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Nanomaterial Modifications for Mitigating Polysulfide Shuttle Effect on Lithium-Sulfur Batteries: A Review

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Abstract. With the rapid development of electric vehicles and large-scale energy storage systems, conventional lithium-ion batteries may be incapable of meeting the gradually increasing energy demands. Accordingly, lithium-sulfur batteries, which feature an ultra-high theoretical energy density, have emerged as a research hotspot worldwide. This review focuses on various strategies for modifying lithium-sulfur batteries using nanomaterials to mitigate the internal polysulfide shuttle effect. This study aims to systematically sort out various effective modification approaches and clarify their underlying functional mechanisms. By adopting the literature analysis method, this work collects, organizes and compares experimental research findings from the past decade concerning two major modification schemes: nanostructured cathode hosts and functional separators. The study reveals that carbon nanotubes combined with polar metal composite materials can achieve a synergistic effect involving a physical barrier, chemical polysulfide trapping and electrocatalysis, which substantially reduces the capacity decay rate and improves the Coulombic efficiency. This review also summarizes several widely recognized bottlenecks for the industrialization of lithium-sulfur batteries and proposes a few directions for future research based on existing literature. Additionally, it aims to accelerate the commercialization process of lithium-sulfur batteries.

Keywords: lithium-sulfur batteries, polysulfide shuttle effect, nanomaterials

1. Introduction

With the rapid development of electric vehicles, the energy storage capacity of traditional lithium-ion batteries has become insufficient to meet the long-term demands of society [1]. What has drawn extensive attention is that the energy density (2600 Wh/kg) and theoretical specific capacity (1675 mAh/g) of lithium-sulfur batteries are both much higher than those of lithium-ion batteries. As the cathode active material, sulfur is abundant in resources, low-cost and environmentally friendly, which further enhances its practical and commercial potential in application [2]. However, polysulfide shuttle effect, one of the main bottlenecks, relates to the reversible migration (during charging) of soluble compounds from one electrode to the other, positive or negative, and to discharging is known to produce a whole range of bad effects such as fast capacity loss, poor Coulombic efficiency and adverse electrode corrosion [3].

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In recent years, with a view to reducing the polysulfide shuttle effect, many researchers have suggested various approaches to this problem and have made use of nanomaterials because of their special structure and properties. Nanomaterials are known to have a specific surface area and pore structure, which make it possible to have substantial chemical interaction with polysulfides, thus helping with their conversion regarding polysulfide limitation. The present review deals mostly with two basic approaches based on nanomaterials to control the polysulfide shuttle in lithium-sulfur batteries, namely positive electrode carriers and functional separators. It sets out, in turn, to be a treatment of the following shuttle process, which has already been much studied by means of theory and experiments.

This review is intended primarily to give a well-organized account based on current findings of nanomaterials used or proposed for lithium-sulfur batteries, with an eye to characterization methods and performance data together with the relevant mechanisms. Additionally, the difficulties of lithium-sulfur batteries and possible areas for later investigation are both brought up here.

2. Strategies for improving lithium-sulfur batteries using nanomaterials

2.1. Nanomaterials as cathode support

The mechanism of action of nano cathode supports is to physically adsorb polysulfides, reducing their dissolution and diffusion. Conventional materials for the cathode support of batteries are carbon nanotubes (CNTs) and metal oxide nanomaterials.

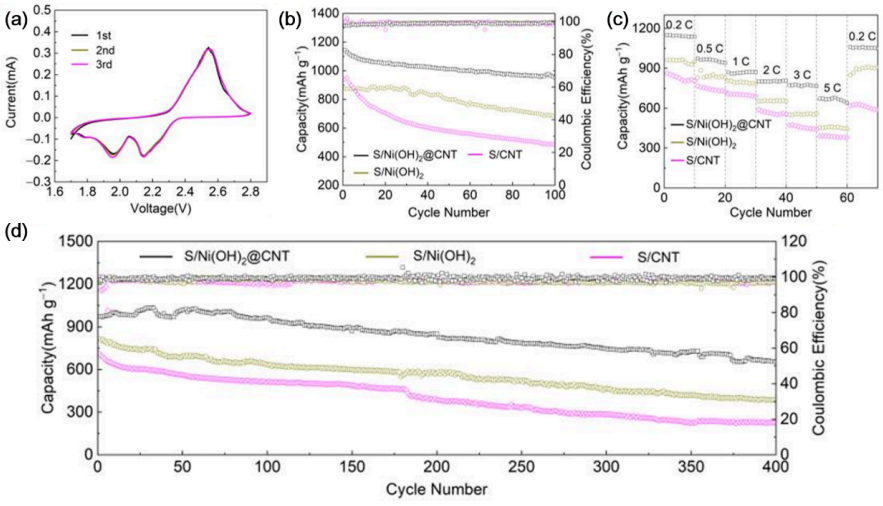

Figure 1. Electrochemical performance of the S/Ni(OH)$_2$@CNT cathode for lithium-sulfur batteries (a) Cyclic-voltammetry curves for Li–S cells assembled with S/Ni(OH)$_2$@CNT cathodes; (b) Cycling behaviors of various electrodes measured at 0.2 C; (c) Galvanostatic cycling profiles of the S/Ni(OH)$_2$@CNT cathode under diverse current rates ranging from 0.2 to 5 C; (d) Long-cycle stability of Li–S cells equipped with various electrodes over 400 cycles at 1 C [4]

Although CNTs have been widely used by researchers, numerous new studies in recent years continue to explore ways to improve them. Jin et al. developed a Ni(OH)$_2$@CNT microsphere with homogeneous hollow mesoporosity, and a melt impregnation method was used to fabricate the S/Ni(OH)$_2$@CNT composites [4]. The designed material features the distinctive spheroidal flower morphology with a 3D framework, which has desirable porosity together with extensive specific surface area. As illustrated in Figure 1a, the CV profiles feature a single oxidation peak alongside

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two reduction peaks, and these three cycles for the composite are almost completely overlapping, indicating its excellent electrochemical stability. As indicated in Figure 1b, diverse electrodes exhibit different electrochemical behaviors measured at 0.2C. Among them, S/Ni(OH)$_2$@CNT demonstrated an extremely high sulfur utilization rate, possessing an initial specific capacity of 1146 mAh/g. After 100 cycles, S/Ni(OH)$_2$@CNT maintains a capacity retention ratio of 83.4%, a much larger value compared with 483 mAh/g for S/CNT and 689 mAh/g for S/Ni(OH)$_2$. As depicted in Figure 1c, the S/Ni(OH)$_2$@CNT also has exceptional rate performance. It was remarkable that the capacity delivered by the S/Ni(OH)$_2$@CNT cathode was able to recover to 1054 mAh/g if the charge/discharge rate was suddenly turned back to 0.2C. A long-term cycling test was conducted on different cathodes (Figure 1d). The S/Ni(OH)$_2$@CNT exhibits a considerable capacity reaching 972 mAh/g at 1C, and even after completing 400 charge-discharge cycles, the discharge capacity remained at 652 mAh/g, which signifies that the per-cycle capacity loss was only 0.081%.

Selenides possess relatively high electrical conductivity and exhibit similar polarity to sulfides and thus have emerged as promising cathode materials applied in lithium-sulfur batteries. Yang et al. pioneered the exploration of the approach for constructing lithium-sulfur battery cathode materials by incorporating zinc selenide nanoparticles into nitrogen-doped carbon as nanoreactors [5]. As shown in Figure 2, researchers synthesized a zeolitic imidazolate framework-8(ZIF-8) precursor powder through a modified precipitation strategy and obtained ZnSe/HNC through annealing treatment of the precursor under a selenium atmosphere. Finally, the melt-diffusion treatment was utilized to introduce sulfur into ZnSe/NHC to prepare S@ZnSe/NHC. The Li_2S_4 adsorption performance of the host materials was evaluated, and the most pronounced faded color was observed in the solution containing ZnSe/NHC, which exhibited the most significant adsorption effect for lithium polysulfide. This was further corroborated by ultraviolet-visible spectroscopy analysis of the supernatant. The dipole-dipole electrostatic interaction between the Lewis acidic lithium atoms in LiPS and the Lewis basic nitrogen heteroatoms doped in carbon materials endow NHC with lithiophilic character. Besides, a strong interaction formed between Zn within ZnSe and S within LiPS confirms the sulfiphilic property of ZnSe within the ZnSe/NHC composite. Specifically, the NHC-based lithiophilic sites and the ZnSe-based sulfiphilic sites induce ZnSe/NHC with a dual chemical adsorption effect and high affinity toward polysulfides, thereby inhibiting the shuttle effect of lithium polysulfides. The experimental observations demonstrate that among three different tested cathode materials, S@ZnSe/NHC exhibits excellent comprehensive performance. It delivers a favorable initial specific capacity of 1475 mAh/g under a current density of 0.1C, with a lower polarization potential (ΔE=157 mV). Additionally, it possesses outstanding rate capacity, achieving an average discharge capacity reached 542 mAh/g at a current density of 3C. After 800 successive cycles at an ultra-high current rate of 3C, the capacity decay in each individual cycle is merely 0.022%. Besides, the Coulombic efficiency remains stably in excess of 99.5%, indicating its excellent long-cycle stability.

Figure 2. Schematic showing the synthesis procedure of S@ZnSe/NHC composites [5]

Azam et al. employed $NiCo_2Ox$-modified CeO_2 nanorods as sulfur hosts; specifically (Figure 3), 10wt% Ni-Co-based bimetallic oxide with a Ni: Co atomic proportion of 1:2 was loaded on CeO_2

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nanorods through a hydrothermal-assisted precipitation-deposition route [6]. In this material, the intrinsic oxygen vacancy sites present on the surface of CeO_2 exhibit strong chemisorption to trap polysulfide anions. Meanwhile, the electrocatalytic effect of $NiCo_2Ox$ nanoclusters accelerates the conversion of polysulfides, thus realizing a dual adsorption-catalysis mechanism. Based on the analysis of characterization results of the kinetic reaction behavior and prolonged cycling stability of lithium-sulfur batteries using $NiCo_2Ox/CeO_2$ nanorods, it can be concluded that, compared with pure carbon cloth and single CeO_2 nanorod electrodes, the proposed host can significantly reduce battery resistance, increase the diffusion coefficient of lithium ions, mitigate polarization, and substantially accelerate the polysulfide conversion. At a sulfur loading of 1.33 mg/cm^2 and a current density of 0.2 C, the starting discharge specific capacity reaches 1236 mAh/g and stabilizes at 1120 mAh/g after 100 cycles, which corresponds to a minimal per-cycle capacity decay of only 0.09%. At high sulfur loadings of 2.67, 4 and 5.33 mg/cm^2, the electrode still retains a superior discharge capacity per unit area after 100 cycles. Characterization of the cathode and anode after cycling confirms that nanorods can catalyze the conversion of polysulfides by generating thiosulfate intermediates, while suppressing the polysulfide shuttle effect, protecting the lithium metal anode, and expanding the cycling lifespan of batteries, thus exhibiting excellent potential for practical applications.

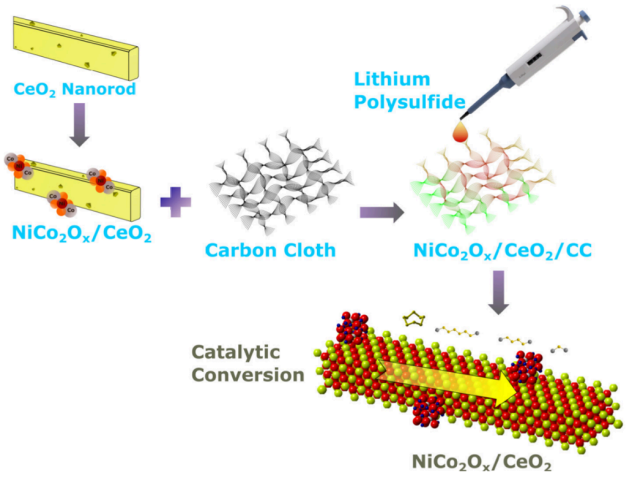

Figure 3. Illustrative scheme describing the synthetic route of Li–S batteries adopting. $NiCo_2O_4/CeO_2$ NR as cathode matrix, demonstrating the dual-function adsorption and catalysis effect on lithium polysulfides [6]

2.2. Separator modified by nanomaterials

Modification of battery separators using nanomaterials is another effective strategy for inhibiting the diffusion of polysulfides. The functional coating formed on the separator surface has the potential to act as both a physical restriction and chemical trapping sites to mitigate the shuttle effect. Conventional lithium battery separators, such as polyethylene, polypropylene and their composite membranes, possess micron-scale pore sizes that are far larger than the dimensions of sulfide ions [7]. Therefore, they cannot effectively block the shuttle effect.

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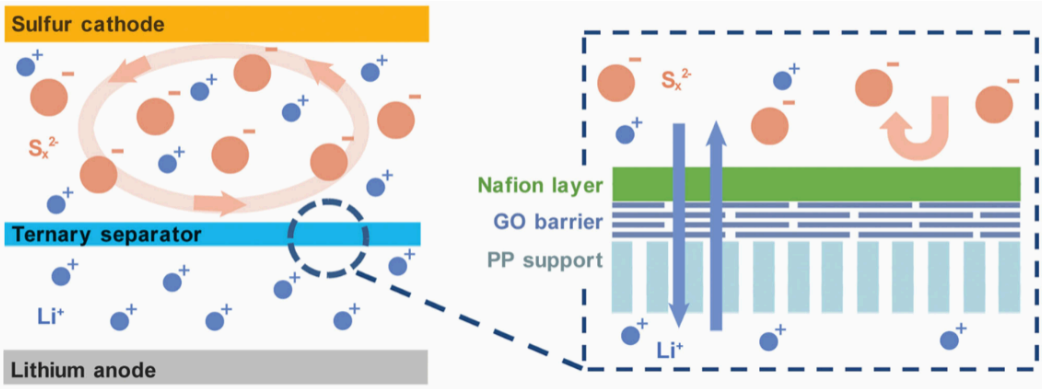

Figure 4. Illustration displaying the structure of a triple-component PP/GO/Nafion separator

Freestanding PP film provides continuous mechanical support. GO sheets with an ultralow loading (0.0032 mg/cm²) cover the macroporous structure of PP and construct physical blocking layers to restrain anionic polysulfide species. A Nafion coating (0.050 mg/cm²) is deposited atop GO, offering $–SO_3^-$ functional moieties. Such groups facilitate rapid Li^+ hopping and hinder the migration of negatively charged S_n^{2-}. The as-designed triple-layer separator realizes elevated Coulombic efficiency and stable capacity retention for cycled Li–S cells [8].

Zhuang et al. constructed a trilayer composite separator composed of a macroporous polypropylene (PP) substrate layer, a graphene oxide (GO) blocking layer, and a Nafion retarding layer [8]. As shown in Figure 4, the PP material serves as a robust insulating matrix with a pore diameter ranging from 20 to 40 nm and a length ranging from 200 to 300 nm. The mass loading per unit area of the ultrathin GO layer stands at merely 0.0032 mg/cm^2 (estimated to consist of roughly 40 layers), which effectively blocks the macroporous framework of the PP substrate. The ion-selective Nafion retarding layer only requires a mass loading of 0.05 mg/cm^2 to endow the separator featuring numerous sulfonic acid moieties and a compact membrane structure, which suppresses the shuttle effect of polysulfides via electrostatic repulsion. The ion diffusion characteristics of the trilayer composite separator are visualized in a customized setup. As illustrated in Figure 5, different separators are placed between the polysulfide solution and the pure solvent to observe color changes. After 16 hours, almost no color change can be detected in the solvent phase of the ternary-layered separator, demonstrating its superior capability to block diffusion. An electrolyte that excludes the protective effect of $LiNO_3$ on the anode was selected to conduct electrochemical performance tests on the ternary-layered separator. The results show that the ternary-layered separator can increase the high plateau of discharge profiles, thereby significantly increasing the primary specific capacity of the sulfur cathodes, which ranges from 969 to 1057 mAh/g. Consistent with the visualization test results presented in Figure 5, this phenomenon indicates that the separator exhibits a significant suppression effect on polysulfides. Furthermore, this effect also significantly increases the Coulombic efficiency from 80.1% to 94.8%. Cycle tests demonstrate that after 200 cycles at 0.5C, the battery assembled with the ternary-layered separator still maintains a Coulombic efficiency of 95%-99%, while the battery with the conventional PP separator only exhibits a Coulombic efficiency of approximately 85%.

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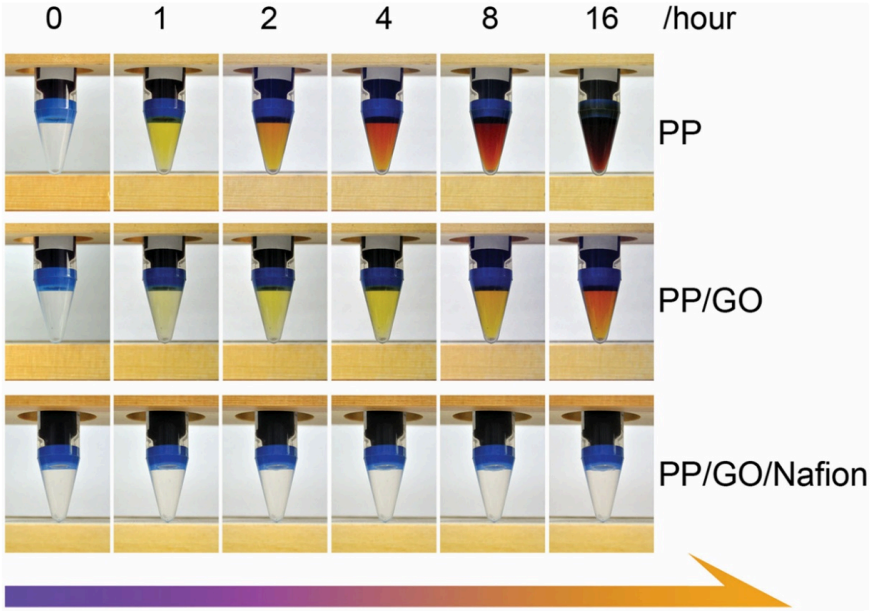

Figure 5. Visual experiment evaluating the shuttle effect suppression capability of the ternary layered separator

Comparison of high-order polysulfide diffusion across a conventional PP separator (top), PP/GO separator (middle), and PP/GO/Nafion triple-layer separator (bottom) after standing for 16 h [8].

Um et al. constructed a heterogeneous Janus architecture host electrode [9]. The cathode is fabricated by bonding a bare carbon nanotube film and a Mo_2C nanoparticle-coated carbon nanotube via a compressive calendaring process, while the anode is obtained by combining a Mo_2C nanoparticle-coated carbon fiber film with a bare carbon fiber film. The mass loading of Mo_2C nanoparticles on both the cathode and anode is 20 wt%. The adsorption efficiency of the Janus film cathode substrate for lithium polysulfides was measured, and the results showed that the Janus film exhibited a faster decolorization rate than the bare carbon nanotube film. Coupled with the spectroscopic absorption characteristics obtained from ultraviolet-visible tests (Figure 6a), it was confirmed that the polysulfide adsorption capability of the Janus film is nearly three times that of the bare carbon nanotube film. Density functional theory (DFT) theoretical calculations reveal that the adsorption capacity of Mo_2C for lithium polysulfides displays an enhancement of nearly 2.4 times the value of the carbon surface. The potentiostatic discharge capacity test was performed on the Janus film cathode cell composed of a lithium metal anode and a cathode with a sulfur loading reaching 5 mg/cm^2, and the cell still maintained a capacity retention percentage of almost 89% over 18 cycles, which is shown in Figure 6b,c. For the Janus carbon fiber anode, cycling tests were conducted on the Janus film with a capacity of 10 mAh/cm2 under a current density of 1 mA/cm^2. The Janus film retains a Coulombic efficiency as high as 99.9% over 100 consecutive cycles, exhibiting stable and outstanding performance. In contrast, the cycling test of the bare carbon fiber film was terminated after around 30 cycles due to significant fluctuations in its Coulombic efficiency. When the Janus films were assembled as a separator into a full cell, the original discharge capacity at 0.1 C reached a record 1461 mAh/g, and as illustrated in Figure 6d, the capacity retention decay rate over 1000 cycles is only 0.048%, which demonstrates excellent long-cycle stability.

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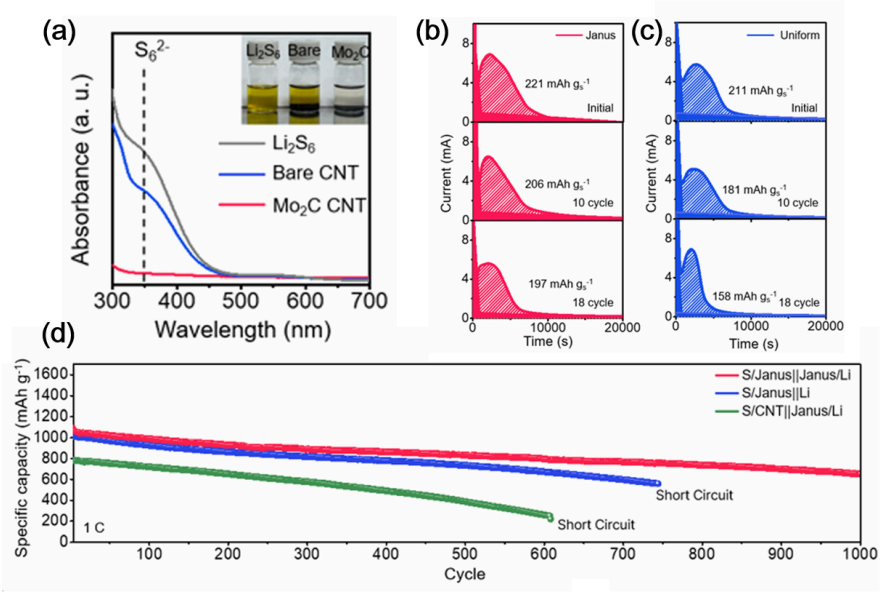

Figure 6. Trapping and conversion capabilities of Janus film toward lithium polysulfides for lithium-sulfur batteries. (a) UV-vis absorption spectra of Li_2S_6 electrolyte soaked with blank substrate and Mo_2C-CNT composite. The inset photograph displays the solution color variation after adsorption treatment; (b) Galvanostatic discharge curves reflecting the conversion process of lithium polysulfides to Li_2S upon cycling in cells equipped with Janus film cathodes; (c) Galvanostatic discharge curves illustrating the LiPS-to-Li_2S conversion behavior during cycling for batteries with uniform film cathodes; (d) long-term cycling [9]

Jiang et al. synthesized $NiFe_2O_4$ nanoparticles via a modified hydrothermal method and prepared a functional coating slurry by mixing the synthesized nanoparticles with Ketjen Black (KB) at a mass ratio of 9: 27 to modify polypropylene separators [10]. SEM images indicate that within the coating, KB particles stack to construct a three-dimensional conductive porous structure capable of accommodating liquid electrolyte. $NiFe_2O_4$ nanoparticles with spinel structure are uniformly dispersed in the porous structure, which captures lithium polysulfides via strong polar chemical bonds and catalyzes their conversion. The synergistic effect of the two components effectively inhibits the polysulfide shuttle effect between the two sides of the separator, and the modified separator membrane has excellent adhesion and stability. Cycle tests have been made of batteries fitted with several separators and the performance has been studied. If one uses a current rate of 0.5 C, then after 100 cycles, the capacity of the battery fitted with the basic PP separator is retained at no more than 49.1%, whereas the battery fitted with the $NiFe_2O_4$/KB-modified separator gives 69.7% capacity retention (nearly 1.5 times the value for the original separator), which is an encouraging result indicate that the separator has very good cycling stability. Furthermore, with a high current density (of 1 C) for more than 1000 consecutive cycles, the average capacity decay per cycle amounts to just 0.051%. The findings listed above show that the $NiFe_2O_4$/KB-modified separator is capable of greatly increasing battery cycle life.

3. Universal challenges

Based on the experimental results and data from the literature reviewed above, various strategies have demonstrated promising performance. However, when it comes to practical industrialization, lithium-sulfur batteries still face numerous challenges. For instance, high surface area nanomaterials

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may undergo certain side reactions to a certain extent with the electrolyte, leading to continuous depletion of the electrolyte. Polar metal oxides inherently suffer from relatively low electrical conductivity, and excessive loading of such materials tends to increase battery internal resistance and polarization. Moreover, these nanomaterials may have drawbacks including complex synthesis procedures, high process production costs, insufficient production stability that hinders large-scale production, among other issues.

4. Future research outlook

Based on literature and practical challenges, several targeted research directions for future investigations are proposed. First, priority should be given to relatively low-cost nanomaterials as alternatives to high-cost precious metals and complexly prepared metal-organic framework derived nanomaterials. Second, it is desirable to plan for more work on materials with hierarchical arrangements as well as defects. Both are helpful in the polysulfide adsorption ability and buffer volume expansion. Third, it is necessary to adjust the functional coating about its location and its thickness to fit cases involving very large sulfur area loads. Effective suppression of the shuttle effect for polysulfides is not something that can be handled by one single method but calls for joint action on several levels. In conclusion, by means of a constant, rational optimization of what modification strategies may be expected for practical uses with lithium-sulfur batteries in the fields of electric vehicles as well as large-scale storage of energy.

5. Conclusion

This review summarizes two typical modification schemes of nanomaterials for lithium-sulfur batteries: sulfur cathode hosts and functional coated separators. Each scheme can achieve physical confinement, chemical capture and electrocatalysis, and these effects synergistically suppress the polysulfide shuttle effect. All the schemes discussed in this review can reduce the capacity decay rate and improve sulfur utilization. Future research still needs to address inherent drawbacks such as poor intrinsic conductivity and complex preparation processes. Continuous optimization through future nanomaterial design will further promote the transition of lithium-sulfur batteries from theoretical research to practical application.

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