelerate LiPS conversion into insoluble Li_2S_2/Li_2S (Li_2S precipitation capacity of 736 mAh g^{-1}) [13]. The S/GCN hybrid realizes a physicochemical synergy to suppress the polysulfide shuttle effect. Its 3D porous graphene@g-C_3N_4 framework provides physical confinement, accommodating sulfur and blocking polysulfide diffusion. Enriched N-sites in g-C_3N_4 form Li-N chemical bonds with polysulfides, achieving strong chemisorption. The interconnected 3D network also boosts fast electron/Li^+ transport, accelerating redox kinetics and further inhibiting polysulfide migration and dissolution [12]. For IP-S, it relies on ionic structure synergism: cationic pyrrolidinium groups form strong electrostatic interaction to anchor anionic $LiPS_x$, while the built-in redox mediation sites lower the Tafel slope to 19.9 mV dec^{-1}, accelerating LiPS conversion and further reducing the accumulation of soluble $LiPS_x$. These synergistic effects enable exceptional battery performance, verifying the superiority of multi-mechanism collaboration [15].

4 Conclusion

The heartbreak that will limit commercialization of lithium-sulfur batteries is the shuttle effect. Basically, it consists of the transfer and response of the lithium polysulfides (LiPS) in both directions, cathode-and anode, to the depletion of the active substances, the harm of the solid electrolyte interphase (SEI) coating, formation of lithium dendrites, which significantly deteriorate the stability of a battery. Despite the present cathode-side approaches including physical confinement with porous matrices of carbon, chemical confinement with polar metal oxides or heteroatom-doped carbon, and catalytic conversion with single-atom catalysts preventing the shuttle effect in the laboratory, each of them is subject to practical drawbacks.

Cathode-side adjustments are extremely more important than non-cathode solutions of lithium-sulfur batteries. Design measures at cathode side directly deal with shuttle effect at the source by confining, anchoring and catalyzing the lithium polysulfides, better than

downstream non-cathode resolutions. In addition, they optimize the energy loading through high sulfur loading/use- necessary to achieve the theoretical capacity of the battery. Also, cathode optimization has been shown to synergistically optimize several key performance metrics, and is applicable to existing manufacturing workflows, which makes cathode optimization the breakthrough of the lithium-sulfur battery development.

These methods have difficulty trying to strike a balance between LiPS adsorption/catalysis and electron conductivity, and a solitary method of modifying the cathode is not able to fully counteract the effect. However, in the future, it is necessary to develop integrated cathode-side systems with synergistic "adsorption-catalysis-confinement" effects, to optimize the structure of cathode composites and to develop low-cost high-performance cathode materials, so as to overcome bottlenecks in application, which will provide a foundation to commercialization of lithium-sulfur batteries with high energy densities.

References

1 L. Zhu, X. Zhang, J. Zhang, H. Ren, Y. Yao, M. Wang, and Y. Song, A Review on Sulfur-Based Composite Cathode Materials for Lithium-Sulfur Batteries: Progress and Prospects. Journal of Alloys and Compounds **1010**, 178282 (2024).

2 M. Wild, L. O'Neill, T. Zhang, R. Purkayastha, G. Minton, M. Marinescu, G.J. Offer, Lithium Sulfur Batteries, a Mechanistic Review. Energy & Environmental Science **8**, 3477 (2015).

3 G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, Revisiting the Role of Polysulfides in Lithium–Sulfur Batteries. Advanced Materials **30**, 1705590 (2018).

4 D. Cai, F. Zheng, Y. Li, C. Zhang, Z. Qin, W. Li, Y. Liu, A. Li, and J. Zhang, Design of Coatings for Sulfur‐Based Cathode Materials in Lithium‐Sulfur Batteries: A Review. Chemistry - an Asian Journal **19**, e202400099(2024).

5 Z. Pan, Dan, G. He, and I. P. Parkin, Progress and Perspectives of Organosulfur for Lithium–Sulfur Batteries. Advanced Energy Materials. **12**, 2103483(2022).

6 Z. W. Seh, Y. Sun, Q. Zhang, and Y. Cui, Designing High-Energy Lithium–Sulfur Batteries. Chemical Society Reviews **45**, 5605(2016).

7 N. Batyrgali, Y. Yerkinbekova, N. Tolganbek, S. Kalybekkyzy, Z. Bakenov, and A. Mentbayeva, Recent Advances on Modification of Separator for Li/S Batteries. ACS Applied Energy Materials **6**, 588(2022).

8 Q. Pang, X. Liang, C. Y. Kwok, and L. F. Nazar, Advances in Lithium–Sulfur Batteries Based on Multifunctional Cathodes and Electrolytes. Nature Energy **1**, 16132(2016).

9 A. Rosenman, E. Markevich, G. Salitra, D. Aurbach, A. Garsuch, and F. F. Chesneau, Review on Li-Sulfur Battery Systems: An Integral Perspective. Advanced Energy Materials **5**, 1500212(2015).

10 Z. Wang et al., Self‐Supported and Flexible Sulfur Cathode Enabled via Synergistic Confinement for High‐Energy‐Density Lithium–Sulfur Batteries. Advanced Materials **31**, 1902228(2019).

11 W. Hu, H. Liu, F. Zhang, X. Wang, L. Pang, S. Wang, and J. Li, Synergistic Coordination Effect of Co@N Active Sites and Multilevel Porous Carbon Confinement Engineering for Boosting Catalytic Conversion Kinetics of Lithium Polysulfides in Li-S Batteries. Chemical Engineering Journal **513**, 163176 (2025).

12 J. Zhang, J. Li, W. Wang, X. Zhang, X. Tan, W. Chu, and Y. Guo, Microemulsion Assisted Assembly of 3D Porous S/Graphene@G‐c_3N_4 Hybrid Sponge as Free‐Standing Cathodes for High Energy Density Li–S Batteries. Advanced Energy Materials **8**, 1702839(2018).

13 Y. Kim, W. I. Kim, H. Park, J. S. Kim, H. Cho, J. S. Yeon, J. Kim, Y. Kim, J. Lee, and H. S. Park, Multifunctional Polymeric Phthalocyanine‐Coated Carbon Nanotubes for Efficient Redox Mediators of Lithium–Sulfur Batteries. Advanced Energy Materials **13**, 2204353(2023).

14 F. Makhlooghiazad, L. Miguel, G. Rollo-Walker, D. Kourati, M. Galceran, F. Chen, M. Deschamps, P. Howlett, L. A. O'Dell, and M. Forsyth, Understanding Polymerized Ionic Liquids as Solid Polymer Electrolytes for Sodium Batteries. Journal of the American Chemical Society **146**, 1992(2024).

15 A. Bhargav, C.-H. Chang, Y. Fu, and A. Manthiram, Rationally Designed High-Sulfur-Content Polymeric Cathode Material for Lithium–Sulfur Batteries. ACS Applied Materials & Interfaces **11**, 6136 (2019).