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Review Article

Progress in Modification Strategies of Manganese-based Cathode Materials for Aqueous Zinc-Ion Batteries: Structural Regulation and Performance Optimization

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Abstract

The global energy transition urgently requires the development of safe, economical, and high-performance energy storage technologies. Aqueous Zinc-Ion Batteries (AZIBs) have emerged as potential candidates for large-scale energy storage due to their inherent safety, environmental friendliness, and abundant resources. Manganese-based cathode materials have become a key component of AZIBs because of their high theoretical capacity ($\sim 308 \text{ mAh g}^{-1}$), relatively high operating voltage, and naturally abundant resources. However, in practical applications, they are still restricted by inherent defects such as low electronic conductivity, manganese dissolution, and capacity fading caused by structural instability. This paper systematically reviews the structural configuration and energy storage mechanism of AZIBs and deeply analyzes the fundamental challenges faced by manganese-based cathodes. We particularly emphasize four breakthrough modification strategies: lattice support regulation, defect state engineering, nanostructure design, and composite material construction. Focusing on discussing breakthrough solutions such as composite hybridization, defect regulation, and innovative structural engineering to address specific issues like particle agglomeration, uneven particle size, and Mn^{3+} disproportionation dissolution. Finally, this paper comprehensively evaluates the synergistic effects and inherent limitations among various modification methods. We propose that future research should focus on stable interface engineering, new dissolution inhibition mechanisms, and scalable manufacturing processes, thus laying the theoretical foundation for advancing high-performance AZIB systems.

Introduction

The escalating global energy demands and environmental degradation have rendered the construction of clean, low-carbon energy systems imperative for achieving carbon peaking and neutrality goals [1]. While renewable energy sources such as wind and solar power offer sustainable alternatives, their inherent intermittency and volatility necessitate reliable energy storage solutions [2,3]. Ideal energy storage devices must satisfy stringent requirements encompassing cost efficiency, high performance, operational safety, extended lifespan, and ecological compatibility. As pivotal electrochemical energy conversion systems, battery technologies have witnessed extensive deployment across various sectors. However, conventional systems including lithium-ion, lead-acid, nickel-cadmium, and fuel cells face critical limitations such as resource scarcity, high costs, environmental pollution, safety concerns, and limited cycle life constraints that substantially compromise their applicability in next-generation energy storage scenarios [4-7]. In this context, aqueous Zn ion batteries have garnered significant attention as promising candidates for large-scale energy storage and portable electronics, owing to their competitive manufacturing costs, exceptional cycling stability, and inherent safety [8,9].

Within Aqueous Zinc-Ion Batteries (AZIBs) systems, cathode materials constitute both the performance-determining component and primary technological bottleneck. Mn-based cathodes, particularly MnO_2 , have emerged as focal research targets due to their exceptional theoretical capacity (308 mAh g^{-1} via single-electron transfer), elevated output voltage, abundant manganese reserves, cost-effectiveness, and environmental benignity [10]. Nevertheless, practical implementation is hindered by intrinsic limitations including poor electronic conductivity, manganese dissolution, and structural degradation during cycling challenges that collectively undermine electrochemical performance and operational durability [11]. These challenges underscore the critical need for developing effective modification strategies to accelerate AZIB commercialization. This review systematically examines the structural characteristics, working mechanisms, and recent advancements in Mn-based cathode materials for AZIBs. Through analysis of emerging modification approaches, we provide looking perspectives on future research directions to bridge the gap between fundamental research and practical applications.

Structure and Energy Storage Mechanism of Aqueous Zn-Ion Batteries

Structure of aqueous Zn-ion batteries

AZIBs primarily consist of four components: a metallic zinc anode, a cathode, an aqueous electrolyte, and a separator [12]. Research focuses on the following areas: development of high-capacity and long-cycle cathode materials, inhibition of zinc dendrite growth and passivation on the anode, design of high-ionic-conductivity electrolytes, and construction of selective separators [13,14]. In the field of electrode material research, anodes include zinc foil, zinc powder, electroplated zinc, and zinc-free anodes [15]. Among these, aqueous secondary batteries predominantly utilize commercially available polished zinc foil as the anode substrate; electrolytes include $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ solutions, ZnSO_4 -based solutions, and ZnCl_2 solutions, among others. Adding MnSO_4 to the electrolyte in manganese-based cathode systems can mitigate the dissolution of cathode materials; battery separators include glass fiber separators and filter paper separators, among others [16]. These separators are characterized by low cost, adequate strength, and high ionic conductivity. The battery structure diagram is shown in Figure 1.

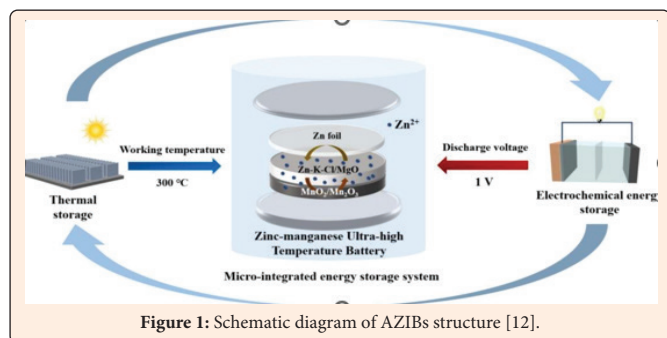


Figure 1: Schematic diagram of AZIBs structure [12].

Energy storage mechanism of aqueous Zn-Mn batteries

The energy storage mechanism of AZIBs exhibits multi-pathway characteristics due to the properties of aqueous electrolytes (proton-active, Zn^{2+} solvation). Currently, the mainstream view primarily encompasses four mechanisms: the most classical Zn^{2+} reversible insertion/extraction mechanism utilizes the 2×2 tunnel structure of $\alpha\text{-MnO}_2$ as a carrier for the reversible insertion/extraction of Zn^{2+} during charge and discharge. This mechanism has been widely confirmed in material systems such as $\delta\text{-MnO}_2$, $\beta\text{-MnO}_2$, and layered vanadium oxides. Among these, Zn-MnO_2 prepared by in situ electrochemical deposition with an expanded interlayer spacing of 0.92 nm exhibits an ultrahigh capacity of 696 mAh g^{-1} and a cycle retention rate of 92.8% [17,18]. In high-proton-concentration electrolyte environments, the $\text{Zn}^{2+}/\text{H}^+$ synergistic insertion mechanism proposed by Sun et al. [19] reveals temporal characteristics: H^+ insertion in high-potential regions and Zn^{2+} insertion in low-potential regions. This system exhibited 10,000 cycles at 6.5 C with only 0.007% capacity decay. Notably, Cui et al. [20] challenged conventional wisdom by finding that Zn^{2+} insertion in $\delta\text{-MnO}_2$ is an irreversible process mediated by ion exchange. The actual charge storage primarily relies on H^+ insertion and extraction, MnO_2 dissolution, and the dissolution-deposition process of zinc-manganese compound minerals explain the capacity decay caused by the irreversible conversion to zinc-manganese compounds during the cycle process. The dissolution-precipitation mechanism of manganese achieves energy storage through the conversion between Mn^{4+} and Mn^{2+} . Yang et al. employed a strategy using KBr carbon to promote Mn^{2+} reprecipitation, achieving a capacity retention rate of 90.4% after 3,000 cycles in an additive-free electrolyte, which significantly enhances system stability [21]. The synergistic and competitive interactions between these mechanisms collectively shape the unique electrochemical behavior of AZIBs, providing multidimensional theoretical support for the development of high-performance batteries.

Characteristics of manganese-based cathode materials

AZIBs have emerged as a sustainable energy storage solution due to their inherent safety, cost-effectiveness, and environmental compatibility [22]. Although vanadium-based materials (such as V_2O_5 derivatives and vanadates) exhibit high specific capacity ($400\text{-}532 \text{ mAh g}^{-1}$) [23], their low operating voltage ($<1.0 \text{ V}$), toxic dissolution issues, and structural instability during cycling limit their practical application [24,25]. Prussian blue analogues (such as NiHCF/RGO composites) exhibit excellent rate performance (80.3% capacity retention after 1000 cycles) [26], but are constrained by their intrinsic theoretical capacity (approximately 50 mAh g^{-1}) [27]. Manganese-based oxides (including MnO_2 , Mn_2O_3 , Mn_3O_4 , MnO , ZnMn_2O_4 , etc.) have emerged as highly promising cathode materials for Aqueous Zinc-Ion Batteries (AZIBs) due to their high operating voltage, high theoretical capacity, multiple valence states, and abundant resources [28].

Among current research, manganese dioxide-based materials have received the most attention due to their unique crystal structure and electrochemical tunability. Liu et al. [29] employed a molybdenum doping strategy to modify $\gamma\text{-MnO}_2$ cathode materials, optimizing ion/electron transport kinetics to achieve a specific discharge capacity of 108.2 mAh g^{-1} at a current density of 2 A g^{-1} and maintain stability over 1000 cycles, thus demonstrating excellent rate performance. For Mn_2O_3 materials (dominated by trivalent manganese), the Jahn-Teller effect of Mn^{3+} can easily induce structural collapse, leading to significant capacity decay and reduced cycle life. To address this issue, Saadi et al. [30] developed a nickel-doped $\text{ZnMn}_2\text{O}_4/\text{Mn}_2\text{O}_3$ composite cathode, achieving significant enhancements in conductivity and electrochemical stability-maintaining a capacity retention of 91.32% after 3,000 cycles at 2 A g^{-1} . However, structurally unstable MnO and Mn_3O_4 materials are prone to phase transitions upon Zn^{2+} insertion. Wang et al. [31] innovatively induced the *in situ* conversion of Mn_3O_4 into $\epsilon\text{-MnO}_2$ layered structures via the electrolyte. This system exhibited a high specific capacity of 221 mAh g^{-1} at 100 mA

g^{-1} and maintained a capacity retention of 92% after 500 cycles, providing new insights for practical applications. To address the challenges of low electrical conductivity and volume expansion in ZnMn_2O_4 cathodes, Qin et al. [32] employed a Ni^{2+} doping strategy to perturb the material's periodic potential field, effectively enhancing the Zn^{2+} diffusion coefficient to $3.74 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The optimized cathode achieved a specific capacity of 175 mAh g^{-1} at 100 mA g^{-1} during the activation stage and maintained a capacity of 120 mAh g^{-1} at a high current density of 1 A g^{-1} , with a stable coulombic efficiency above 97%. These studies demonstrate that component regulation and structural design can effectively mitigate the intrinsic defects of manganese-based oxides, laying the foundation for their practical application in AZIBs.

Challenges of Manganese-Based Cathode Materials

Manganese-based cathode materials demonstrate significant potential in aqueous zinc-ion batteries, but they still face three core challenges: intrinsic conductivity limitations, irreversible manganese dissolution, and dynamic structural instability. First, the semiconductor properties of manganese oxides result in intrinsic conductivity values generally below $10^{-5} \text{ S cm}^{-1}$ [33], severely limiting the insertion/extraction kinetics of Zn^{2+} . This manifests as rate performance degradation (capacity loss exceeding 60% when rates increase from 0.5 C to 5 C) and exacerbated polarization in high-load electrodes. Second, during charging and discharging, the Jahn-Teller distortion of Mn^{3+} easily triggers a disproportionation reaction. Dissolved Mn^{2+} (with concentrations reaching 0.1-0.3 M) not only disrupts the crystalline integrity of the cathode but also migrates to the zinc anode surface, forming an insulating layer and triggering dendrite growth-both of which accelerate capacity decay (capacity retention rate $<70\%$ after 100 cycles). Although adding Mn^{2+} salts to the electrolyte can partially compensate for active material loss [34], this strategy cannot fundamentally address the dissolution-migration-deposition chain reaction. Additionally, phase transitions induced by charging and discharging (layered to spinel structure transformation) are accompanied by lattice distortion (volume change $>15\%$), leading to particle microcracks and conductive network fractures that further exacerbate capacity degradation [35]. These multi-scale, multi-physics-coupled failure mechanisms result in the actual energy density of manganese-based cathodes typically being more than 50% below the theoretical value, making it a key bottleneck constraining the commercialization of aqueous zinc-ion batteries.

Improvement Strategies for Manganese-Based Cathode Materials

Lattice support regulation engineering

To address lattice distortion and structural degradation in tunnel-type and layered manganese-based cathodes during electrochemical cycling, researchers have widely adopted pre-embedding guest ions to enhance structural stability via a lattice support system. Liu et al. [36] used a self-template sacrificial method to fix potassium ions in situ as structural stabilizers within the $\alpha\text{-MnO}_2$ crystal framework. Their studies showed that when K^+ occupies specific lattice sites, a three-dimensional support network forms in the framework, effectively suppressing structural relaxation during charging and discharging. Notably, the stoichiometric ratio of pre-embedded ions strongly regulates electrochemical performance. By systematically controlling alkali metal doping, researchers constructed $\alpha\text{-K}_{0.19}\text{MnO}_2$ cathodes with the optimal K^+ ratio, achieving a 127% increase in specific capacity retention vs. the unmodified system and demonstrating excellent cycling stability.

Defect state regulation engineering

Defect engineering, as a technical approach to optimize charge transport kinetics, primarily enables performance breakthroughs in modifying manganese-based electrodes through constructing oxygen vacancies and regulating cation defects. Xiong et al. [37] pioneered using plasma etching to construct an MnO_2 heterostructure with gradient-distributed oxygen vacancies. The underlying mechanism involves combining density functional theory simulations with electrochemical in situ characterization to confirm that the optimized vacancy configuration has an optimal Gibbs free energy for Zn^{2+} adsorption-desorption. Exposure of electrochemical active sites in the modified MnO_2 was markedly enhanced, resulting in a doubled capacity relative to the original material.

Engineering control of nanostructures

Engineered control of nanostructures is one of the strategies for optimizing the performance of manganese-based energy storage materials. Precise control of material morphology and structure (multi-level pores and special morphologies) increases the electrochemical active interface and shortens ion migration paths. Wang et al. [38] synthesized flower-shaped MnO_2 nanospheres with Zn^{2+} as pillars via a simple chemical



reaction between zinc powder and potassium permanganate. This unique structure provides a high specific surface area and mesoporous structure, facilitating effective electrolyte-electrode contact and enhancing electrochemical kinetics. At a current density of 0.3 A g^{-1} , a reversible specific capacity of 358 Ma h g^{-1} was achieved after 100 cycles; at a high current density of 3.0 A g^{-1} , a high-rate capacity of 124 Ma h g^{-1} was achieved. Additionally, the structure exhibits excellent stability, closely linked to the battery of a good reversibility and superior long-term cycle stability

Construction of nano-composite

The construction of nanocomposite systems is an effective strategy for enhancing the stability of manganese-based electrodes. By constructing a heterogeneous composite system, a conductive interface modification layer forms on the surface of manganese oxide, effectively suppressing active component leaching and significantly improving charge transport efficiency. Wang et al. [39] developed self-supporting MnO_2/rGO membranes, where MnO_2 nanowires and rGO intertwine to form a hybrid structure with face-to-line contact, establishing long-range conductive pathways to enhance electron transport; the interwoven structure suppresses rGO stacking and MnO_2 agglomeration, maintaining electrode integrity and enhancing mechanical flexibility. The rGO coating reduces the dissolution rate of the cathode material, and the optimized composite electrode exhibits a high energy density of 436 Wh kg^{-1} , demonstrating its application potential. Cheng et al. [40] designed a Mn_3O_4 tetrahedral double pyramid-loaded nitrogen-doped layered porous carbon (Mn_3O_{45}

TB/NHPC) composite material, utilizing the three-dimensional structure of NHPC to uniformly disperse Mn_3O_4 and improve electrical performance. Sayyed et al. [41] used dynamic potential electrodeposition to prepare Mn_3O_4 films on flexible stainless-steel substrates via a simple and effective process, and the material exhibited significant pseudocapacitance and good stability.

Summarized and Prospected

AZIBs offer a promising future as a safe, environmentally friendly, and cost-effective energy storage technology. Manganese-based cathode materials-with their high capacity, high voltage, and abundant resources-are key to enabling AZIBs to achieve high performance. This paper systematically reviews four main modification strategies developed to address the key challenges of manganese-based cathode materials (particularly MnO_2 and Mn_3O_4): lattice support regulation, defect state regulation, nanostructure engineering, and composite nanomaterial construction. These strategies have achieved significant results in enhancing structural stability, suppressing dissolution, improving conductivity, optimizing reaction kinetics, and extending cycle life.

Future research on manganese-based Aqueous Zinc-Ion Batteries (AZIBs) should focus on performance optimization and industrialization. First, advanced in situ characterization techniques should be used to thoroughly analyze the dynamic phase transformation mechanisms of Mn_3O_4 , MnO , and other materials, as well as the $\text{H}^+/\text{Zn}^{2+}$ synergistic storage mechanisms, to clarify the fundamental causes of capacity decay. Building on these insights, novel dissolution inhibition strategies beyond traditional Mn^{2+} electrolyte additives should be developed, exploring in situ SEI film formation, lattice stabilization, and multifunctional electrolyte additive systems. Simultaneously, we need to optimize composite material interface interaction mechanisms, innovate carbon-based composite carrier designs, and develop controlled synthesis processes to improve the dispersion uniformity of Mn_3O_4 . Additionally, new material systems such as binary/ternary manganese-based chalcogenides should be explored to exploit their structural advantages.

Finally, when applying modification technologies, it is essential to comprehensively consider production cost scalability, environmental compatibility, and compatibility with other battery components (high-stability anodes and functional separators). This will facilitate the transition of high-performance manganese-based AZIBs from laboratory research to practical applications. Through continuous in-depth mechanistic research and material engineering innovation, the performance bottlenecks of manganese-based cathode materials for aqueous zinc-ion batteries can be continuously overcome, accelerating the large-scale deployment of AZIBs in fields such as renewable energy storage and portable electronic devices.

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