

Research Progress of Structural Optimization of Lithium-Sulfur Battery Cathode Materials for Suppressing the Polysulfide Shuttle Effect

Yuetong Jia

*Department of Chemistry and Material Science, Xi'an Jiaotong-Liverpool University, Suzhou, China
Yuetong.Jia23@student.xjtlu.edu.cn*

Abstract. Since lithium-sulfur (Li-S) batteries are inexpensive, environmentally friendly, and have an extraordinary theoretical energy density (2600 Wh/kg), they have emerged as viable candidates for future energy storage systems. However, the polysulfide shuttle effect leads to the loss of active material, capacity degradation, and reduced cycle stability which severely hindering their practical application. This review elaborates on the working principles of lithium-sulfur batteries, analyzes mechanisms behind the shuttle effect and its impact on battery performance, and summarizes recent strategies for optimizing cathode materials including nano-modification (e.g., Co-PB@S and Fe₃C/PB@S cathode materials), polymer modification (e.g., PEDOT-S@PAN nanofiber structures) and composite modification (e.g., multifunctional MXene/CNT-1Zr and Ti₃C₂/S@PDA composites). These materials effectively suppress polysulfide migration through physical confinement, chemical adsorption, and catalytic conversion mechanisms, thereby improving sulfur utilization and cycling stability. Finally, this review emphasizes that upcoming studies should prioritize evaluating performance in practical scenarios, including minimal electrolyte amounts and high sulfur loading, to advance the practical application of Li-S batteries. The findings provide theoretical insights and technical prospects for improving Li-S batteries.

Keywords: Lithium-sulfur battery, shuttle effect, modification strategy, cathode material

1. Introduction

The rise of smart living has led to the widespread adoption of electronic devices, fueling an increasing need for energy storage solutions. A major focus in current research is the development of high-performance, safe, and economical electrode materials. Lithium-sulfur (Li-S) batteries, functioning as rechargeable energy storage devices, operate through sulfur's reversible redox reactions, where electrical energy is stored and released via the cleavage and reformation of S-S bonds. Owing to their distinctive benefits, they have become a promising contender for future rechargeable energy storage solutions. Specifically, sulfur cathode materials possess outstanding advantages: low cost and natural abundance, excellent safety characteristics, and an extraordinary theoretical specific capacity of 1675 mAh/g, which enables ultrahigh theoretical energy density of 2600 Wh/kg [1].

The discharge process of Li-S batteries includes four distinct stages: Stage 1: Transformation from solid-to-liquid occurs as initial S_8 reacts to form highly soluble Li_2S_8 . Stage 2: The Li_2S_8 undergoes rapid reduction to Li_2S_4 . Stage 3: Soluble Li_2S_4 experiences a transformation from liquid to solid phase and converting to Li_2S_2 . Stage 4: The transformation of solid-to-solid from Li_2S_2 to Li_2S [2].

Nevertheless, the application of Li-S batteries encounters a significant challenge -- shuttle effect. Throughout cycling, polysulfides (Li_2S_n , $n=4, 6, 8$) dissolve into the electrolyte to form soluble lithium polysulfides species ($LiPS_s$). Their migration between polarity leads to capacity fading, shortened cycle life and decreased Coulombic efficiency. Notably, modification technologies for cathode materials have emerged as a core direction for breaking through these performance bottlenecks.

For cathode material optimization, the most common approaches involve nano-modification, polymer modification and composite modification [3]. The enhancement of sulfur loading efficiency through nanoscale structural design, coupled with the reduction of ion transport pathways. Effectively mitigates polysulfide migration via chemical adsorption between polar functional groups and lithium polysulfides ($LiPS_s$). And the synergistic effects of electron conduction and physical confinement are achieved through the integration of carbon-based/metal oxide composites with sulfur. These material systems have demonstrated significant progress in alleviating the shuttle effect by suppressing polysulfide dissolution, improving sulfur utilization, and accelerating electron conduction [3-5]. For instance, carbon-sulfur composites physically immobilize $LiPS_s$ through porous structures while enhancing electron transport via carbon networks, whereas polymer-coated cathodes reduce $LiPS_s$ loss through chemical anchoring mechanisms.

This review systematically examines the working principles of Li-S batteries during cycling processes, analyzes the mechanism and detrimental impacts of the polysulfide shuttle effect, and comprehensively discusses cathode material optimization strategies through three key approaches: nanomaterial modification, polymer modification, and composite material modification. Furthermore, it provides insightful perspectives on future research directions, offering valuable theoretical guidance for engineering application of high-performance Li-S batteries. This review integrates fundamental mechanisms with practical material design considerations, presenting a holistic view of current challenges and potential solutions in this promising energy storage technology.

2. Working principles of lithium-sulfur battery and its main problem

2.1. Working principles of lithium-sulfur battery

Lithium-sulfur (Li-S) battery systems employ a fundamental electrochemical architecture comprising metallic lithium anode and crystalline sulfur (S_8) cathode [6]. According to the Figure 1, the discharge process initiates with lithium oxidation at the anode, where metallic Li undergoes delithiation ($Li \rightarrow Li^+ + e^-$). The liberated lithium ions subsequently diffuse through the organic electrolyte medium, while the concomitant electrons traverse the external circuit, establishing the charge transfer pathway. Concurrently at the cathode compartment, the S_8 molecules undergo a complex multistep reduction sequence, ultimately yielding lithium sulfide (Li_2S) through the net reaction: $S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$, which provides the remarkable theoretical capacity of 1675 mA h/g.

Charging process constitutes the exact reverse transformation, where lithium ions are reduced and replated onto the anode substrate ($Li^+ + e^- \rightarrow Li$), while the cathodic Li_2S is electrochemically

oxidized back to elemental sulfur through $8\text{Li}_2\text{S} \rightarrow \text{S}_8 + 16\text{Li}^+ + 16\text{e}^-$ [7]. This distinctive conversion-type electrochemical mechanism, fundamentally different from conventional intercalation chemistry, theoretically enables Li-S batteries to achieve extraordinary energy densities up to 2600 Wh/kg. However, the commercial implementation of this battery chemistry faces substantial obstacles from multiple intrinsic limitations, specifically: (1) the polysulfide shuttle phenomenon causing active cathode material loss, (2) significant volumetric expansion exceeding 80% during cycling processes, and (3) the poor electrical conductivity of both sulfur and its reduction products. These fundamental issues synergistically lead to accelerated capacity decay and restricted cycling durability in realistic battery configurations.

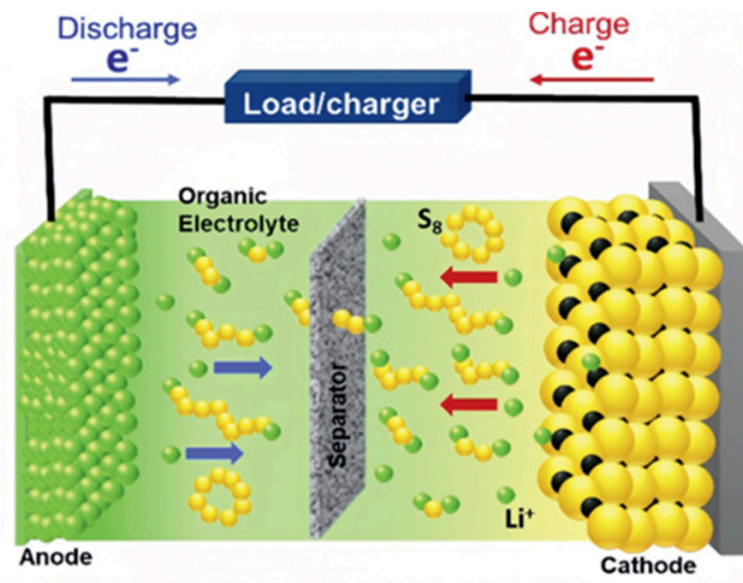
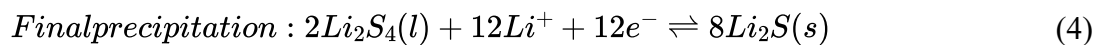
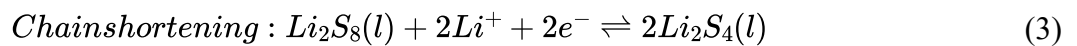
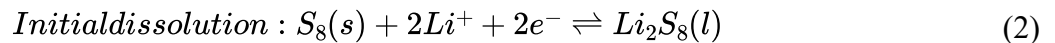
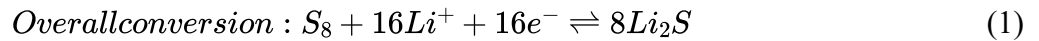


Figure 1. Schematic illustration of Li-S batteries [8]

2.2. Mechanism and impacts of the shuttle effect

The shuttle effect represents a fundamental challenge in lithium-sulfur battery systems, describing the detrimental electrochemical process wherein soluble lithium polysulfide intermediates (LiPS_x , Li_2S_x where $4 \leq x \leq 8$) undergo continuous migration between electrodes during cycling [9]. This phenomenon originates from the stepwise reduction of elemental sulfur (S_8) during discharging, which proceeds through a series of complex phase transformations. The complete electrochemical pathway can be described by four key reactions:



Equations (2) and (3) govern the generation of soluble higher-order polysulfides (Li_2S_8 and Li_2S_4), while Equation (4) represents the critical liquid-to-solid transition where soluble Li_2S_4 ultimately converts to insoluble Li_2S [2]. The dissolved polysulfide species then diffuse across the

electrolyte medium, driven by concentration gradients, establishing a dynamic equilibrium between the polarity.

The migrating polysulfides undergo parasitic reactions at the anode interface through three main pathways: (1) chemical reduction to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, (2) continuous consumption of lithium metal, and (3) formation of passivating surface layers. This process establishes a cyclic shuttle loop as the lower polysulfides diffuse back to the cathode for re-oxidation [10, 11], ultimately leading to four critical failure modes: accelerated capacity fade ($>0.2\%/cycle$), reduced Coulombic efficiency ($<95\%$), irreversible active material loss, and severe cycle life limitations (<200 cycles) in conventional designs [12, 13]. Understanding these reaction dynamics and transport phenomena is essential for developing effective mitigation strategies in advanced Li-S battery systems.

3. Optimization strategies for cathode materials and future research perspectives

In contemporary lithium-sulfur battery research, three principal cathode optimization strategies have emerged to address the polysulfide shuttle effect through distinct yet complementary mechanisms. Nano-modification techniques employ precisely engineered nanostructures to provide exceptional surface areas and tunable pore architectures for physical confinement and enhanced conversion kinetics. Polymer modification approaches utilize functional conductive matrices that combine flexible frameworks with tailored chemical functionalities for polysulfide immobilization, while simultaneously accommodating the 80% volume expansion during cycling. Composite modification strategies integrate hybrid material systems that synergistically combine conductive networks with polar adsorption sites, achieving multifunctional performance through precisely designed component interactions. These approaches collectively target the shuttle phenomenon via: (1) physical confinement through nanoscale architectures, (2) chemical immobilization via polar interactions, and (3) catalytic enhancement of conversion kinetics - while current research challenges focus on optimizing these systems for practical high-loading conditions ($>5 \text{ mg/cm}^2$) and scalable manufacturing processes to bridge the gap between laboratory achievements and commercial viability.

3.1. Nano-modification

Nanomaterials effectively mitigate the lithium polysulfide shuttle effect through nanostructural confinement while enhancing ionic conductivity and transport efficiency. A representative example is the cherry blossom-derived micro-carbon sheets embedded with Co-based nanoparticles developed by Liu et al. (Figure 2). The material exhibits a multiscale structure composed of microsheets with dimensions varying between 100 nm and 1 nm, with the introduced Co atoms substantially enhancing both the specific surface area ($2768.2 \text{ m}^2\text{g}^{-1}$) and pore volume ($1.63 \text{ cm}^3\text{g}^{-1}$). The Co atoms further form Co-N derivatives that chemically anchor polysulfides through strong adsorption, effectively suppressing the shuttle effect. This synergistic physical-chemical confinement strategy achieves outstanding electrochemical performance: the Co-PB@S cathode exhibits initial discharge capacity which is 933 mA h g^{-1} , retains 550 mA h g^{-1} after 500 cycles at 0.5C, showcasing excellent cycling durability and capacity preservation [14].

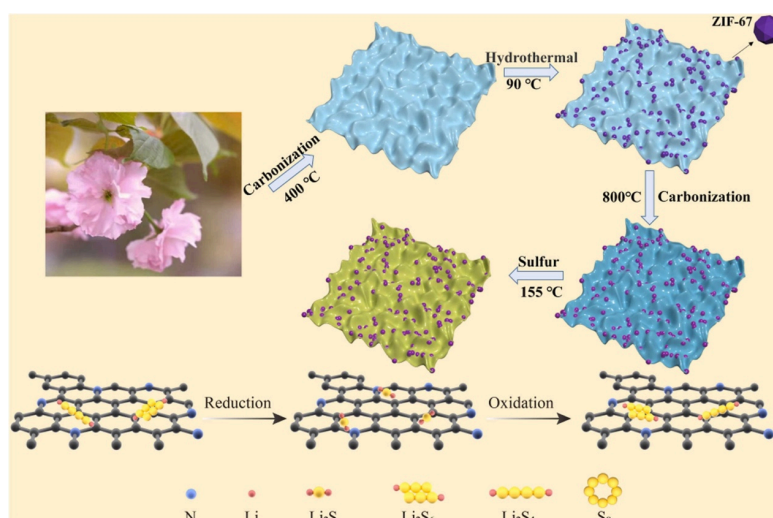


Figure 2. The preparation process, structure and mechanism of action on polysulfides of Co-PB@S [14]

Furthermore, Lei et al. (Figure 3) developed an innovative Fe_3C nanoparticle-modified biochar (PB) sulfur cathode, where the Fe_3C nanoparticles efficiently immobilize polysulfides via robust chemical interactions, significantly suppressing the shuttle effect and enhancing cycling stability. The synthesized $\text{Fe}_3\text{C}/\text{PB}$ composite exhibits an exceptionally large specific surface area ($2732 \text{ m}^2\text{g}^{-1}$) and cumulative pore volume ($1.60 \text{ cm}^3\text{g}^{-1}$). The $\text{Fe}_3\text{C}/\text{PB@S}$ cathode, featuring a substantial sulfur content of 69.6 wt% demonstrates outstanding electrochemical performance: achieving initial discharge capacity which is $1347.74 \text{ mA h g}^{-1}$ at 1C rate, stabilizes at 837.6 mAh g^{-1} after 5 cycles, maintains remarkable capacity of $555.25 \text{ mA h g}^{-1}$ after 250 cycles [15]. The enhanced performance stems from combined action of the porous carbon framework's physical entrapment capability and the Fe_3C active sites' dual function in chemical binding and reaction rate enhancement.

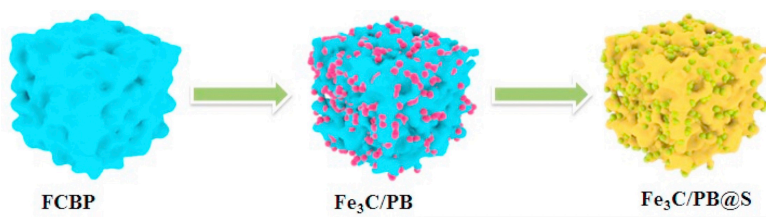


Figure 3. Schematic illustrations of the fabrication procedure of $\text{Fe}_3\text{C}/\text{PB@S}$ [15]

3.2. Polymer modification

Polymer-modified cathodes effectively address polysulfide migration through dual mechanisms: physical blocking via nanoscale pore structures and chemical adsorption to accelerate conversion kinetics. A breakthrough example is the core-shell electrospun nanofiber developed by Raulo et al. (Figure 4), featuring an in-situ grown sulfur core encapsulated in porous polyacrylonitrile (PAN) shells (S@PAN), further coated with a conductive poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) layer to create PEDOT- S@PAN nanofibers. This hierarchical design demonstrates superior performance compared to conventional sulfur-carbon (S/C) cathodes: at discharge rates of 0.1C, 0.2C, 0.5C, 1C and 2C, the S/C/PEDOT- S@PAN hybrid cathode delivers capacities of 735, 594, 447, 355 and 294 mA h g^{-1} respectively, significantly outperforming S/C

cathodes (670, 417, 336, 263 and 159 mA h g⁻¹ under identical conditions). Remarkably, when the current rate returns to 0.1C after high-rate cycling, the hybrid cathode recovers 607 mA h g⁻¹ (82.6% retention), showing 17% higher capacity recovery than conventional S/C electrodes [16].

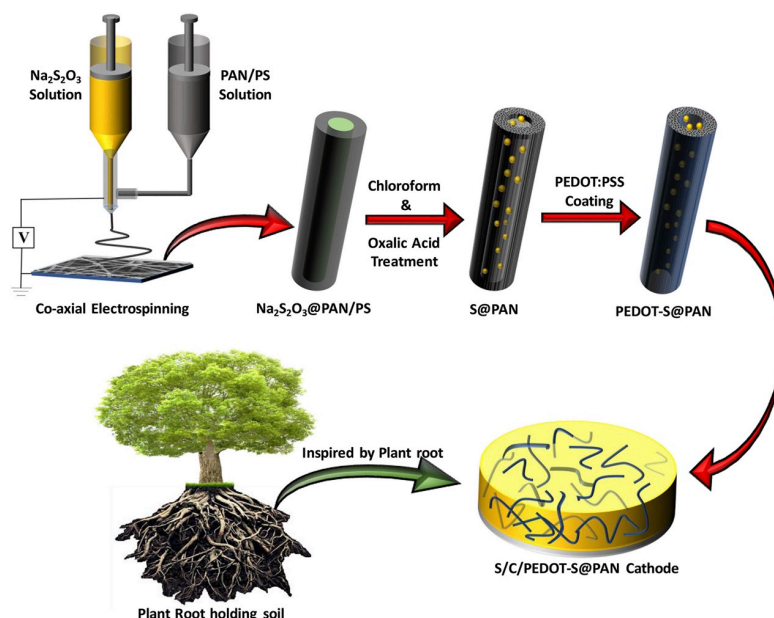


Figure 4. Schematic illustration of plant root inspired design and fabrication of PEDOT-S@PAN electrospun nanofiber and its incorporation in LSB hybrid cathode [16]

3.3. Composite modification

Composite materials effectively suppress the polysulfide shuttle effect through hierarchical porous structures that enable dual physical-chemical adsorption, significantly enhancing polysulfide conversion efficiency. A representative example is the multifunctional MXene/CNT-1Zr composite developed by Xie et al. (Figure 5), which serves as advanced sulfur host material. The S@MXene/CNT-1Zr electrode exhibits outstanding cycling performance in Li-S batteries under a 2.0 mg cm⁻² sulfur loading: achieving initial capacity of 904.8 mAh g⁻¹ at 1.0C with 381.1 mAh g⁻¹ retained after 1000 cycles, corresponding to an impressive 43.6% capacity retention. Particularly noteworthy is the ultralow capacity fade rate of merely 0.057% per cycle, establishing new standards for long-term cycling in Li-S battery systems [17].

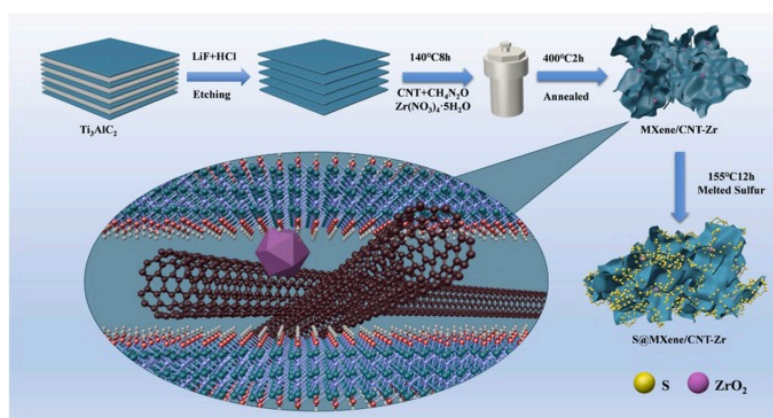


Figure 5. Schematic synthesis of S@MXene/CNT-Zr composites [17]

Furthermore, Wang et al. (Figure 6) developed a high-performance $\text{Ti}_3\text{C}_2/\text{S@PDA}$ composite cathode for lithium-sulfur batteries, where the polydopamine (PDA) coating effectively immobilizes lithium polysulfides (Li_2S_x) through strong chemical interactions while MXene (Ti_3C_2) substrate provides excellent electrical conductivity. This novel configuration exhibits outstanding battery performance under industrially relevant high-sulfur-loading conditions, achieving initial capacity which is 1001 mAh g^{-1} at 0.2C with 651 mAh g^{-1} retained after 1000 cycles - equivalent to an exceptionally low-capacity fade rate of just 0.035% per cycle. The exceptional cycle life stems from the cooperative action of PDA's polar groups enabling strong polysulfide binding and Ti_3C_2 's metallic conduction facilitating rapid electron transport, marking a crucial step forward in developing commercially viable high-energy Li-S batteries [18].

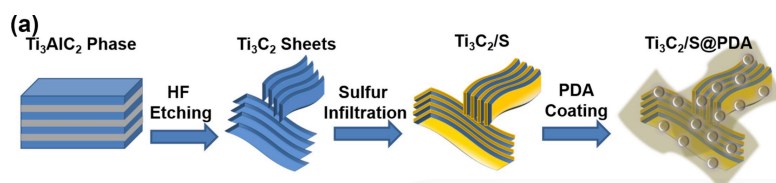


Figure 6. Schematic illustration of the fabrication of $\text{Ti}_3\text{C}_2/\text{S@PDA}$ composite [18]

The three primary modification approaches each present unique advantages and challenges in addressing polysulfide shuttling. Nanomaterials (e.g., Co-PB@S , $\text{Fe}_3\text{C/PB}$) offer exceptional surface areas ($>2700 \text{ m}^2/\text{g}$) and strong chemisorption sites, delivering high initial capacities ($900\text{-}1300 \text{ mAh/g}$) but face scalability challenges. Polymer modifications (e.g., PEDOT-S@PAN) provide cost-effective solutions with excellent mechanical flexibility and capacity recovery (82.6%), though with relatively lower energy densities. Composite materials (e.g., MXene/CNT-Zr , $\text{Ti}_3\text{C}_2/\text{S@PDA}$) demonstrate superior cycling stability ($1000+$ cycles, $<0.06\%$ decay/cycle) and high-loading capability (5 mg/cm^2), but involve complex fabrication and higher costs. Currently, nanomaterials show the highest technology readiness for moderate-load applications, polymers offer the best cost-performance balance, while composites represent the most promising but least mature solution for high-energy systems. Future development should focus on hybrid strategies that combine the merits of these approaches while addressing their respective limitations in scalability and cost.

Currently, the majority of lithium-sulfur (Li-S) battery research is conducted under idealized laboratory conditions characterized by high sulfur content ratios, low sulfur loadings (typically $<2 \text{ mg cm}^{-2}$), and modest current densities (often $\leq 0.5\text{C}$). While these conditions facilitate fundamental mechanism studies and produce impressive initial performance metrics, they fail to address the complex operational requirements for practical energy storage applications. To comprehensively assess Li-S batteries, it is essential to perform thorough evaluations under practical operating conditions that account for various key factors:

- (1) Practical Energy Density Requirements: Industrial applications demand high-sulfur loadings ($>5 \text{ mg cm}^{-2}$) to achieve competitive energy densities.
- (2) Real-world Operating Conditions: Performance validation across wider temperature ranges (-20°C to 60°C). And assessment under varying mechanical stresses and vibration scenarios.
- (3) Scalability Considerations: Evaluation of manufacturing feasibility for proposed material architectures. And cost analysis of advanced material systems.
- (4) System-level Integration Challenges: Performance in pouch cell configurations and long-term stability under potential voltage fluctuations.

The transition from idealized laboratory conditions to practical evaluation frameworks will enable more accurate assessment of Li-S technology's true potential while identifying remaining

challenges for commercialization. Future research should prioritize developing standardized testing protocols that better simulate real-world operating scenarios while maintaining scientific rigor in performance characterization [19, 20].

4. Conclusion

This review provides a comprehensive analysis of Li-S battery, highlighting its advantages and challenges. Li-S batteries demonstrate significant potential as advanced secondary battery systems due to the sulfur cathode's inherent benefits of low cost, high theoretical energy density, and enhanced safety. The review examines the unique "solid-liquid-solid" multiphase conversion reaction mechanism and investigates the detrimental effects of polysulfide shuttling, including active material loss, reduced Coulombic efficiency, rapid capacity fading, and shortened cycle life. To address these issues, three major optimization strategies are systematically summarized: nanomaterial modification (physical confinement/chemical adsorption), polymer coating, and composite structure design. While laboratory achievements such as exceeding 1000 cycles have been made, commercialization still requires overcoming critical technical barriers including stability under high sulfur loading and performance across wide temperature ranges. Future research should prioritize establishing more practical evaluation systems and employing multi-scale regulation and interface engineering strategies to enhance reliability under complex operating conditions. Only by resolving these engineering challenges can Li-S batteries fully realize their theoretical advantages and achieve large-scale applications in energy storage power stations, electric vehicles, and other fields, ultimately meeting the demand for the future green energy systems.

References

- [1] Wang, T., Tan, X., Ma, Y., Ma, Y., & Wu, Y. (2025). High-entropy materials regulating lithium polysulfides for advanced lithium-sulfur batteries. *Chemical Engineering Journal*, 165580.
- [2] Tian, K., Yuan, M., Zhang, Z., & Wang, C. (2025). Rational design of catalysts for lithium-sulfur batteries based on descriptors: progress and prospects. *Energy Storage Materials*, 80, 104429.
- [3] Jan, W., Khan, A. D., Iftikhar, F. J., Abbasi, M. Z., Ali, G., Iwuoha, E., Shahzad, S., Ahmad, F., & Ahmad, N. (2025). Electrolyte design for lithium-sulfur batteries: Progress and challenges. *Renewable and Sustainable Energy Reviews*, 221, 115916.
- [4] Feng, J., Meng, Y., Qi, D., Du, W., Xiang, Q., & Zhu, F. (2025). Recent progress and application frontiers of 2D layered double hydroxides in lithium-sulfur batteries. *Journal of Energy Storage*, 131, 117447.
- [5] Sun, L., Liu, H., Gui, X., Liu, L., Li, D., Sun, X., Xue, Y., Luo, C., & Xu, K. (2025). A novel sulfur-containing polythiophene cathode active material for reducing shuttle effect in lithium sulfur battery. *Journal of Energy Storage*, 129, 117376.
- [6] Li, Z., Li, B.-Q., Bi, C.-X., Li, X.-Y., Zhao, M., & Zhang, Q. (2025). A review of lithium-sulfur batteries at different working conditions: The role of ambient temperature, external force, and electromagnetic field. *Materials Science and Engineering: R: Reports*, 164, 100955.
- [7] Xia, S., Xu, X., Wu, W., Chen, Y., Liu, L., Wang, G., Fu, L., Zhang, Q., Wang, T., He, J., & Wu, Y. (2025). Advancements in functionalized high-performance separators for lithium-sulfur batteries. *Materials Science and Engineering: R: Reports*, 163, 100924.
- [8] Mendeiev Nitou, M. V., Yu, W., Muhammad, W., Zhang, Z., Chen, D., Yu, H., Tang, M., Fang, X., Liu, R., Pang, Y., Samynathan, A., Sondra, B. D., Niu, Y., Lv, W., & Chen, Y. (2025). Advances in Cathode's Microstructure Modification to Boost Performance of Lithium-Sulfur Batteries. *Green Energy & Environment*.
- [9] Santos, É. A., Policano, M. C., Pinzón, M. J., Galantini, I., Gonçalves, V. A., Maia, F. C. B., Macedo, L. J. A., Doubek, G., Freitas, R. G., & Zanin, H. (2024). Operando FTIR study on water additive in lithium-sulfur batteries to mitigate shuttle effect. *Journal of Energy Chemistry*, 98, 702-713.
- [10] Wang, J., Wang, H., Jia, S., Zhao, Q., Zheng, Q., Ma, Y., Ma, T., & Li, X. (2023). Recent advances in inhibiting shuttle effect of polysulfide in lithium-sulfur batteries. *Journal of Energy Storage*, 72, 108372.

- [11] Ren, W., Ma, W., Zhang, S., & Tang, B. (2019). Recent advances in shuttle effect inhibition for lithium sulfur batteries. *Energy Storage Materials*, 23, 707-732.
- [12] Mao, D., Fu, Y., Ba, J., Li, J., Yin, X., Wang, C., Wei, Y., & Wang, Y. (2025). Synergistic vanadium carbide/oxide heterostructures within layered carbon for enhanced lithium–sulfur battery performance. *Journal of Colloid and Interface Science*, 693, 137646.
- [13] Prasad, C., & Sarkar, A. (2025). Reduced-order multicycle electrochemical modelling of lithium-sulphur batteries with shuttle effect and capacity degradation. *Journal of Energy Storage*, 132, 117698.
- [14] Liu, Z., Wang, Q., Wang, Z., Ma, Y., Wang, Y., Du, Y., & Lei, W. (2024). Cherry blossom derived micron carbon sheets loaded with Co based particles served as sulfur host for lithium sulfur batteries. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 685, 133171.
- [15] Lei, W., Wang, X., Zhang, Y., Luo, Z., Xia, P., Zou, Y., Ma, Z., Pan, Y., & Lin, S. (2021). Facile synthesis of Fe₃C nano-particles/porous biochar cathode materials for lithium sulfur battery. *Journal of Alloys and Compounds*, 853, 157024.
- [16] Raulo, A., Bandyopadhyay, S., Ahamad, S., Gupta, A., Srivastava, R., Formanek, P., & Nandan, B. (2019). Bio-inspired poly(3, 4-ethylenedioxythiophene): Poly(styrene sulfonate)-sulfur@polyacrylonitrile electrospun nanofibers for lithium-sulfur batteries. *Journal of Power Sources*, 431, 250-258.
- [17] Xie, J., Li, Y., Li, J., Wu, Z., Huang, Y., Huang, H., Liang, X., Li, G., Qing, P., Huang, D., Liu, H., Lan, Z., & Zhou, W. (2025). Multifunctional MXene/CNT-Zr 3D composite cathode for long cycling stability in high-performance lithium-sulfur batteries. *Journal of Alloys and Compounds*, 1036, 181797.
- [18] Wang, X., Yang, C., Xiong, X., Chen, G., Huang, M., Wang, J.-H., Liu, Y., Liu, M., & Huang, K. (2019). A robust sulfur host with dual lithium polysulfide immobilization mechanism for long cycle life and high capacity Li-S batteries. *Energy Storage Materials*, 16, 344-353.
- [19] Chen, S., Miao, K., & Zhou, J. (2025). Advances in lithium-sulfur batteries for commercialization. *Sustainable Materials and Technologies*, 45, e01500.
- [20] Chen, H., Wu, Z., Zheng, M., Liu, T., Yan, C., Lu, J., & Zhang, S. (2022). Catalytic materials for lithium-sulfur batteries: mechanisms, design strategies and future perspective. *Materials Today*, 52, 364-388.