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Investigation of the Microstructure and Performance of Composite Cathodes in Sulfide-Based Solid-State Batteries

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Abstract

Sulfide-based solid-state batteries have emerged as a leading candidate for next-generation energy storage solutions, owing to their superior safety characteristics and high energy density potential. The composite cathode, as a critical component of sulfide-based solid-state batteries, requires precise microstructure optimization to significantly enhance overall battery performance. This paper compiles and synthesizes current research advancements, providing a comprehensive review of how sulfide electrolyte particle size distribution, active material loading ratios, and interface engineering critically influence composite cathode performance. The study also examines methods and mechanisms for developing high-loading cathodes to enhance cycling stability and rate capability, while summarizing associated challenges and potential strategies. Currently, this field faces notable challenges, including discrepancies between experimental and practical performance, reliance on static models, and difficulties in achieving low impedance with high-loading electrodes. To overcome these limitations and enable widespread application in electric vehicles and large-scale energy storage, we must establish multi-scale in-situ characterization platforms, develop multi-physics dynamic models, investigate novel interfacial materials, and optimize electrode manufacturing processes.

Keywords

sulfide-based solid-state batteries, composite cathode, microstructure regulation

1. Introduction

Lithium-ion batteries have become the core energy storage technology for portable electronics, electric vehicles, and large-scale energy storage systems. however, the energy density of conventional liquid lithium-ion batteries is approaching its theoretical limit. Furthermore, the flammable organic electrolytes are prone to side reactions, posing significant safety risks.

Consequently, the development of all-solid-state lithium-ion batteries utilizing solid electrolytes has emerged as a promising solution. These batteries not only enhance safety but are also compatible with high-energy electrode materials like lithium metal, thereby breaking through energy density limitations. Among them, sulfide-based solid electrolytes exhibit room-temperature ionic conductivity on the order of 10^{-2} $S \cdot cm^{-1}$, along with excellent processability and electrode compatibility, making them a key research focus for all-solid-state batteries.

The composite cathode serves as a critical component in sulfide-based solid-state batteries, where its microstructure governs the continuity of ion/electron transport and the quality of interfacial contact, thereby directly determining essential performance metrics such as capacity and rate capability. Mismatched electrolyte and active material particle sizes may form porous structures that disrupt ion transport paths. While excessive active material loading causes component imbalance, insufficient loading fails to achieve high energy density. Therefore, investigating the “microstructure-electrochemical performance” relationship in composite cathodes is crucial for practical battery development.

Recent studies have demonstrated notable progress in this field: Using fine-grained sulfide electrolytes significantly increases contact area with active materials, thereby enhancing charge transfer efficiency. Composite cathodes prepared with NCM811 and small-particle electrolytes exhibit substantially higher initial discharge capacity compared to large-particle counterparts(Schlautmann et al., 2023). At a mass ratio of 70:30 between NCM and Li_6PS_5Cl, optimal conductivity matching is achieved, maintaining capacity growth even when current rates increase from 0.05C to 1C. The application of LLSTO as an interfacial coating effectively mitigates lithium distribution inhomogeneity in thick cathodes, reducing the maximum lithiation gradient(Δx)by approximately 30% in coated versus uncoated samples (Stavola et al., 2023).

Nevertheless, the practical application of composite cathodes faces significant challenges. Most experiments are conducted under idealized conditions (25°C, 50MPa constant pressure), creating substantial gaps between laboratory data and real-world performance. Existing microstructure models fail to account for dynamic interfacial and bulk phase evolution during cycling, limiting accurate capacity fade prediction. Furthermore, achieving both high active material loading and low transport impedance remains particularly difficult. For instance, when NMC loading reaches 80%, the ionic transport tortuosity coefficient (τ^2) in the Li_6PS_5Cl phase dramatically increases from 7.78 to 17.24, resulting in sharply elevated transport resistance (Stavola et al., 2023).

This review will systematically examine the intrinsic “microstructure-electrochemical performance” relationship in composite cathodes, summarize prevailing optimization strategies while identifying their limitations, and subsequently propose an integrated research framework combining multi-scale characterization with dynamic modeling. The ultimate objectives are to design composite cathodes with high active material loading, low transport impedance, and stable interfaces, thereby providing valuable insights for advancing sulfide-based solid-state battery technology.

2. Overview of Composite Cathodes for Sulfide-Based Solid-State Batteries

2.1 Component Systems

The composite cathode of sulfide-based solid-state batteries consists of active material NCM811, solid electrolyte Li_6PS_5Cl, and conductive additives.

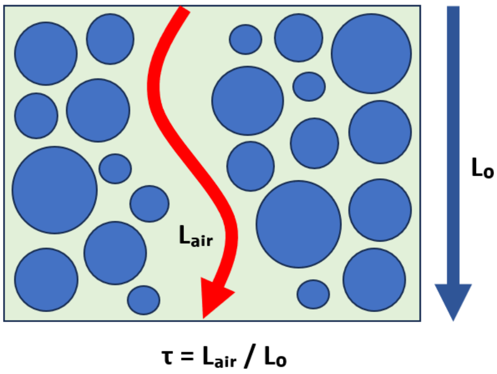
The active material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) is a high-nickel ternary compound with a theoretical specific capacity of 220 $mAh\cdot g^{-1}$. Its layered structure enables reversible lithium-ion intercalation and deintercalation. However, challenges such as structural phase transitions during charge/discharge cycles and high surface reactivity with electrolytes must be addressed. Interface modification is typically employed to enhance its stability. The sulfide solid electrolyte Li_6PS_5Cl exhibits a room-temperature ionic conductivity of 10^{-2} $S\cdot cm^{-1}$, serving roles in ion conduction, interfacial contact, and mechanical buffering. Conductive additive (activated carbon), with electronic conductivity >100 $S\cdot cm^{-1}$, constructs a continuous electron network to compensate for the low conductivity of NCM811 ($\approx 10^{-8}$ $S\cdot cm^{-1}$). Its content is typically controlled at 2–5 wt%; excessive amounts reduce energy density, while insufficient amounts disrupt electron network continuity.

2.2 Key Microstructural Parameters

Critical parameters governing the composite cathode structure in sulfide-based solid-state batteries include particle size distribution, porosity, active material loading, and tortuosity.

Particle size distribution is characterized by median particle size and distribution width. Smaller Li_6PS_5Cl particles enhance contact area with NCM811, while larger particles may cause ion transport pathway discontinuities. The distribution width should be maintained between 0.5-0.8, as excessive polydispersity readily induces particle agglomeration. Porosity refers to the volume fraction of voids within the electrode and should be maintained between 20% and 30%. Excessively low porosity compromises ion transport pathways, while overly high porosity reduces active material loading and structural integrity. This balance ensures simultaneous optimization of ion transport efficiency and energy density requirements, Active material loading typically needs to exceed 10 mg·cm^{-2} to enhance energy density. However, excessively high loading (>80 wt%) leads to insufficient electrolyte content, increased ion transport tortuosity, and sharply elevated resistance. Conversely, loading below 50 wt% fails to meet energy requirements. Tortuosity reflects the convoluted nature of ion/electron transport paths, as schematically illustrated in Fig. 1. The ideal tortuosity value ranges from 2 to 3, whereas conventional electrodes typically exhibit values exceeding 5. High active material loading or particle size mismatch can cause rapid tortuosity increase (e.g., τ_2 in Li_6PS_5Cl phase may rise from 7.78 to 17.24), significantly elevating transport resistance.

Figure 1: Schematic diagram of tortuosity.



2.3 Structure-Performance Relationship

Cells with well-matched particle sizes and balanced active material-to-electrolyte ratios demonstrate superior performance.Li_6PS_5Cl (1–10 μm) with particle size compatible to NCM811 reduces tortuosity and enhances initial capacity (198 mAh·g^{-1} in fine-particle group vs. 152 mAh·g^{-1} in coarse-particle group).Cells with balanced active material-to-electrolyte ratio (NCM811:Li_6PS_5Cl mass ratio = 70:30) form dual-continuous ion-electron conduction networks, enabling capacity increase even when rate rises from 0.05C to 1C.

Low tortuosity and optimized porosity effectively suppress interfacial side reactions. For instance, aligned pore channels enable high-loading cathodes to maintain over 80% capacity retention. Incorporating activated carbon enhances electron transport, thereby mitigating rate capability degradation.

3. Composite Cathode Structural Regulation Strategies

3.1 Sulfide Electrolyte Particle Size Regulation

Fine particles (D_{50}=4μm) improve capacity and cycling performance, though excessively small sizes risk agglomeration. A particle size range of 1-10μm with optimized distribution is recommended.

Particle size distribution of sulfide solid electrolytes constitutes a critical controlling factor for composite cathode microstructure, directly governing ion transport continuity and interfacial contact quality. Schlautmann et al. (Schlautmann et al., 2023) conducted a detailed study on the particle size effect of Li_6PS_5Cl electrolyte. When composite cathodes were prepared with fine-grained electrolyte (D_{50}=4μm), the active material interparticle voids were more effectively filled, resulting in enhanced interfacial contact area, reduced ion transport tortuosity, and improved charge transfer efficiency. This configuration achieved an initial discharge capacity of 198 mAh·g^{-1}, significantly surpassing the 152 mAh·g^{-1} obtained with large-grained electrolyte (D_{50}=40μm).Fine-grained electrolytes form homogeneous ion conduction networks, effectively preventing current density localization and polarization, buffering volume changes of active materials, suppressing interfacial side reactions, and ultimately enhancing cycling stability. Furthermore, cathode materials with reduced particle dimensions also enhance battery performance. Wu et al. developed submicron-sized SC-LRMO cathodes (300-700 nm), which delivered a reversible capacity of 316 mAh/g at 0.05C and maintained 90% capacity retention after 50 cycles under high loading conditions of 20 mg/cm² (Wu et al., 2024).

However, smaller particle size is not always preferable. Excessively fine particles exhibit high surface energy, leading to agglomeration during ball milling and mixing processes, which ultimately disrupts the ion conduction network. Balancing research requirements and industrial feasibility, the optimal electrolyte particle size should be controlled within 1-10 μm. Additionally, employing suitable dispersants or blending particles of different sizes can effectively regulat size distribution and optimize the ion conduction network structure (Jiang et al., 2023).

3.2 Optimization of Active Material to Electrolyte Ratio

A mass ratio around 70:30 facilitates the formation of a bicontinuous percolation network, though specific adjustments should be made according to active material properties, manufacturing processes, and application requirements.

The mass ratio between active material and electrolyte directly governs the ion-electron transport balance in composite cathodes, consequently determining battery performance. Active material loading exceeding 80wt% leads to insufficient electrolyte content, obstructed ion transport, and degraded rate capability, while loading below 50wt% fails to meet high energy density requirements.

Employing operando energy-dispersive X-ray diffraction (EDXRD), Stavola et al. (2023) dynamically monitored and investigated the lithiation gradient within a thick NMC111-argyrodite composite cathode with a thickness approaching 110 μm. They observed that at 70wt% active material content, ionic and electronic conductivities achieve optimal matching, enabling continued capacity growth even when the current rate increases from 0.05C to 1C, attributable to the formation of a bicontinuous percolation network. When the loading reaches 80%, the tortuosity coefficient(τ)of Li_6PS_5Cl electrolyte surges from 7.78 to 17.24, causing a sharp increase in ion transport resistance due to compressed electrolyte particles failing to form continuous conduction pathways.

Theoretically, active materials and electrolytes must form a continuous transport network with low tortuosity in three-dimensional space. Current research indicates that a mass ratio between 60:40 and 70:30 most readily achieves this balance. For practical optimization, high-nickel NCM materials with superior electronic conductivity may accommodate increased electrolyte proportions. In thick electrodes (>100μm), elevating electrolyte content helps alleviate ion transport constraints, whereas thinner electrodes or high-energy-density designs can tolerate higher active material loadings (Cao, 2020).

3.3 Interface Modification

Hybrid sulfide-polymer coatings, bulk doping, and synergistic interfacial modification strategies effectively suppress side reactions while enhancing interfacial stability.

Interfacial side reactions constitute a primary cause of capacity degradation in composite cathodes. The interface between high-voltage cathode materials and sulfide electrolytes is prone to reactions that generate high-resistance byproducts, impeding ion transport. Interface coating technology has proven effective in addressing this challenge, with oxide and polymer coatings demonstrating particularly favorable results.

To address interfacial stability issues in high-nickel single-crystal $Li[Ni_{0.92}Co_{0.06}Mn_{0.02}]O_2$(SC-Ni92), Liu et al. innovatively constructed a hybrid $LiNbO_3$-Li_3BO_3 coating on its surface. The crystalline $LiNbO_3$ establishes ion-conducting channels while isolating active material from electrolyte, while amorphous Li_3BO_3 fills surface defects of the active material. As shown in Figure 4, the coated sample maintained 88.4% capacity retention after 100 cycles at 1C rate, significantly surpassing the 75% retention of uncoated samples. XPS analysis confirmed the coating effectively suppressed S^{2-} oxidation and electrolyte decomposition (Liu et al., 2025).

Lin et al. proposed a synergistic interfacial modification strategy for $LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$ (NCM83125) active material through Zr/F co-doping combined with cPAN coating. The Zr/F co-doping enhances bulk structural stability, while the cPAN coating simultaneously suppresses interfacial reactions and constructs an electron conduction network. Density functional theory (DFT) calculations demonstrate this approach reduces the driving force for interfacial reactions. The modified composite cathode delivers a stable capacity of 109 $mAh \cdot g^{-1}$ even at 3C rate (Lin et al., 2024).

Furthermore, Zhao et al. proposed a P-CNT modification strategy to address interfacial contact and stability issues between the cathode and electrolyte, achieving 70.4% capacity retention after 1400 cycles (Zhao et al., 2023). Additional interfacial regulation approaches including sulfide electrolyte coatings and two-dimensional material interlayers, provide valuable pathways for enhancing battery performance.

4. Challenges and Strategies

4.1 Challenges and Strategies for High-Loading Cathode Design

Achieving high active material loading (typically>10 $mg \cdot cm^{-2}$) is critical for enhancing the energy density of sulfide-based solid-state batteries to meet application requirements in electric vehicles and large-scale energy storage systems. However, the design and fabrication of high-loading cathodes face significant challenges: as active material loading increases, electrode thickness typically grows substantially, leading to considerably extended ion transport paths within the electrode. Concurrently, the tortuosity of these ion transport pathways rises, resulting in a sharp increase in ion transport resistance. Furthermore, high loading may lead to uneven porosity distribution and discontinuous electron conduction networks within the electrode, further exacerbating charge transport bottlenecks.

To overcome the performance limitations of high-loading cathodes, microstructure design has become a breakthrough approach. Precise regulation of electrode porosity and ion transport tortuosity can significantly enhance ionic conductivity. Additionally, reinforcing the electron conduction network serves as an effective strategy to address challenges in high-loading cathode systems.

Another innovative research direction involves replacing polycrystalline active materials with single-crystal alternatives. Polycrystalline particles contain numerous grain boundaries, which can act as barriers to ion transport and frequently serve as hotspots for interfacial side reactions. During charge-discharge cycling, structural degradation and byproduct accumulation tend to occur near grain boundaries, leading to increased interfacial impedance. Single-crystal active material particles, being devoid of internal grain boundaries, mitigate ion transport barriers and reduce sites for interfacial side reactions. Their superior mechanical strength enables withstand high-pressure compaction during electrode fabrication, minimizing structural damage to the electrode.

4.2 Strategies for Enhancing Cycling Stability and Rate Capability

Cycling stability and rate capability represent core metrics for evaluating the practical viability of composite cathodes in sulfide-based solid-state batteries. Beyond the previously discussed strategies, additional approaches, including intrinsic material modification, thermal management optimization, and enhanced ion transport kinetics, play crucial roles in performance enhancement.

In intrinsic material modification, elemental doping to regulate the crystal structure and electronic properties of active materials serves as an effective approach to enhance the cycling stability of composite cathodes (Rana et al., 2023). Additionally, modifying the phase composition of electrolytes can significantly improve rate capability (Suo et al., 2024).

Regarding thermal management, sulfide electrolytes are highly temperature-sensitive: they decompose above 80°C and suffer drastic conductivity loss below 0°C. Maintaining an operating temperature of 50-60°C is essential to balance stability and conductivity, though safety and cost considerations must be addressed.

External pressure regulation serves as a key method for improving interfacial contact in composite cathodes and enhancing cycling stability. In sulfide-based solid-state batteries, applied pressure effectively reduces interfacial gaps, thereby facilitating ion conduction. Maintaining an external pressure of 10-50MPa enables optimal interfacial contact between the composite cathode and electrolyte, significantly reducing interfacial impedance. Excessive pressure may compromise pore structure, while insufficient pressure leads to poor contact, necessitating dynamic adjustment based on electrode parameters.

The enhancement of rate capability primarily depends on achieving fast ion transport kinetics, where the lithium-ion diffusion coefficient (DLi^+) serves as a key indicator of ion transport efficiency. Enhancing DLi^+through interface coating optimization and electrode structure design has emerged as a core strategy for improving the rate capability of composite cathodes. Beyond coating optimization, rational design of electrode thickness also serves as an effective approach to enhance rate capability. Reducing electrode thickness significantly shortens the Li^+transport path within the electrode, decreasing ion transit time and thereby enhancing the battery's rate response.

5. Conclusion

This review summarizes key regulation strategies and discusses multidisciplinary research progress, leading to the following conclusions: Regarding electrolyte particle size regulation, smaller particles increase contact area and reduce transport path tortuosity but are prone to agglomeration, necessitating control within the 1-10μm range; When the active material-to-electrolyte mass ratio reaches approximately 70:30, a bicontinuous percolation network forms, achieving optimal conductivity matching to ensure both high energy density and superior rate capability; In interface engineering, oxide-polymer hybrid coatings effectively isolate active materials from electrolytes, suppress side reactions, and provide ion transport pathways, significantly enhancing interfacial stability; For high-loading cathode design, aligned pore channels, single-crystal active materials, and conductive additives address transport and side reaction challenges under high loading conditions; Regarding cycling and rate performance enhancement, elemental doping, temperature-pressure control, and diffusion coefficient optimization serve as critical strategies.

Looking forward to advancing sulfide-based solid-state battery composite cathodes, the following research directions deserve emphasis: First, establishing multi-scale in-situ observation platforms; second, developing multi-physics dynamic models incorporating electro-chemo-mechanical coupling effects; third, exploring novel interfacial coatings and modified materials; fourth, optimizing electrode manufacturing processes to provide technical support for large-scale production of high-loading, low-impedance cathodes.

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