Progress in the Application of Vanadium Oxides in the Cathode of Lithium-Sulfur Batteries

Chaofan Hu

School of Materials Science and Engineering, Shaanxi University of Technology, Hanzhong 723001, China

Abstract: ***Lithium-sulfur batteries have become a research hotspot in the energy storage field due to their high theoretical specific energy (2600 Wh/kg) and low cost. However, their commercialization is limited by the shuttle effect of polysulfides (LiPSs), resulting in a decrease in cycle stability and Coulomb efficiency. Vanadium oxides, with their unique structure, multiple oxidation states, and excellent catalytic/adsorption properties, have become key materials for suppressing the shuttle effect. This paper systematically reviews the research progress of vanadium oxide-based cathode modifications, classifies and summarizes the cathodes from four aspects: morphology design, ion doping, heterostructure, and composite conductive framework, and prospects the future research directions of lithium-sulfur battery cathodes.***

Keywords: Lithium-sulfur battery; Shuttle effect; Vanadium oxide; Polysulfide; Cycle stability.

1. INTRODUCTION

As a highly promising next-generation high-energy-density energy storage system, lithium-sulfur batteries have received extensive attention from the academic and industrial communities in recent years. Under the background of the increasingly urgent global energy transformation and environmental protection needs, it is of great significance to develop new battery technologies with high specific energy, long life, low cost, and environmental friendliness. Lithium-sulfur batteries, with a theoretical energy density of up to 2600 Wh/kg and a theoretical specific capacity of $1675\mathrm{mAh/g}$, far exceed the performance of traditional lithium-ion batteries. Moreover, the positive electrode active material uses sulfur powder, which has the advantages of rich reserves, low price, and green non-toxicity, and is considered to be one of the candidates for future electric vehicles, large-scale energy storage, and other fields. Wang and Lai (2026) proposed a novel strategy to enhance upper-room ultraviolet germicidal irradiation (UVGI) performance by employing a rotating UV source under poorly-mixed ventilation conditions, which could effectively improve disinfection efficacy in spaces where conventional fixed-source systems are limited by uneven airflow [1]. Narouei et al. (2025) investigated the effects of germicidal far-UVC (222 nm) on ozone and particulate matter in a conference room, finding that the irradiation not only inactivated airborne microorganisms but also induced secondary chemical reactions that altered ozone concentrations and fine particle levels, thereby raising important considerations for indoor air quality management [2]. Xiao et al. (2022) developed an ultrasmall Fe_3O_4-decorated polydopamine hybrid nanozyme that enables continuous conversion of dissolved oxygen into highly toxic hydroxyl radicals through a glutathione-depleted cascade redox reaction, and they demonstrated that this nanozyme system provides intensive wound disinfection with excellent biocompatibility and therapeutic potential [3].

2. WORKING PRINCIPLE AND EXISTING PROBLEMS OF LITHIUM-SULFUR BATTERIES

2.1 Working Principle

The lithium-sulfur battery uses elemental sulfur as the positive electrode and metallic lithium as the negative electrode. Its energy storage mechanism is based on the multi-electron redox reaction between sulfur and lithium ions, which is different from the insertion/extraction mechanism of lithium-ion batteries. During discharge, solid S_8 molecules undergo multiple reduction reactions, successively generating long-chain polysulfides (Li_2S_8, Li_2S_6, etc.) and short-chain polysulfides (Li_2S_4, Li_2S_2), and finally forming insoluble Li_2S. This process is accompanied by a "solid-liquid-solid" three-phase transformation, involving complex electrochemical and chemical reaction paths. The reaction platforms are located at approximately 2.4 V and 2.1 V respectively. The charging process is the reverse reaction of this. Subsequently, insoluble Li_2S_2 and Li_2S are generated. The overall reaction equation of the lithium-sulfur battery is $S_8 + 16Li^+ + 16e^- = 8Li_2S$. S_8 undergoes multiple

reactions during the cycle as follows.

$$3S_8^{2-} + 2e^- \rightarrow 4S_6^{2-} \quad (1)$$

$$2S_6^{2-} + 2e^- \rightarrow 3S_4^{2-} \quad (2)$$

$$3S_4^{2-} + 4\mathrm{Li}^+ + 2e^- \rightarrow 2\mathrm{Li}_2\ \mathrm{S}_2 \quad (3)$$

$$2\mathrm{Li}_2\ \mathrm{S}_2 + 2\mathrm{Li}^+ + 2e^- \rightarrow 2\mathrm{Li}_2\ \mathrm{S}_2 \quad (4)$$

2.2 Existing Problems

Although lithium-sulfur batteries have significant theoretical advantages, their practical applications still face many challenges: (1) The sulfur conductivity is extremely low (about $5 \times 10^{-30}\ \mathrm{S/cm}$), and the discharge product $\mathrm{Li}_2\ \mathrm{S}/\mathrm{Li}_2\ \mathrm{S}_2$ is an electron and ion insulator, seriously affecting the reaction kinetics and utilization rate of active materials. (2) The reaction intermediate polysulfides are soluble in ether-based electrolytes, causing a serious "shuttle effect", resulting in an increase in electrolyte viscosity and poor cycle performance. Moreover, these polysulfides also react with the lithium anode to form irreversible insoluble polysulfides ($\mathrm{Li}_2\ \mathrm{S}/\mathrm{Li}_2\ \mathrm{S}_2$) in the electrolyte, and their deposition non-uniformity and conversion kinetics will cause problems such as loss of active materials, increase in battery internal resistance, and reduction of Coulomb efficiency. (3) The volume of sulfur expands by up to about 80% during the reaction, and repeated charge and discharge are likely to cause electrode structure damage and shedding of active materials, restricting the cycle life of the battery [3]. (4) The uneven deposition of lithium on the negative electrode leads to the growth of lithium dendrites, which may pierce the separator, resulting in potential short circuits and safety hazards. To overcome the bottleneck of lithium-sulfur batteries, the research on modifying the cathode material focuses on improving conductivity, anchoring polysulfides, and optimizing reaction kinetics. This paper systematically reviews the mechanisms of enhancing the cycle performance of lithium-sulfur batteries through strategies such as morphology design, ion doping, heterostructure, and composite conductive frameworks, and prospects the future research directions.

3. INTRODUCTION TO VANADIUM OXIDES

Since the discovery of the metal-insulator phase transition in vanadium oxide by Morin [4] in VO_2 in 1959, vanadium oxide has become a hot topic in the research of functional materials due to its unique 3d electronic configuration and multivalent state characteristics $(+3、+4、+5)$. $\mathrm{V}_2\mathrm{O}_5$、VO_2 and $\mathrm{V}_2\mathrm{O}_3$, as typical vanadium oxides, have tunable crystal structures and electrical properties, showing broad prospects in energy storage.

$\mathrm{V}_2\mathrm{O}_5$ has a layered structure, consisting of distorted $[\mathrm{VO}_6]$ octahedra forming a two-dimensional lamellar structure, stacked by van der Waals forces between layers, endowing the material with excellent ion intercalation ability and high surface activity. This material has electrochemical activity within the 1.5~4V voltage range and can contribute to the capacity in cooperation with the sulfur cathode. In addition, $\mathrm{V}_2\mathrm{O}_5$ can act as a redox mediator, oxidizing polysulfides to sulfur-oxygen species with its high potential (>3V) and chemically anchoring them on the surface. The $\mathrm{V}^{5+}/\mathrm{V}^{4+}$ variable valence state further catalyzes the liquid-solid conversion of polysulfides, enhancing the reaction kinetics. VO_2 is characterized by a metal-insulator phase transition close to room temperature, and its electronic structure is sensitive to external stimuli, which is closely related to its electrocatalytic performance. Research shows that its redox potential is higher than that of polysulfides (>2.4V), with the ability to anchor thiosulfates [5], accelerating $\mathrm{Li}_2\mathrm{S}$ deposition/decomposition and reducing the reaction overpotential. $\mathrm{V}_2\mathrm{O}_3$ has a corundum-type structure, undergoes a metal-insulator transition at about $150\ \mathrm{K}$, and is in a metallic state at room temperature with excellent conductivity. It chemically adsorbs and anchors polysulfides through V^{3+} sites, inhibits the shuttle effect, and simultaneously has conductivity and catalytic activity, synergistically enhancing the reaction kinetics and cycle stability.

4. APPLICATION OF VANADIUM OXIDES IN THE CATHODE OF LITHIUM-SULFUR BATTERIES

4.1 Morphology Design

In the design of the lithium-sulfur battery cathode, by regulating the microstructure of vanadium oxides, the synergistic physical confinement and chemical adsorption effects can effectively enhance the anchoring and catalytic conversion ability of polysulfides, which is a key strategy to inhibit the shuttle effect and improve the

electrochemical performance.

The VO_2 nanobelts prepared by Yang Ruoxuan [5] are based on the reversible conversion mechanism of " Li_2S_n - sulfate-polysulfate". At a high sulfur loading of $10.6mg/cm^2$, the flexible pouch cell achieves an initial capacity of 1075.1 mAh/g at 0.2C, with a capacity retention rate of 97.8% and an actual energy density of 327.6 Wh/kg. Li Xin et al. [6] prepared V_2O_3 hollow spheres by a high-temperature reduction method assisted by NH_3. The $S-V_2O_3$ cathode has an initial discharge specific capacity of 1375 mAh/g at 0.2C and still maintains 815 mAh/g after 100 cycles, showing excellent cycle stability, mainly attributed to the strong adsorption of polysulfides by V_2O_3 and the physical confinement effect of its hollow structure on the active material. The VO_2 nanorods prepared by Chen Bing [7] have a width of about 50 - 200 nm (Figure 1 (a) $\lambda Li_2\ S_6$). The adsorption experiment shows that the supernatant is clear and transparent after adding the VO_2 nanorods (Figure 1 (b)), confirming the strong adsorption of this material to $Li_2\ S_6$.

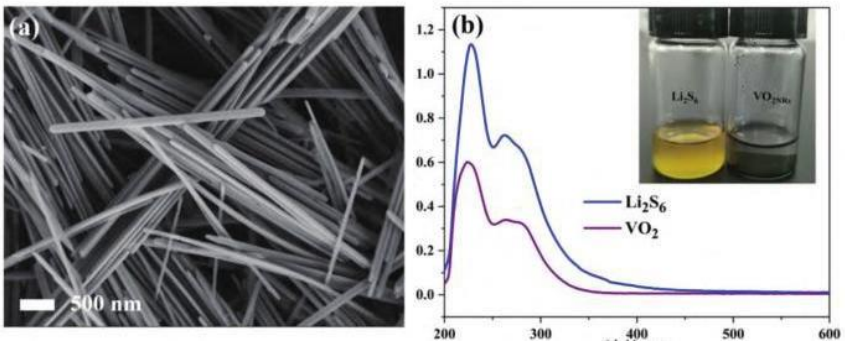

Figure 1: (a) Scanning electron microscope photograph of the VO_2 nanorods; (b) Visual photograph and ultraviolet-visible spectrum of the VO_2 after adsorbing the $Li_2\ S_6$ solution

4.2 Ion Doping

Ion doping of vanadium oxides can enrich surface active sites, optimize lattice defects and conductivity by introducing transition metals or single atoms, thus synergistically enhancing the chemical anchoring and catalytic conversion ability of polysulfides and effectively improving the electrochemical performance.

Liu Fanjun [8] prepared $Fe/Co/Ni$ -doped V_2O_5 yolk-shell microspheres (M-V2O5-YS) by hydrothermal method. Doping effectively introduced lattice defects and improved conductivity, enhancing the anchoring and catalytic ability of polysulfides. At $6\,\mu L/mg$ low electrolyte dosage and $4.9mg/cm^2$ high sulfur loading, the initial capacity of the S/Co- V_2O_5-YS cathode reached $1168.1mAh/g$ at 0.3C, and the decay per cycle was only 0.11% after 300 cycles at 0.5 C. Pang et al. [9] developed a single-atom iron-doped VO_2 nanoribbon ($Fe-VO_2$) catalyst, which regulated the electronic structure through electron metal-support interaction (EMSI), significantly reducing the energy barriers for polysulfide conversion and lithium-ion diffusion. The capacity retention rate of this cathode was 67% after 500 cycles at 1 C, and the decay per cycle was 0.066%. This study confirmed the effective role of EMSI in improving the catalytic performance of lithium-sulfur batteries.

4.3 Heterostructures

Heterostructure design effectively inhibits polysulfide shuttling and enhances reaction kinetics by constructing a vanadium oxide composite interface and leveraging the synergistic effect between components, providing a new path for the innovation of cathode materials for lithium-sulfur batteries.

The [10] -developed VN/V_2O_5 nanoporous heterojunction by Liu et al. achieved a $963mAh/g$ specific capacity at 5C high rates as a sulfur host and an $12.12mAh/cm^2$ areal capacity at $9.02mg/cm^2$ ultra-high sulfur loading. This performance stems from the synergistic catalysis between the rapid capture of polysulfides by V_2O_5 and the electron/ion transport channels provided by VN. Cai et al. [11] used 3D printing technology to construct a $V_8C_7-VO_2$ heterostructure bifunctional scaffold with both polysulfide anchoring-catalysis and lithium deposition regulation functions. This material exhibited only 0.061% capacity decay per cycle after 900 cycles at 4C and achieved uniform lithium deposition at $5mA/cm^2$, providing a new solution for high-energy-density lithium-sulfur batteries.

4.4 Composite Conductive Framework

The composite conductive framework is an important strategy to enhance the ability of vanadium oxides to inhibit the shuttle effect and the overall performance of the battery. Combining vanadium oxides with materials with excellent conductivity such as graphene and carbon nanotubes can play a synergistic role and effectively improve the performance of electrode materials.

Dan et al. [12] prepared $Co^{-}CNTs/C@V_2O_3$ coral-like composite materials through a hydrothermal-annealing method. V_2O_3 nanorods provide strong adsorption, and $Co-CNTs$ synergistically enhances the electron conduction and mass transfer efficiency. The S@Co-CNTs/C@V_2O_3 cathode achieves $880mAh/g$ reversible capacity at $0.5C$ under $4.52mg/cm^2$ high loading. Yang Yadong [13] constructed a three-dimensional nitrogen-doped graphene-supported V_2O_3/VN heterojunction, combining the strong anchoring of V_2O_3 and the high catalytic activity of VN to achieve efficient fixation and rapid conversion of polysulfides. After 300 cycles at $5C$, the capacity decay rate of this electrode is as low as 0.1%, demonstrating excellent long-cycle stability and interfacial synergistic advantages. The dual-core-shell structure $S@V_2O_5@G0$ material prepared by Chen Bing is. After 200 cycles, the discharge specific capacity of the $S@V_2O_5@G0$ electrode is $562.1mAh/g$, with a single-cycle decay of 0.015%, showing excellent electrochemical performance.

5. SUMMARY AND OUTLOOK

Through strategies such as morphology design, ion doping, heterostructure, and composite conductive frameworks, vanadium oxides can synergistically enhance their physical confinement, chemical adsorption, and catalytic functions, significantly improving the cycle stability, rate performance, and reaction kinetics of lithium-sulfur batteries. Despite the remarkable progress, this system still faces the following challenges: (1) The understanding of the mechanism is not yet complete. The description of the "adsorption-catalysis" synergistic mechanism is still relatively brief, and the analysis of microscopic mechanisms such as electronic structure regulation and interfacial reaction pathways is insufficient. (2) The material preparation process needs to be optimized. There are still technical bottlenecks in the large-scale and low-cost synthesis of high-quality vanadium oxide-based materials, and their structural stability and electrochemical consistency also need to be improved. (3) The research on practical conditions is insufficient. In cases close to actual applications such as high sulfur loading ($> 10mg/cm^2$), lean electrolyte, etc., the long-term performance and compatibility of the materials urgently need to be systematically evaluated.

Future research can be carried out in the following directions: First, with the help of in-situ characterization techniques and theoretical calculations, deeply explore microscopic mechanisms such as interfacial electron transfer and orbital coupling, and clarify the essence of the adsorption-catalysis synergistic effect; second, develop green and controllable synthesis methods to achieve the large-scale and low-cost preparation of vanadium oxide-based materials; third, expand the applicability of the materials in complex scenarios such as flexible devices and low-temperature environments, and construct a "structure-function-application" integrated material system; fourth, composite vanadium oxides with new materials such as two-dimensional materials and single-atom catalysts to construct a functional host system with multiple synergistic effects, and through cross-scale structural design and multi-mechanism coordination, promote the development of lithium-sulfur batteries towards high efficiency, stability, and practicality, providing a material basis for the next generation of high-energy-density energy storage systems.

FUND PROJECT

Provincial College Students' Innovation and Entrepreneurship Training Program Project (S202410720062); Scientific Research Start-up Project for Introduced Talents of Shaanxi University of Technology (SLGRCQD2519).

REFERENCES

[1] Narouei, F. H., Tang, Z., Wang, S. I., Hashmi, R. H., Welch, D., Sethuraman, S., ... & McNeill, V. F. (2025). Effects of germicidal far-UVC on ozone and particulate matter in a conference room. Plos one, 20(8), e0328224.

[2] Xiao, J., Hai, L., Li, Y., Li, H., Gong, M., Wang, Z., ... & He, D. (2022). An Ultrasmall Fe3O4 ‐ Decorated Polydopamine Hybrid Nanozyme Enables Continuous Conversion of Oxygen into Toxic Hydroxyl Radical via GSH ‐ Depleted Cascade Redox Reactions for Intensive Wound Disinfection. Small, 18(9), 2105465.
[3] Li, J. F., Niu, Z. H., Guo, C., et al. (2021). Catalyzing the polysulfide conversion for promoting lithium sulfur battery performances: A review. Journal of Energy Chemistry, 54, 434–451.
[4] Morin, F. J. (1959). Oxides which show a metal-to-insulator transition at the Neel temperature. Physical Review Letters, 3(1), 34–36.
[5] Yang, R. (2024). Research on the regulation of the performance of vanadium dioxide in lithium-sulfur soft-pack batteries [Doctoral dissertation, Southwest University of Science and Technology].
[6] Li, X., Chen, L., Ma, X., et al. (2019). Preparation of V_2O_3 hollow spheres and their application in lithium-sulfur batteries. Chemical Journal of Chinese Universities, 40(9), 1972–1978.
[7] Chen, B. (2023). Electrochemical performance research on low-dimensional vanadium oxide cathode materials for lithium-sulfur batteries [Doctoral dissertation, Xi'an University of Architecture and Technology].
[8] Liu, F. (2023). Preparation of metal cation-doped V_2O_5 microsphere materials and their application research in lithium-sulfur batteries [Doctoral dissertation, Nanchang University].
[9] Pang, Y. S., Xie, M. S., Lu, X. H., et al. (2024). Electronic metal-support interactions in atomically dispersed Fe(III)-VO_2 nanoribbons for high-performance lithium-sulfur batteries. Advanced Functional Materials, 34(2), 2308849.
[10] Liu, B. T., Li, H., Shi, C. L., et al. (2022). Multifunctional integrated VN/V_2O_5 heterostructure sulfur hosts for advanced lithium-sulfur batteries. Nanoscale, 14(12), 4557–4565.
[11] Cai, J. S., Jin, J., Fan, Z. D., et al. (2020). 3D printing of a V_8C_7-VO_2 bifunctional scaffold as an effective polysulfide immobilizer and lithium stabilizer for Li-S batteries. Advanced Materials, 32(50), 2005967.
[12] Dan, J. C., Zhou, W., Chen, M. Z., et al. (2023). Cobalt-carbon nanotubes supported on V_2O_3 nanorods as sulfur hosts for high-performance lithium-sulfur batteries. Journal of Colloid and Interface Science, 64, 877–889.
[13] Yang, Y. (2021). Preparation of vanadium-based heterojunctions and their application in lithium-sulfur batteries [Doctoral dissertation, Wuhan University of Science and Technology].

Author Profile

Chaofan Hu (2002-), male, Han nationality, from Xi'an, Shaanxi, undergraduate, research direction: lithium-sulfur batteries.