Review article

Mn-oxide cathode material for aqueous Zn-ion battery: structure, mechanism, and performance

Xue Ke\textsuperscript{a}, Li Li\textsuperscript{b}, Shan Wang\textsuperscript{c}, Anyang Wang\textsuperscript{a}, Zhuo Jiang\textsuperscript{a}, Feng Ryan Wang\textsuperscript{d}, Chunguang Kuai\textsuperscript{a,}\textsuperscript{*}, Yuzheng Guo\textsuperscript{a,}\textsuperscript{b,}\textsuperscript{c,}\textsuperscript{d,}\textsuperscript{e,}\textsuperscript{f,}\textsuperscript{g}

\textsuperscript{a} School of Electrical Engineering and Automation, Wuhan University, Wuhan, China
\textsuperscript{b} The Institute of Technological Sciences, Wuhan University, Wuhan, China
\textsuperscript{c} Department of Anesthesiology, Zhongnan Hospital of Wuhan University, Wuhan, China
\textsuperscript{d} Department of Chemical Engineering, University College London, London, UK
\textsuperscript{e} School of Electronics Science and Technology, Wuhan University, Wuhan, China
\textsuperscript{f} School of Biological Sciences, Wuhan University, Wuhan, China
\textsuperscript{g} School of Life Science, Wuhan University, Wuhan, China

Abstract

The wide-scale expansion of renewable energy sources has triggered the demand for advanced energy storage technologies. Aqueous zinc ion batteries (AZIBs) have been widely noticed in recent years because of their intrinsic safety, abundant raw materials, and environmental friendliness. Among the reported cathode materials for ZIBs, Mn-oxide materials stand out as one of the most promising candidates with their diverse structures, high capacity, and cost-effectiveness. However, the complex energy storage mechanism and unstable electrochemical properties persistently obstruct the practical application of this technology. It has been realized that these disturbances are related to the structural evolution of Mn-oxide materials during the charge/discharge process, and considerable relevant research was carried out. In this review, we present an up-to-date review of the most recent advancements and challenges concerning Mn-oxide cathode materials for aqueous zinc ion batteries. Firstly, we offer a concise summary and categorization of several widely recognized energy storage mechanisms and crystal structures. Then, we focused on sorting out the structural evolution path of Mn-oxide materials, and explored the relevant influencing factors and the relationship between phase evolution and property fluctuations. Finally, we distill key optimization strategies and provide a forward-looking perspective on future research.

1. Introduction

In the quest for effective cathode materials in aqueous zinc-ion batteries, manganese oxides have risen to the forefront of research and development. This prominence stems from their abundant availability, cost-effectiveness, low toxicity, and their notable theoretical capacity, all underpinned by a favorable redox potential [1–5]. However, despite significant strides in the field over the past decade, certain fundamental challenges continue to hinder the commercialization of manganese oxides for use in aqueous Zn-ion batteries, particularly in understanding their energy storage mechanisms and structural evolution [6–8].

The energy storage processes in these batteries are intricate, involving complex interfacial reactions during both charging and discharging [9–13]. These reactions encompass phase changes, dissolution and redeposition of Mn ions, co-intercalation and deintercalation of other cations aside from Zn\textsuperscript{2+}, water oxidation, and more. The resulting complexity of these interfacial reactions has impeded our ability to identify the precise energy storage mechanism\textsuperscript{3}. Further challenges, including sluggish kinetics and limited cycle stability, persist due to the strong electrostatic repulsion of divalent zinc ions, leading to substantial mechanical stress on manganese oxides and undesirable volume fluctuations and structural instability [14]. Moreover, the intrinsic low electronic conductivity of Mn-oxide materials hampers reaction rates and promotes undesirable side reactions [15,16]. The Jahn-Teller effect of Mn\textsuperscript{3+} exacerbates the problem by triggering disproportionation and manganese dissolution [17]. Understanding the crystal structure evolution can provide insight into the above issues.

The intercalation process of Zn\textsuperscript{2+}/H\textsuperscript{+} cations is intrinsically tied to the crystal structure of manganese oxides, notably the channel structure [18–20]. Mn elements can adopt multiple oxidation states and form diverse crystal structures, which contributes to the challenges of unstable crystal structures and complex phase transition processes. Crystalline phases with wide channel structures tend to offer higher discharge capacity and faster ion diffusion rates [21]. Hence, α-MnO\textsubscript{2},

\textsuperscript{*} Corresponding authors.
E-mail addresses: chuangk@whu.edu.cn (C. Kuai), yguo@whu.edu.cn (Y. Guo).

https://doi.org/10.1016/j.nxener.2023.100095
Received 31 October 2023; Received in revised form 21 December 2023; Accepted 29 December 2023
Available online 22 January 2024
2949-821X/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
with its expansive tunneling space, initially garnered attention [22,23], but it was later discovered that tunnel-like manganese oxides tend to convert to a layered structure [24–26]. Consequently, δ-MnO₂, with its relatively stable structure and broader two-dimensional diffusion channels, has taken the spotlight [27]. In addition, manganese oxides with non-tunnel structures or narrow tunnel spaces [12,28–30], such as Akhtenite-type MnO₂, amorphous MnO₂, and ZnMn₂O₄, exhibit notable discharge capacity and kinetic performance due to their low crystallinity or structural modifications. However, the diverse crystalline structures of manganese oxides are susceptible to varying degrees of manganese dissolution and structural collapse, resulting in rapid performance degradation [31]. Furthermore, the intercalation behavior of cations can indirectly induce reversible phase transitions of Mn oxides (between solid phases or solid-liquid phases), as documented in numerous studies, albeit with ongoing debates regarding the pathway of phase evolution [32–36]. Moreover, the manganese oxide cathode experiences irreversible phase changes during the cycling process, introducing variability in the mechanism and performance across different cycling stages [37–39].

The complexity of these phase transition processes arises from sensitivity to various environmental factors, such as the morphological particle size, complex composition, anions, and minority functional electrolyte additives [40]. Furthermore, the redox potentials of different reactions, current density, and voltage window influence the phase evolution process. To address these challenges, researchers have proposed various modification strategies, including heterogeneous doping and nanostructure engineering, to enhance reversibility, inhibit manganese dissolution, and support structural stability. These strategies have effectively improved the cycling ability and specific capacity of Mn-oxide materials [41].

This review paper delves into Mn-oxide cathode materials for aqueous zinc-ion batteries, focusing on their active substance structure and its influence on the reaction mechanism and electrochemical performance. (Fig. 1) We categorize Mn-oxide materials based on their channel structures, discuss important mechanisms, unravel the complex phase evolution paths, explore strategies to improve structural stability, and address the current challenges and future research directions in this promising field.

### 2. Mn-oxides cathode material

Mn-oxide have attracted considerable attention as promising cathode materials for aqueous zinc ion batteries (AZIBs) due to their remarkable activity, cost-effectiveness, and environmental compatibility. However, the performance of manganese dioxide can be influenced by its diverse structures and variations in morphology and particle size reported in different literature. These discrepancies may give rise to distinct underlying mechanisms and performance characteristics. Therefore, in this paper, we present an overarching review of recent advancements in the field, focusing on energy storage mechanisms, crystal structures, and interactions with the anode, with the objective of elucidating these aspects.

#### 2.1. Energy storage mechanism

In the realm of scientific research, a multitude of investigations have been conducted in previous years to unravel the intricacies of the reaction mechanism employed in lithium-ion batteries. Consequently, researchers have reached a relatively consensual understanding regarding this matter. Nevertheless, in the context of aqueous zinc batteries with a Mn-oxide cathode, the energy storage mechanism presents itself as considerably more intricate and contentious. The complexity arises from the inherent instability of Mn-oxides and the intricate nature of the aqueous phase environment surrounding them. Over the course of the past decade, tireless exploration has yielded recognition for four prevalent mechanisms (Fig. 2) [2]. These coincide with the following: (1) The Zn²⁺ insertion mechanism; (2) The conversion reaction mechanism; (3) The H⁺/Zn²⁺ co-insertion mechanism; and (4) The dissolution-deposition mechanism. This section will briefly describe these four mechanisms.

##### 2.1.1. Zn²⁺ insertion/extraction

In a manner akin to the "rocking chair" phenomenon observed in lithium-ion batteries, the energy storage mechanism in aqueous rechargeable zinc-ion batteries relies on the reversible migration of Zn²⁺ between the cathode and anode. Notably, this reaction mechanism was initially put forth and substantiated by Kang et al., employing α-MnO₂ (2 x 2 tunnel) as the anode material [9,10]. Consequently, the reaction equations pertaining to this particular mechanism can be expressed as follows:

\[
\begin{align*}
\text{Zn}^{2+} + \text{e}^- & \rightarrow \text{Zn} \\
\text{MnO}_2 & \rightarrow \text{MnO} + \text{O}_2
\end{align*}
\]
In addition to the Zn\(^{2+}\) insertion/extraction mechanism, the cathode host material. The galvanostatic charge and discharge curves exhibit two distinct discharge plateaus, as depicted in Fig. 3e. Notably, with an increase in the charge and discharge rate from 0.3 to 6.5 C, the capacity contributed by the second plateau (region II) undergoes a more rapid decrease compared to the first plateau (region I), indicating the presence of two different kinetic rates for the reaction. This observation is more prominently evident in the discharge galvanostatic intermittent titration technique (GITT) profiles (Fig. 3f), where region II demonstrates a more pronounced overpotential. This disparity can be attributed to the varying transfer rates between different ions. Furthermore, subsequent experiments revealed that the insertion of H\(^+\) with a faster kinetic rate occurs initially and contributes to region I, followed by the insertion of Zn\(^{2+}\) associated with region II.

In a subsequent study, Gao et al. demonstrated the H\(^+/\text{Zn}^{2+}\) co-insertion mechanism of the α-MnO\(_2\) cathode in aqueous zinc-ion batteries (ZIBs) [52]. They further explored this mechanism through in-situ XRD, non-in-situ TEM, and electrochemical methods. The results indicate that while the Zn\(^{2+}\) insertion step may lead to the formation of irreversible spinel phases, the H\(^+\) insertion process exhibits superior reversibility compared to Zn\(^{2+}\). Hence, the insertion/extraction of H\(^+\) plays a pivotal role in upholding the performance of ZIBs during the charge/discharge process.

### 2.1.4. \(\text{MnO}_2/\text{Mn}^{2+}\) dissolution-deposition

In addition to the aforementioned three single-electron transfer mechanisms, researchers have recently observed a new deposition-dissolution mechanism [53]. Lee et al. [13] investigated the relationship between the concentrations of Mn\(^{2+}\) and Zn\(^{2+}\) ions, as well as the pH value in the electrolyte, during the charging and discharging processes of rechargeable zinc-manganese batteries. As shown in Fig. 3g and Fig. 3h, during discharge, the concentration of Mn\(^{2+}\) ions increases, accompanied by an increase in pH value, reaching its peak at the end of discharge, while the concentration of Zn\(^{2+}\) ions decreases to its lowest point. Subsequently, the opposite trend is observed during the charging process.

A subsequent series of studies have confirmed that this phenomenon is attributed to the dual-electron reaction of MnO\(_2\)/Mn\(^{2+}\) in the cathode [54]. The dissolution of Mn consumes a significant amount of H\(^+\), leading to an increase in pH. At the same time, Zn\(^{2+}\) combines with OH\(^-\) to form precipitates in alkaline conditions. During the charging process, the precipitation of Mn\(^{2+}\) occurs, resulting in a decrease in pH and the dissolution of ZHS,

\[
\text{MnO}_2 + 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{Mn}^{2+} + 4\text{OH}^-
\]

\[
4\text{Zn}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow \text{Zn}_4(\text{OH})_6\text{SO}_4\cdot 5\text{H}_2\text{O}.
\]

The mechanisms mentioned above will be the main focus of subsequent discussions.

### 2.2. Diverse crystal structures

The element manganese displays a wide range of oxidation states (ranging from +2 in MnO to +4 in MnO\(_2\)). Among these, MnO\(_2\) has emerged as the most extensively studied, with its fundamental structural unit being the MnO\(_6\) octahedron. By connecting MnO\(_6\) octahedra in different configurations, various polycrystalline substances with distinct structures are formed. These include tunnel-like structures represented by α-, β-, γ-, and todorokite-types, layered structures represented by δ-, spinel structures represented by ε-, and dense structures represented by ν-. Additionally, other Mn-oxides, such as amorphous manganese dioxide, spinel MnMn\(_2\)O\(_4\), MnO, MnO\(_3\), and MnO\(_2\) have also exhibited potential as cathode materials for zinc batteries. Importantly, it has been discovered that the properties, mechanism, and stability of Mn-oxides are intimately linked to their crystal structures. Consequently, this section aims to classify and examine these Mn-oxides based on their crystal structures (Fig. 4).

#### 2.2.1. Tunnel-like structure

Manganese oxides possessing tunnel structures have been extensively investigated due to their capacity to function as direct hosts and provide pathways for cation diffusion. Based on differences of tunnel structure, these manganese oxides can be further classified into tunnel-like, layered, and spinel structures. Among the tunnel-like structures, commonly studied examples include α-MnO\(_2\), β-MnO\(_2\), γ-MnO\(_2\), and others, distinguished primarily by variations in tunnel size. In the Zn/ MnO\(_2\) system, the size of the tunnel plays a significant role in determining the capabilities for cation insertion and diffusion, as well as the stability of the material itself. A thorough discussion of these aspects will follow in subsequent sections.
2.2.1.1. \( \beta - \text{MnO}_2 (1 \times 1 \text{ tunnel}) \). The pyrolusite-type \( \text{MnO}_2 \) (\( \beta - \text{MnO}_2 \)) comprises single chains of shared-edge \( \text{MnO}_6 \) octahedra, forming one-dimensional (1 × 1) tunnels, which possess the narrowest size (~1.89 Å) among tunneled manganese oxides [57]. Consequently, this structure is often limited by sluggish cation insertion kinetics and a low storage capacity [58–60]. For instance, an earlier study compared the first discharge capacities of \( \text{MnO}_2 \) with different channel structures at a small current density of 0.1 A/g (\( \alpha - \text{MnO}_2 \): 234 mAh/g; \( \beta - \text{MnO}_2 \): 201 mAh/g; \( \gamma - \text{MnO}_2 \): 213 mAh/g; \( \delta - \text{MnO}_2 \): 269 mAh/g) and found that \( \beta - \text{MnO}_2 \) exhibited the lowest discharge capacity due to its smaller tunneling structure [57].

In a study conducted in 2020, the co-insertion and deinsertion processes of \( \text{H}^+ \) and \( \text{Zn}^{2+} \) in \( \beta - \text{MnO}_2 \) during charge and discharge were demonstrated [60]. Density functional theory calculations further provided insights into the preference of \( \beta - \text{MnO}_2 \) host structure to accommodate \( \text{H}^+ \) rather than \( \text{Zn}^{2+} \) due to the smaller ionic radius of \( \text{H}^+ \). A recent report proposed that the early cycles in the \( \text{H}^+/\text{Zn}^{2+} \) co-insertion process are primarily dominated by proton conversion reactions, with the involvement of \( \text{Zn}^{2+} \) in the formation of ZHS [61]. Interestingly, they observed that the higher Zn content on the cathode in the discharged state was primarily contributed by ZHS rather than direct \( \text{Zn}^{2+} \) insertion.

2.2.1.1.1. \( R - \text{MnO}_2 (1 \times 2 \text{ tunnel}) \). The ramsdellite type \( \text{MnO}_2 \) (\( R - \text{MnO}_2 \)) contains a double chain formed by the shared assembly of \( \text{MnO}_6 \) octahedral edges, thus presenting a framework structure of (1 × 2) tunneling.

The activity of \( R - \text{MnO}_2 \) has received relatively less attention in past studies. However, Wilkinson et al. introduced the preparation and utilization of highly crystalline \( R - \text{MnO}_2 \) as a cathode material for aqueous zinc-based batteries in 2019 [55]. Analysis of discharge curves (Fig. 5a)
and cycling characteristics plots (Fig. 5b) revealed that R-MnO₂ exhibits a moderate capacity (approximately 140 mAh/g) and favorable cycling performance (maintaining over 65% of its initial capacity during 1000 cycles) at a current density of 0.1 mA g⁻¹.

A recent study employed electrochemical analysis to demonstrate that R-MnO₂ acts as a host and enables Zn²⁺/H⁺ insertion/extraction [62]. Intriguingly, R-MnO₂ also exhibited lower solubility compared to other MnO₂ polymorphs, which effectively inhibits performance degradation.

2.2.1.1.2. γ-MnO₂ (1 × 1 and 1 × 2 tunnel). In Nsutite type MnO₂ (γ-MnO₂), 1 × 1 and 1 × 2 cross sections exist simultaneously and are interspersed, so it can be regarded as a symbiosis between β-MnO₂ and R-MnO₂ [57].

The current widely accepted energy storage mechanism for γ-MnO₂ comes from a report published in 2015 by Alfaruqi et al. [44]. They revealed the complex phase transition mechanism of γ-MnO₂ occurring during Zn²⁺ insertion/extraction by means of characterization based on in situ x-ray absorption near edge structure (XANES) and in situ simultaneous XRD.

2.2.1.1.3. α-MnO₂ (2 × 2 tunnel). In the case of Hollandite-type MnO₂ (α-MnO₂), the double chains of MnO₆ octahedra combine to form a 2 × 2 tunneling structure with a comparatively larger size...
X. Ke et al.

oxide cathode materials [65]. Similar to tunneled manganese oxides, the discharge curves exhibit distinctive double discharge plateaus, later impressive discharge capacities reaching up to 250 mAh/g [66].

2.2.3. Spinel structure

The spinel structure, characterized by its three-dimensional ion diffusion channels, theoretically possesses faster kinetic properties compared to other manganese oxides. For example, spinel-type LiMnO$_2$ has proven to be a promising host material for Li-ion insertion [72, 73]. However, the insertion process of Zn$^{2+}$ in ZnMnO$_4$ is hampered by the stronger electrostatic interaction of Zn$^{2+}$ and the limited tunneling space within the structure [74]. In 2014, Yuan et al. obtained spinel $\lambda$-MnO$_2$ through acid leaching treatment [43], but subsequent electrochemical tests revealed unsatisfactory rate performance and specific capacity (Fig. 5c). Moreover, ab initio calculations presented in another study indicated the low mobility of Zn$^{2+}$ in the spinel structure [75]. Such reduced activity is likely related to the lower specific surface area and total pore volume in this structure [57]. Therefore, the transition of the structure to ZnMnO$_4$ during the cycling of MnO$_2$ with alternative structures is often regarded as an important factor contributing to capacity decay [46]. As a result, the pristine spinel structure is not suitable as a cathode material for ZIBs, prompting the common practice of introducing manganese vacancies into the spinel structure as a modification method [74].

In contrast to ZnMnO$_4$, MnMnO$_3$ consists of the divalent manganese species Mn$^{2+}$ and exhibits a reaction mechanism akin to that of lower valent manganese oxides, including Mn$_3$O$_4$ and MnO, wherein the metal transforms into other active phases during the initial cycles. For instance, the conversion of MnMnO$_3$ to Zn-birnessite [76] or Akkhen-skite MnO$_2$ [77], MnO [78], and other phases exemplifies this phenomenon, which will be discussed in detail later. This further underscores the complexity associated with the reaction mechanism of MnMnO$_3$.

2.2.4. Other structures

In addition to the crystal types mentioned above, other types of Mn-oxides primarily consist of densely structured $\epsilon$-MnO$_2$, amorphous MnO$_4$, as well as lower valence Mn$_3$O$_4$ and MnO. These Mn-oxides inherently lack cation diffusion pathways, leading to limited ion transport kinetics. However, they often possess abundant defects and lower crystallinity, which can facilitate slow kinetic properties. Moreover, manganese oxides are prone to electrochemically induced phase transitions, which, paradoxically, present certain opportunities for these materials.

2.2.4.1. Dense. Akkhen-skite MnO$_2$ ($\epsilon$-MnO$_2$) is a dense structure consisting of the co-faceted combination of an equivalent proportion of Mn$_3$O$_4$ and (YO$_6$) octahedra (Y indicates vacancy) [79,80].

It has been contended that the dense structure of $\epsilon$-MnO$_2$ is not inherently conducive to rapid intercalation and delamination of metal ions during energy storage [81]. However, it is intriguing to note that the initial discovery of the H$^+$/Zn$^{2+}$ co-insertion/deinsertion mechanism as discussed earlier was conducted in such a dense structure, which may be attributed to its abundance of cation vacancies [12]. Furthermore, the small particle size resulting from in situ deposition of $\epsilon$-MnO$_2$ can yield a multitude of electrode/electrolyte contact interfaces and reduce the diffusion path length for ions, thereby greatly enhancing the kinetic performance of the electrochemical reaction. Nonetheless, the kinetics of cation insertion into $\epsilon$-MnO$_2$ necessitate further investigation due to the absence of a tunnel-like structure [19].

Recent findings indicate that this particular structure is well-suited for exploiting the deposition dissolution reaction mechanism inherent to Mn$^{2+}$/MnO$_2$ chemistry [53]. For instance, the electrolytic MnO$_2$ cell proposed by Chao et al. exhibits a capacity of 570 mAh/g, which closely approaches the theoretical capacity of 616 mAh/g [82], simultaneously showcasing an output voltage of up to 1.9 V. Hence, this structure holds great promise for grid energy storage applications. Further details on this topic will be expounded upon in a subsequent section.
2.2.4.2. Amorphous. In contrast to crystalline materials, amorphous materials exhibit irregularly spaced short-range ordering and a random arrangement of atoms [28,83]. Despite the presence of certain pseudo-capacitance effects [84], amorphous manganese oxides are often disregarded in the context of ZIBs [28] due to their perceived low capacity resulting from the absence of well-defined cationic host structures and transport channels [85]. Nonetheless, recent studies have unveiled that the highly disordered structure of amorphous MnO imparts numerous active sites, superior structural strain resistance, and enhanced kinetic properties [28]. Furthermore, the observation of two reduction peaks in the cyclic voltammetry curve and two voltage plateaus in the discharge curve further indicates an \( \text{H}^+ / \text{Zn}^{2+} \) co-insertion mechanism (Figs. 5d and 5e) [56,84,86]. Zn/A-MnO\(_2\) also showcases excellent rate performance, delivering a discharge capacity of 308.5 mAh/g at a high rate of 0.97 C (Fig. 5d) [28].

It has also been reported that the newly deposited MnO\(_2\) during circulation can inhibit the dissolution of Mn to some extent, thus improving the circulation capacity. [8,26].

2.2.4.3. Other low valued manganese oxides. Among the common non-tunnel types are low-valent manganese oxides, including MnO\(_2\) and MnO. MnO\(_2\) exhibits a bizbyte structure, where Mn\(^{3+}\) are octahedrally coordinated while each O ion is surrounded by four Mn ions [35]. On the other hand, MnO possesses a rock salt structure and has proven to be effective as a cathode material for lithium-ion batteries [87–89]. However, the absence of a tunnel structure initially rendered these two materials inactive for ZIBs, leading to their frequent neglect [81].

Recent studies have demonstrated that both materials can indeed be utilized as cathodes for ZIBs with certain modifications. These modifications involve the introduction of specific defects to facilitate solid-state diffusion of cations [90,91], or the electrochemically induced phase transformations to form oxide types with tunnel structures capable of hosting cations [92–95]. Further details on these modifications will be explored in a subsequent section.

2.3. Interplay with zinc anode

Zinc metal, as a historically significant and extensively utilized anode material, plays a crucial role in the field of batteries. It possesses not only a high theoretical capacity (820 mAh/g and 5854 mAh/cm\(^3\)) but also a low standard electrode potential (–0.76 V vs. SHE). In addition to these favorable electrochemical properties, zinc metal is characterized by its relative abundance, low cost, and environmentally-friendly nature. Furthermore, it exhibits exceptional stability in both non-aqueous and aqueous electrolytes, regardless of their alkaline or acidic nature [96]. Such remarkable stability renders zinc metal an essential component for various battery systems.

Traditional alkaline zinc-manganese batteries have enjoyed widespread application owing to their higher energy density and environmental safety. However, the low Coulomb efficiency and irreversible side reactions inherent in these batteries hinder their further development as secondary batteries.

In recent years, there has been increasing attention towards aqueous zinc-manganese dioxide batteries, driven by deeper understanding of the mild aqueous zinc storage mechanisms and the growing demand for large-scale energy storage applications [53]. However, research in this area is still in its early stages, and there is a significant road ahead before achieving widespread commercial utilization of these batteries.

2.3.1. Operating voltage and pH

From a thermodynamic perspective, the electrochemical stability window of water is limited to 1.23 V. Voltages beyond this range would result in water decomposition and the generation of oxygen evolution reactions (OER) and hydrogen evolution reactions (HER), thereby restricting the compatibility of aqueous batteries with high-voltage electrode materials (Fig. 6a) [97,101]. However, fortunately, zinc metal, as an anode material, plays a crucial role in suppressing HER due to its high overpotential, despite having a lower standard electrode potential. This property enables aqueous batteries to operate within a higher voltage range (Fig. 6b) [98].

Additionally, the rates of OER and HER are influenced by the concentration of hydroxide ions (OH\(^-\)) and hydrogen ions (H\(^+\)) in the solution. The pH value of the electrolyte, serving as an indicator of acidity or alkalinity, plays a key role in regulating the kinetics of redox reactions involving H\(^+\) and OH\(^-\) [102]. Therefore, the proper selection and adjustment of the electrolyte’s pH value are essential to ensure its compatibility with the working voltage range of both cathode and anode materials. In particular, for aqueous zinc-manganese dioxide batteries, a near-neutral electrolyte environment can effectively suppress the occurrence of HER and OER side reactions.

Furthermore, maintaining a near-neutral pH environment also inhibits zinc dendrite growth and the formation of corrosive byproducts at the anode to a certain extent. Hence, in the design of aqueous zinc-manganese dioxide batteries, it is of significant importance to ensure that the electrolyte maintains an appropriate near-neutral pH environment, as it enhances battery stability and reduces potential issues that may arise at the anode [2].

2.3.2. Carrier electrostatic interaction

The primary charge carrier in aqueous Zn-MnO\(_2\) batteries is divalent zinc ions. Compared to single-valent ion-based batteries, these batteries exhibit higher capacity density within the same volume, particularly because zinc is currently the only metal that can be directly used as the anode in aqueous batteries. Furthermore, manganese dioxide has been proven to be an excellent host material for lithium ions, and Zn\(^{2+}\) shares similar ionic radii with Li\(^+\) (Table 1). However, Zn\(^{2+}\) ions experience stronger electrostatic repulsion, which not only limits ion diffusion rates but also subjects manganese dioxide to significant mechanical stress, leading to severe volume fluctuations and structural instability [81]. Moreover, the strong interaction between Zn\(^{2+}\) and solvation water molecules results in substantial desolvation penalties that impede the intercalation kinetics of Zn\(^{2+}\), thereby reducing electrochemical performance [16].

Additionally, during delithiation, electroplating, and/or insertion of Zn\(^{2+}\) into either electrode, it is unlikely for single-charged species to form stable intermediates via a single electron transfer. These singly charged species, due to their inherent instability, exhibit high reactivity and may give rise to various parasitic reactions, including electrolyte decomposition and/or electrode passivation, thereby hindering electrochemical performance [103].

2.3.3. Impact analysis of ZHS

Zinc sulfate is the most widely used salt in aqueous zinc-ion batteries due to its low cost and favorable electrochemical performance. However, it is worth noting that at the electrode-electrolyte interface, local pH changes result in the reversible deposition-dissolution of Zn\(_x\)(OH)\(_{4-x}\)SO\(_4\)\(_x\)xH\(_2\)O (ZHS):

\[4\text{Zn}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} + x\text{H}_2\text{O} \rightarrow \text{Zn}_x(\text{OH})_{4-x}\text{SO}_4\cdot x\text{H}_2\text{O}\]

This phenomenon is common at both the cathode and anode. For the zinc anode, this low conductivity byproduct has been demonstrated as a significant factor causing uneven deposition of zinc ions and promoting dendritic growth (Fig. 6c) [99,104,105]. In contrast, the mechanism and role of this product for cathode are controversial [81,106].
Chen et al. [100] argue that ZHS plays a crucial role in facilitating favorable phase evolution of manganese dioxide (Fig. 6d), while Nazar et al.’s research [107] suggests that the reversible formation/disappearance of ZHS has a negligible impact on the electrochemical performance. Xia et al. [108], however, propose that the formation of ZHS leads to a rapid decline in capacity during initial cycles, but is beneficial for maintaining stability of the positive electrode material in subsequent cycles. Nevertheless, ZHS does exhibit a certain influence in suppressing pH fluctuations and maintaining a stable solution environment. Detailed exploration of this mechanism will be carried out in the following sections.

3. The evolution of the structure

Due to their inherent instability and diverse crystal structures, Mn-oxide cathodes in ZIBs often undergo complex structural evolutions during cycling. On the one hand, this characteristic serves as the root of controversies regarding reaction mechanisms and product formation in the academic community. On the other hand, it also leads to distinct mechanisms and performance characteristics exhibited by ZIBs in different reaction processes. Extensive research efforts have been dedicated to unraveling the evolutionary pattern in this regard. Accordingly, this section provides a systematic review of the primary evolution paths of manganese oxide cathodes in ZIBs, explores the associated influencing factors, and investigates their relationship with structural stability.

3.1. Main evolution path

During the occurrence of structural evolution, the element Mn undergoes transfers between different phases, including transitions from solid to liquid phase and between different solid phases. Based on the sequence of Mn element in these phases, existing literature has identified three primary evolution paths: the solid-phase evolution path, the liquid-phase evolution path, and the mixed evolution path that encompasses both. In the subsequent sections, this paper will delve into a thorough discussion of these three evolution paths.

3.1.1. Solid-phase evolution path

The solid-phase evolution path, which will be discussed in this study, pertains to the direct conversion between different solid phases during the cycling process. Layered oxides and spinel oxides are frequently encountered in these solid-phase evolution paths [31,81]. Consequently, the solid-phase evolution paths can be categorized into three distinct forms based on the position of these two oxides along the pathway and their reversible relationships.

3.1.1.1. Reversible structural evolution with layered structure.

In various studies, the presence of layered manganese dioxide was commonly observed during characterization, even when different manganese oxides were used as initial phases. However, there remains significant controversy regarding the evolutionary pathway of these phases and the reversibility of phase transitions. Early investigations initially proposed that the transformation of layered manganese dioxide with other phases primarily involved reversible phase changes. In 2014, Lee et al. put forth the concept of a reversible phase transition from α-MnO₂ to Zn-buserite during Zn²⁺ intercalation/deintercalation (Fig. 7a) [24]. Further research conducted by Lee et al. determined that the actual discharge product should be Zn-buserite, characterized by wider layer spacing,
which subsequently loses water molecules and $\text{Zn}^{2+}$ to form the previously observed Zn-birnessite (Fig. 7b) [25]. Subsequent studies have also reported reversible phase transitions from tunneled $\alpha$-MnO$_2$ to layered structures (Figs. 7c and 7d) [109,110].

Additionally, a recent study has highlighted the presence of a reversible phase transition between $\gamma$-MnO$_2$ and the layered structure during the charging-discharging process, as revealed through in situ Raman analysis (Figs. 8a and 8b) [111].

Interestingly, a study on low-valent manganese oxides reported similar findings regarding the phase transition process (Fig. 8c) [35].

![Figure 7: Schematic illustrating the reversible phase transition from $\alpha$-MnO$_2$ to layered Zn$_x$MnO$_2$ with zinc intercalation. (a) The reversible phase transition between $\alpha$-MnO$_2$ and Zn-birnessite. (b) The reversible phase transition between $\alpha$-MnO$_2$ and Zn-birnessite. The reversible phase transition with pre-intercalation ions of Al$^{3+}$ (c) and K$^+$ (d). (a) Reproduced from ref. [24] with permission. (b) Reproduced from ref. [25] with permission. (c) Reproduced from ref. [109] with permission. (d) Reproduced from ref. [110] with permission.](image1)

![Figure 8: (a) Schematic illustration of the reversible phase transformation between $\gamma$-MnO$_2$ and layered birnessite, and (b) in situ Raman spectra acquired at different potentials and the corresponding GCD curves (current density of 100 mA g$^{-1}$). Reaction mechanism of $\alpha$-Mn$_2$O$_3$ as cathode material for zinc ion battery: (c) schematics of phase transition, and (d) XRD patterns at original state, zinc ion extraction state and zinc ion insertion state. (a) Reproduced from ref. [111] with permission. (b) Reproduced from ref. [35] with permission.](image2)
Specifically, during the charging/discharging process, the presence of layered Zn-birnessite was observed through HR-TEM patterns. This led the researchers to conclude that there is a direct transition from $\alpha$-Mn$_2$O$_3$ to the layered Zn-birnessite phase (Fig. 8d). The conclusion was further supported by a combined analysis of XRD and SEM, which also indicated the reversibility of the structural transformation.

Another study illustrated that the layered manganese dioxide transforms into a multiphase mixture of Mn$_3$O$_4$, MnO, and ZnMn$_2$O$_4$·H$_2$O at a specific discharge voltage [69]. Upon charging, these forms are converted back to birnessite-MnO$_2$.

### 3.1.1.2. Irreversible structural evolution with layered structure.

The aforementioned studies provide support for reversible transformations between layered MnO$_2$ and other phases. However, the existence of contradictory evolutionary pathways indicates controversies in the mechanism. Subsequent studies have largely concluded that solid-phase transformations involving layered manganese dioxide are predominantly irreversible. For instance, Zhang et al. present a comprehensive mechanism detailing the irreversible transition process from tunnelled $\beta$-MnO$_2$ to layered Zn-buserite during the first cycle (Fig. 9a) [26]. The subsequent charging/discharging processes primarily involve reversible intercalation/deintercalation of Zn ions into the formed layered phase cathode. Significant differences between the initial and subsequent cycles are observed in the cyclic voltammetry curves (Fig. 9b), while changes in peak intensity in the in situ XRD images (Figs. 9c and 9d) demonstrate the alteration of the physical phase during the first discharge. Furthermore, they also observed similar phase transition processes in $\alpha$-MnO$_2$ and $\gamma$-MnO$_2$, which may reveal a shared evolution mechanism among tunnel-structured manganese oxides.

This phenomenon of phase transition induction in the initial cycle is also observed in certain low-valent manganese oxides. For instance, MnO, a non-tunnel structured low-valent manganese oxide, is not ideal as a host material for ion intercalation. Therefore, it undergoes a phase transition process in the first cycle to induce the formation of porous layered MnO$_2$ nanosheets, as demonstrated in a recent study (Fig. 10a) [112]. XPS analysis conducted during charging and discharging revealed a decrease in the binding energy separation of the dual peaks from 5.83 eV to 4.7 eV after three cycles, corresponding to a Mn valence state transition from +2 to +3.9 (Fig. 10b). Further XRD analysis provided clear confirmation of the presence of layered MnO$_2$ nanosheets (Figs. 10c and 10d), which subsequently act as electroactive sites for the reversible co-intercalation of Zn$^{2+}$/H$^+$. These findings were further supported in subsequent studies involving different MnO doping strategies (Figs. 10e and 10f) [113,114].

The findings from these studies indicate that various manganese oxides, particularly those with tunnel-like structures, tend to undergo a phase transition towards layered manganese oxidation. As a result, two-dimensional layered manganese dioxide, which exhibits relative structural stability and provides a larger diffusion space, has attracted increased attention. However, this type of manganese dioxide still encounters phase transitions during cycling, leading to a rapid capacity decrease.

### 3.1.1.3. Structural evolution with spinel structure.

In addition to the layered structure, researchers have also discovered a propensity for various types of manganese oxides to undergo transformation towards spinel structures. For instance, in earlier studies, Xu et al. observed the emergence of a new phase in $\alpha$-MnO$_2$ during charge-discharge processes [34], which were identified as spinel ZnMn$_2$O$_4$ [26]. This was further supported by a subsequent study conducted by Alfaruqi et al. (Fig. 11a) [23], where ex-situ synchrotron XRD analysis confirmed the presence of spinel ZnMn$_2$O$_4$ peaks during discharging. However, this transformation was considered reversible.

Subsequently, the layered structure of $\delta$-MnO$_2$ also exhibits a phenomenon of transformation to spinel structure during long-term cycling. Alfaruqi et al. further investigated its structural transformation and electrochemical mechanisms during extended cycling processes [46]. Considering that spinel ZnMn$_2$O$_4$ is not conducive to the insertion/extraction of Zn$^{2+}$[74], this study suggests that the layered $\delta$-MnO$_2$ gradually and irreversibly converts to spinel ZnMn$_2$O$_4$, leading to a loss of activity during prolonged cycling.

Recently, a study focusing on amorphous Mn$_2$O$_3$ also reported a similar process of structural evolution [56]. However, in this case, the formation of spinel ZnMn$_2$O$_4$ was considered a favorable factor contributing to capacity enhancement during the initial cycles (Fig. 11b). From the in situ grazing incidence X-ray diffraction (GIXRD) spectra, it can be observed that two peaks corresponding to the spinel ZnMn$_2$O$_4$ phase appeared after five cycles, while another X-ray diffraction pattern emerged after 200 cycles and became more pronounced after 500 cycles (Fig. 11c).

### 3.1.1.4. Transition among other structures.

These aforementioned reports suggest a propensity for various Mn oxides to undergo conversions to layered or spinel structures. However, there are also studies documenting other phase transitions in these materials. For instance, Wang et al. discovered a transformation from ball-milled Mn$_3$O$_4$ to $\varepsilon$-MnO$_2$.

![Fig. 9. Electrochemical and structural evolution of $\beta$-MnO$_2$ in Zn-MnO$_2$ cell.](image)

(a) schematic illustration of irreversible phase transformation, (b) cyclic voltammograms at a scan rate of 0.1 mV s$^{-1}$ from 0.8 to 1.9 V, and (c) typical charge/discharge curves for the initial two cycles with (d) corresponding XRD patterns. Reproduced from ref. [26] with permission.
during the initial activation process of the cathode material [77]. The XRD peaks shown in Figs. 11d and 11e clearly correspond to ε-MnO$_2$, while the Mn$_3$O$_4$ peaks disappear, demonstrating this phase transition. Another interesting report proposed a novel reaction mechanism for Mn$_3$O$_4$ used as a cathode in a zinc aqueous battery with a water-in-salt electrolyte (WiSE) containing a concentrated solution of 20 M ZnCl$_2$ + 5 M NH$_4$Cl. This mechanism entails an irreversible reductive insertion of Zn$^{2+}$ into Mn$_3$O$_4$, resulting in the formation of Zn$_{0.2}$Mn$_3$O$_4$ [115], which subsequently acts as the host material for the reversible intercalation of chloride ions (Fig. 12a). However, further research is necessary.
to gain a more comprehensive understanding of the underlying details of these processes.

Additionally, Mn$_2$O$_3$ has been identified as a promising cathode material due to its Zn$^{2+}$/H$^+$ intercalation mechanism accompanied by reversible phase transformations. Feng et al. investigated the use of mesoporous amorphous MnO$_x$ in zinc batteries and observed the occurrence of Zn$^{2+}$/H$^+$ intercalations during charging and discharging processes [116]. As Zn$^{2+}$ is inserted into the cathode structure, an insertion phase called Zn$_2$Mn$_2$O$_5$ is formed. Simultaneously, the inserted protons react with Mn$_2$O$_3$, leading to the extraction of oxygen from the host material, resulting in the formation of H$_2$O and a new phase of MnO (Fig. 12b). This transformation is reversible throughout cycling, and the cathode reaction mechanism can be represented as follows:

$$x\text{Zn}^{2+} + 2\text{e}^- + \text{Mn}_2\text{O}_3 \leftrightarrow \text{Zn}_x\text{Mn}_2\text{O}_3.$$
Mn₂O₃ + 2 H⁺ + 2e⁻ ↔ 2MnO + H₂O.

A latest report came to a similar conclusion where an urchin-like hierarchical porous Mn₂O₃ was used as cathode [92]. However, this work revealed that the intercalation of proton into Mn₂O₃ resulted in the formation of Mn₃O₄ rather than the MnO (Fig. 12c).

3.1.2. Liquid phase evolution path

In the previously discussed solid phase evolution pathway, the presence of dissolved Mn²⁺ is often considered as a significant factor contributing to capacity decay [24,25,44]. However, it is worth noting from Section 2.1.4 that dissolved Mn³⁺ can also participate in the energy storage mechanism of ZIBs. This review will further explore the Jahn-Teller effect associated with dissolved manganese and delve into the role played by dissolved Mn⁴⁺ in the charge/discharge and phase evolution processes. On one hand, the process of dissolution redeposition of Mn elements indirectly contributes to the transition between solid phases. On the other hand, the presence of dissolved Mn²⁺ in the solution itself can actively participate in the charge/discharge process as a Mn phase, thereby providing an important energy storage mechanism for direct phase change during charge/discharge. This mechanism has been widely studied in the context of high energy density systems.

Therefore, in this review, the phase evolution process involving the dissolution redeposition of manganese will be categorized as the liquid phase evolution pathway.

3.1.2.1. Jahn-Teller effect

In the discussed solid-state transformation process, Mn elements often undergo transitions between +3 and +4 oxidation states. However, it should be noted that the +3 oxidation state of manganese is not stable. This phenomenon can be attributed to a general principle proposed by Jahn Teller, stating that non-linear symmetric molecules in a degenerate orbital state (higher energy level) become unstable [117,118]. To reduce symmetry and relieve degeneracy, the molecules undergo distortions (Fig. 13a). Specifically, in the MnO₆ octahedral structure, the electronic orbitals of Mn²⁺ and Mn⁴⁺ exhibit non-degenerate t₂g e_g and t²g e_g configurations, respectively (Fig. 13b). On the other hand, Mn³⁺ exhibits a t²g e_g configuration with only one electron in the doubly degenerate e_g orbitals. This leads to an uneven distribution of electrons and distortion in the crystal structure [119]. Consequently, Mn³⁺ readily undergoes disproportionation reactions, transforming into Mn²⁺ and Mn⁴⁺ (2Mn³⁺ → Mn⁴⁺(aq) + Mn²⁺(aq)) [122], with Mn⁴⁺ dissolving in the electrolyte. This phenomenon is detrimental to the structural stability of manganese oxides during the ion insertion and extraction processes. It is generally acknowledged that the Jahn-Teller effect is one of the significant reasons contributing to structural collapse and manganese ion dissolution in Mn-oxide materials.

Previous studies have often attempted to suppress the Jahn-Teller effect and maintain the stability of crystal structures in manganese oxides by adjusting the oxidation states and introducing element doping. However, these methods have proven challenging in fundamentally eliminating the persistent effects of Jahn-Teller distortion and inherent structural instability in manganese oxides. In recent years, researchers have discovered that harnessing the deposition-dissolution process of manganese not only allows for self-repair of active materials against losses caused by the Jahn-Teller effect in cathode materials but also exhibits significant potential as an energy storage mechanism.

3.1.2.2. Reversible structural evolution between solid and liquid phases

Scholars have discovered that the solid-liquid phase structural evolution involving Mn elements also holds significant importance. Subsequent studies have concentrated on investigating the phase evolution mechanisms related to Mn²⁺ in the liquid phase. Guo X. et al. conducted a study on the energy storage mechanism of tunnelled α-MnO₂ and layered δ-MnO₂, and categorized the process into two stages, as depicted in Fig. 13 [36]. During the initial discharge process, a major portion of MnO₂ reacts with water, forming dissolved Mn²⁺ and OH-. Subsequently, in the charging process, Mn²⁺ are deposited as layered birnessite-MnO₂, replacing the original host MnO₂. In the subsequent charge and discharge cycles, the layered birnessite-MnO₂ undergoes reversible deposition and dissolution, serving as the new host material. Additionally, a portion of the original MnO₂ remains as the host material for reversible Zn²⁺/H⁺ co-embedding. The dissolution-redeposition process of MnO₂ accounts for the majority of the capacity and serves as the primary mode of energy storage conversion. It is entirely

Fig. 13. (a) Distortion of the Jahn Teller effect. (b) The electronic orbitals of Mn²⁺/Mn³⁺/Mn⁴⁺ ions. (c) The schematic illustration of dissolution-conversion mechanism in Zn/MnO₂ battery. (d) Schematic illustration of the reaction mechanism of α-MnO₂ in an aqueous ZIB. Zn/α-MnO₂ cell is most likely dominated by reversible formation of ZHS and Zn₅H₈O₃·3 H₂O during cycling, as α-MnO₂ experiences structural irreversibility from continuous dissolution. (e) Schematic illustration for reaction mechanism of the in situ formed Zn/Mn-d-ZMO@C battery. (f) The reaction path of β-MnO₂ during cycling.

(a) Reproduced from ref. [119] with permission. (b) Reproduced from ref. [36] with permission. (c) Reproduced from ref. [120] with permission. (d) Reproduced from ref. [30] with permission. (e) Reproduced from ref. [61] with permission.
reasonable to conclude that different Mn-oxides are redeposited as the same product following dissolution. However, there is controversy regarding the specific products of redeposition. Recent studies propose a contrasting view, suggesting that the dissolved Mn\(^{2+}\) ions undergo reversible deposition as ZnMnO\(_2\) and MnO, as shown in Fig. 13d and 13e [30,120]. Nevertheless, subsequent investigations indicate that the dense structure ε-MnO\(_2\) appears to be suitable for the dissolution-redeposition process (Fig. 13f) [61,81,82,121]. A wide range of noteworthy research has emerged based on the dissolution-redeposition mechanism of ε-MnO\(_2\).

### 3.1.2.3. Battery design based on the deposition-dissolution mechanism.

Compared to previously reported energy storage mechanisms such as cation intercalation and proton conversion, the deposition-dissolution mechanism involving reversible phase transitions between liquid and solid phases provides a two-electron transfer process, resulting in higher voltage and larger capacity (Fig. 14a) [54]. This has led to a recent trend in battery design based on the Mn\(^{3+}\)/MnO\(_2\) deposition-dissolution mechanism [53].

In 2018, W. Chen et al. first applied the manganese deposition/dissolution reaction mechanism to the manganese-hydrogen (Mn-H) battery, achieving high energy density and ultra-long cycle life [122]. This groundbreaking study sparked a new research focus on the use of Mn\(^{3+}\)/MnO\(_2\) cathodes matched with different anodes to form batteries, such as MnO\(_2\)-Zn [123,123–128], MnO\(_2\)-Cu [129,130], MnO\(_2\)-Pb [131] and MnO\(_2\)-Sn [132]. Inspired by this work, Chao et al. further investigated the energy storage behavior of Zn-Mn batteries and discovered a two-electron transfer reaction at the high-voltage region [82]. Consequently, they proposed a new electrolytic Zn-MnO\(_2\) battery (Figs. 14b and 14c). By enhancing the proton and electron transfer dynamics, the electrochemical activity of Mn\(^{3+}\)/MnO\(_2\) was further activated, significantly extending the high-voltage discharge region. This battery design achieved a high output voltage of 1.95 V and a remarkable gravimetric capability of approximately 570 mAh/g.

Due to the crucial role of proton regulation, Liang et al. proposed a more detailed description of the dissolution process of MnO\(_2\) involving three-step reactions [54]:

\[
\text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnOOH} \quad \text{(i)},
\]

\[
\text{MnOOH} + 3 \text{H}^+ \rightarrow \text{Mn}^{3+} + 2 \text{H}_2\text{O} \quad \text{(ii)},
\]

\[
\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+} \quad \text{(iii)}.
\]

Reactions (i) and (iii) are electrochemical reactions, while reaction (ii) is a chemical reaction. In essence, this process includes a proton conversion reaction from Mn\(^{3+}\) to Mn\(^{2+}\) and a disproportionation reaction of MnOOH from Mn\(^{4+}\) to Mn\(^{3+}\) [64,133].

The presence of an acid electrolyte promotes the dissolution of manganese; however, it can lead to zinc anode corrosion and hydrogen evolution reaction [82,134]. Additionally, the poor electrical conductivity and incomplete dissolution of MnO\(_2\) impose limitations on its use in high areal capacity applications [135,136]. In subsequent studies, scientists have explored various strategies to address these challenges, including the use of acid buffer solutions [124,134,137,138], cation regulation [133,135,136], and cathode structural adjustments [123,139,140], which will be discussed in detail later.

### 3.1.2.4. Decoupling electrolytes towards high voltage.

The Mn\(^{3+}\)/MnO\(_2\) chemistry, which exhibits a high redox potential, is predominantly influenced by acidic conditions. On the other hand, the anode Zn/Zn (OH)\(_2\) redox couple operates with lower potential in alkaline electrolytes compared to Mn\(^{3+}\)/Mn in mild electrolytes. The use of decoupled electrolytes creates an advantageous environment for the cathode and the anode separately, resulting in higher energy density and long-term stable operation. The reactions for this chemistry are as follows [126,141]:

**Cathode:**

\[
\text{MnO}_2 + 4 \text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O} \quad \text{E}_0 = 1.22 \text{ V vs SHE.}
\]

**Anode:**

\[
\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 2e^- \quad \text{E}_0 = -1.22 \text{ V vs SHE.}
\]

**Overall:**

\[
\text{Zn} + \text{MnO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{Mn}^{2+} \quad \text{E}_0 = 2.44 \text{ V vs Zn/Zn (OH)\(_2\).}
\]

Liu et al. were the first to design an aqueous battery system utilizing an acid-alkaline dual electrolyte separated by an ion-selective membrane [126], achieving an ultrahigh energy density of up to 1503 Wh/kg (Fig. 15a).

Subsequently, Chao et al. proposed a new generation of electrolytic Zn-MnO\(_2\) battery that incorporated a decoupled electrolyte and Ni\(^{2+}\) catalysis to enhance the reversible Mn\(^{3+}\)/MnO\(_2\) conversion, building upon their previous research (Fig. 15b) [82,125].

More recently, Zhong et al. further developed the electrolyte-decoupling strategy by employing a neutral electrolyte as buffered solutions to separate an alkaline electrolyte for the Zn anode and an acidic electrolyte for the MnO\(_2\) cathode, utilizing two chambers and two
membranes (Fig. 15c) [121]. This innovative two-membrane three-chamber design significantly increased the open-circuit voltage to an impressive 2.83 V, resulting in an excellent energy density of 1621.7 Wh/kg.

3.1.3. Mixed evolution path

As research on the energy storage mechanism of zinc-ion aqueous batteries advances, an increasing number of researchers have recognized the existence of a complex mechanism system that encompasses multiple structural evolution paths for Mn-oxide cathodes.

Huang et al. unraveled an intricate reaction mechanism and the evolution of physical phases in aqueous Zn/MnO$_2$ batteries with Mn$^{2+}$ additives [142]. Upon initial discharge, Zn$^{2+}$ insertion occurs around 1.4 V, followed by H$^+$ insertion and conversion between 1.0 and 1.3 V (Fig. 16). This leads to the formation of \( \alpha\)-Zn$_x$MnO$_2$, MnOOH, phase transition product Mn$_2$O$_3$, and the byproduct ZHS. During the initial charge, the discharge products Zn$_x$MnO$_4$, MnOOH, and Mn$_2$O$_3$ are transformed back to the pristine tunnel structure of \( \alpha\)-MnO$_2$, with the detachment of Zn$^{2+}$ and inverse conversion. Simultaneously, the BZSP phase undergoes transformation to ZnMn$_3$O$_7$⋅3 H$_2$O in the presence of Mn$^{2+}$. Subsequent cycles involve not only the aforementioned transition processes but also the emergence of new phases such as ZnMn$_2$O$_4$ and ZnMn$_2$O$_{12}$, which act as host materials for Zn$^{2+}$ intercalation/deintercalation and dissolved Mn$^{2+}$ dissolution/redeposition. However, this mechanism is highly intricate, and further exploration is warranted to elucidate specific details. For instance, some scholars have pointed out that the sequence of Zn$^{2+}$ and H$^+$ insertion in this mechanism differs from the previously reported co-intercalation mechanism.

---

**Fig. 15.** (a) The schematic illustration and mechanism of Zn-Mn$^{2+}$ battery using an acid-alkaline dual electrolyte. (b) Schematic illustration of Zn-Mn hybrid aqueous battery. (c) two-membrane and three-chamber design for electrolyte decoupling. (a) Reproduced from ref. [126] with permission. (b) Reproduced from ref. [125] with permission.(c) Reproduced from ref. [121] with permission.

**Fig. 16.** Phase evolution of MnO$_2$ cathode during (a) the first discharge process, (b) the first charge process, and (c) the repeated charge/discharge processes after the first charge/discharge cycle, respectively. Reproduced from ref. [142] with permission.
Recent studies have reported a two-electron reaction mechanism for nanostructured layered birnessite MnO₂ with low crystallinity (Figs. 17a and 17b) [143,144]. In contrast to previous reports, this mechanism reveals an additional step of solid-phase transition from layered δ-MnO₂ to spinel ZnMnO₄ phase, involving the insertion of Zn²⁺ before Mn³⁺ dissolution [36,54,82]. This step aligns with the Mn⁴⁺/Mn³⁺ single-electron reaction previously observed in studies on the phase transition mechanism of layered δ-MnO₂ [81]. The Mn⁴⁺/Mn³⁺ reaction in this mechanism is attributed to the low crystallinity of birnessite MnO₂.

A recent study proposed an evolution path for α-MnO₂ cathodes (Fig. 17c) [145]. During the initial discharge, α-MnO₂ undergoes an electrochemical-induced structural conversion to a layered-type L-Zn₂MnO₄, which is accompanied by irreversible structure changes and the dissolution of Mn²⁺. In subsequent cycles, L-Zn₂MnO₄ acts as the host for Zn²⁺ intercalation/deintercalation, while the dissolved Mn²⁺ undergoes reversible deposition/dissolution in layered δ-MnO₂. This finding differs from an earlier report that suggested irreversible structure conversion without the presence of layered-type MnO₂ [35].

It is noteworthy that significant byproducts, such as ZHS, have been observed in the previously discussed reports due to the dissolution of Mn²⁺ with increasing pH value. These byproducts have been directly used as cathodes in other works, as subsequently discussed.

Zhao et al. designed a novel rechargeable Zn/MnO₂ battery in which ZHS served as the cathode material [146]. Active MnO₂ was deposited from the dissolved Mn²⁺ in the electrolyte during the charging process. Specifically, the battery initially undergoes a charging process in which Mn²⁺ deposits as spinel ZnMnO₄ and then converts to layered Zn-birnessite, while ZHS dissolves into the electrolyte (Figs. 18a and 18b). Subsequent discharge exhibits reversible evolution, and the subsequent cycles follow a mechanism similar to the one discussed previously [143,144].

However, Chen et al. suggested that the intermediate phase during the dissolution of MnO₂ deposition is not ZnMnO₄ but rather ZnMnO(OH)₂ (Fig. 18c) [100]. Their recent report further proposes a new model for ZSH-assisted deposition–dissolution, asserting that the capacity contribution of aqueous Zn-Mn batteries mainly stems from the reversible conversion of ZHS and ZnMnO(OH)₂ (Fig. 18d) [147]. The report also concluded that the MnO₂ cathode only induces the generation of ZHS during the discharge process and does not require the assistance of Mn²⁺. Therefore, MnO₂ can be replaced by other materials, such as ZnO or CaO, in an electrolyte containing Mn²⁺. However, several aspects of this report still require further validation.

3.2. Influence factor

While the structure evolution of zinc-ion batteries has been extensively studied, the experimental observations of different evolutionary products can vary due to various factors, including electrode materials, electrolyte solutions, and operating conditions. These factors can introduce interference and complicate the investigation of the actual mechanism. Therefore, there is an immediate and pressing need to systematically summarize and analyze these potential influencing factors to gain a comprehensive understanding of the zinc-ion battery system.

3.2.1. Electrode materials

From the preceding discussion, it is evident that the channel structure and particle size morphology of a material play a significant role in the energy storage mechanism and structural evolution pathway.

In particular, tunnel-like structures tend to undergo an irreversible phase transition to a layered structure during the initial charge/discharge process. Previous studies indicated that tunnel-structured manganese oxides exhibit reversible phase transitions with other phases (such as layered or spinel-like structures) upon Zn²⁺ insertion/extraction. However, Zhang challenged this perspective by proposing that tunnel-structured manganese oxides experience irreversible transformation to the layered phase only during the initial charge/discharge process [26]. This study suggests that the tunnelled phase is not a stable structure for MnO₂ and has consequently led to extensive research on the relatively more stable layered phase, δ-MnO₂.

The non-tunnel structures of ε-MnO₂ and A-MnO₂ inherently present challenges in accommodating cations and facilitating rapid diffusion. However, their smaller particle sizes and abundant defects make the originally slow electrochemical reactions more favorable.

However, neither the tunnelled, layered, nor non-tunnel structured manganese oxides can circumvent the transition to the inactive spinel phase ZnMnO₄ [37,66]. As discussed earlier, this spinel-phase ZnMnO₄ possesses a three-dimensional channel structure that tends to have a low capacity due to its narrow tunneling space and substantial electrostatic repulsion, which is generally unfavorable for the diffusion of divalent ions. Consequently, it often necessitates relying on defective structures as anode materials for zinc-ion batteries.

Mn-oxide materials also exhibit a general characteristic of being susceptible to dissolution and conversion into a liquid phase during
been studied and compared, revealing that R-MnO₂ undergoes structural evolution at the beginning of the cycle, transitioning into tetravalent manganese oxides that serve as the true cation hosts. Examples of such tetravalent manganese oxides include MnO₂₃⁺ and MnO₂₄⁺ [62]. In addition to the structural aspects, the valence state of manganese elements also plays a significant role in the evolution mechanism. Considering the stability of Mn⁴⁺, low-valent manganese oxides tend to undergo a structural evolution process at the beginning of the cycle, transitioning into tetravalent manganese oxides that serve as the true cation hosts. Examples of such tetravalent manganese oxides include MnO₈⁶⁺, Mn₃O₇²⁻, and Mn₄O₉⁶⁺ [76,148] as discussed in the previous section.

3.2.2. Electrolytes

Besides, the electrolyte environment has a very critical influence on the structural evolution, especially the liquid phase evolution path.

Early studies have suggested that manganese dissolution was an important cause of capacity decay. This dissolution of manganese has often been considered as a significant contributor to capacity decay [24]. However, recent research has challenged this degradation mechanism and demonstrated that dissolved manganese can be redeposited as manganese oxides when it reaches a certain concentration [62]. In 2016, Pan et al. found that by pre-adding a specific concentration of manganese ions to the electrolyte, the cycling stability of the battery was significantly improved [11]. This study concluded that the deposition of dissolved manganese as manganese oxides could offset the loss of pristine manganese dioxide through dissolution. In 2017, Zhang et al. discovered that Mn²⁺ forms uniform porous nanostructured MnO₂ films on the cathode’s surface, effectively protecting the electrode from aggregation of OH⁻ near the cathode results in the precipitation of ZHS with Zn²⁺ and SO₄²⁻, which inhibits pH rise [13,150]. Moreover, Qiao et al. discovered that the addition of certain acids to the electrolyte battery can promote the deposition-dissolution reaction of manganese [82], suggesting that this effect is due to proton activation. On the other hand, Liang et al. found that ZHS hampers the contact between the cathode material and water molecules [36], thus impeding the dissolution of manganese. Therefore, it can be inferred that the dissolution of manganese is more likely to occur under acidic conditions without the presence of ZHS.

3.2.3. Working conditions

The evolution of the structure is also influenced by various operating conditions. It is well established that each electrochemical reaction corresponds to a specific redox potential, and different charging and discharging platforms correspond to distinct reaction mechanisms. Previous studies have often assumed that the Zn/MnO₂ system exhibits two discharge platforms, corresponding to the insertion processes of Zn²⁺ and H⁺, respectively [11]. However, Qiao et al. conducted a study on the e-MnO₂ cathode, prepared through constant voltage charging at 2.2 V [82], and observed distinct triple discharge regions during the discharge process (Fig. 14c). These regions represent three different discharge mechanisms. The medium-pressure region (D2: 1.7 to 1.4 V) and the low-pressure region (D3: 1.4 to 0.8 V) correspond to the previously reported insertion reactions of Zn²⁺ and H⁺, respectively. Remarkably, they also discovered a high-pressure region (D1: 2.0 to 1.7 V) attributed to the electrolytic reaction of manganese. This finding not only enabled achieving a higher output voltage in Zn/MnO₂ batteries but also significantly improved the specific capacity of the MnO₂ cathode material. This discovery provides valuable insights into the reaction mechanisms and opens up new possibilities for enhancing the performance of Zn/MnO₂ batteries.

Moreover, a series of subsequent studies have demonstrated that cycling at high voltages is more favorable for improving the cycle life of MnO₂ cathodes. Several reasons support this observation: 1) The deposition-dissolution of manganese effectively mitigates the structural collapse that conventional manganese oxides experience during cation insertion/extraction processes. 2) Irreversible conversion reactions are more prone to occur at low voltages. A study combining experiments and density functional theory (DFT) calculations found that in the Zn/MnO₂ system [69], the H⁺/Zn²⁺ co-insertion and conversion reactions occur at 1.40 V and 1.26 V, respectively (Fig. 19a). Notably, the irreversible chemical reaction at low voltages is a significant factor contributing to capacity decay. The cycling performance was compared under different voltage ranges (1.0–1.8 V and 1.3–1.8 V) (Fig. 20a), and although the capacity of ZIBs was limited in the range of 1.3–1.8 V, it exhibited better cycling performance compared to the voltage range of 1.0–1.8 V.

Manganese deposition occurs at high voltages, which helps
compensate for the capacity loss caused by manganese dissolution. Chen et al. found that Zn/MnO$_2$ batteries with Mn$^{3+}$ additives still exhibited rapid capacity drops when cycled between 0.8 and 1.6 V [100]. It was confirmed that the improved cycling performance attributed to the Mn$^{2+}$ additive was actually due to the redeposition of Mn$^{2+}$ at high potentials (>1.6 V) (Figs. 20b and 20c). Another study also reached a similar conclusion [133]. Cyclic voltammetry measurements obtained by scanning over wide potentials clearly show the reduction peak of manganese deposition above 1.6 V (Fig. 20d). The cycling performance of ZIBs was investigated under different voltage ranges, and it was observed that capacity decay occurred rapidly in the low voltage range, while the cycling performance significantly improved at high and full voltages (Fig. 20e). Collectively, these findings highlight the importance of operating at higher voltages to enhance the cycling performance and stability of MnO$_2$ cathodes in Zn-ion batteries.

Furthermore, in addition to voltage, it is evident that the charge and discharge rate also have a significant impact on the evolution process. Due to differences in ionic radii, the kinetic properties of H$^+$ and Zn$^{2+}$ vary considerably [12]. The literature further presents an analysis of the charge/discharge rate, along with demonstrating that irreversibility at low voltages leads to capacity decay (Fig. 19b) [69]. The results indicate that the change in current density affects the kinetic performance of the two reactions differently. An increase in current density notably enhances the Gibbs free energy barrier of the conversion reaction at low voltage, while its effect on the insertion reaction at high voltage is negligible. This suggests that higher current densities contribute to the suppression of irreversible phase transitions at low voltages, resulting in improved cycling performance. Comparisons of the cycling performance at different rates confirm the capacity retention at high current densities (Fig. 20f). Thus, it is evident that controlling the charge and discharge rate is crucial for optimizing the cycling stability and capacity retention of MnO$_2$ cathodes in Zn-ion batteries.

Interestingly, a recent study has discovered that lower current densities can promote the self-healing of the cathode material [123]. The redeposition effect of Mn$^{2+}$ at high potentials was compared at different current densities using carboxy-modified carbon nanotubes (cCNTs) as cathode substrates for aqueous Zn/MnO$_2$ batteries (Fig. 19c). The findings show that lower current densities lead to better manganese deposition, which was further confirmed through cycling tests (Fig. 19d).

However, it is important to note that the mechanism of how current density affects the energy storage mechanism and structural evolution is quite complex. Various factors such as different current collectors, electrolyte concentrations, and other sensitive parameters can interfere with the analysis results. Therefore, accurately determining the mechanism of the reaction products under different current densities remains a significant challenge. Further research is needed to elucidate the intricate interplay between current density, structural evolution, and energy storage mechanisms in order to optimize the performance and stability of MnO$_2$ cathodes in Zn-ion batteries.

3.3. The impact of structural stability on performance and mechanisms

The previous section introduced the main pathways and influencing factors of structural evolution in manganese oxide. It is worth noting that manganese oxide may undergo multiple phase transitions throughout the entire lifecycle of ZIBs, and these structural changes further impact the performance and mechanisms of the battery at different stages. For example, an initial increase in capacity during cycling, a mid-term capacity retention, and an inevitable capacity decay during long-term cycling. Therefore, a deeper analysis of the evolution rules of phases is necessary to understand the mechanism of this capacity change. Through years of exploration, various reaction products have been observed during the operation of Zn/MnO$_2$ batteries, such as ZnMn$_2$O$_4$, MnOOH, Zn-birnessite, Zn-buserite, ZHS, MnO$_x$, ε-MnO$_2$, Mn$^{2+}$, and others. Although the debate regarding the reaction mechanism is ongoing, the academic consensus on the evolution mechanism has gradually shifted from early single-step phase transition to a complex multi-step competitive phase evolution. Throughout this process, the reversibility of the reactions has always been discussed. Therefore, this subsection first briefly summarizes the impact of the reversibility of various structural evolution pathways on the performance and mechanisms, and then explores the latest research on the evolution rules of manganese oxide structure, mechanisms, and performance during long-term battery cycling.

3.3.1. Reversible phase change and energy storage mechanisms

The reversible phase transition of Mn oxides corresponds to the energy storage and release process, which may be attributed to either the insertion and extraction of cations or the deposition-dissolution mechanism of Mn [151]. Concerning the solid-phase evolution pathway, various reaction products have been successively discovered since Xu...
et al. proposed the reversible phase transition of $\alpha$-MnO$_2$ ↔ ZnMn$_2$O$_4$ [34]. Consequently, scholars have put forth several explanations for different reversible phase transitions, such as $\alpha$-MnO$_2$ ↔ Zn-burnessite [24] and $\alpha$-MnO$_2$ ↔ Zn-buserite [25], etc. However, Zhang et al.’s study seems to question the stability of tunnel-like materials, particularly during cycling (Fig. 9a) [26]. Subsequently, numerous scholars have employed methods like pre-insertion to stabilize such non-layered structures, and it has been found that certain reversible phase transitions of the solid-phase can still be observed [109,111].

Furthermore, the selection of a more reversible liquid-phase evolutionary pathway appears to be a preferable option. However, the phase of deposited manganese remains a topic of debate. Different literature reports have proposed five distinct forms of Mn-deposited phases, which include amorphous MnO$_x$ [26], $\gamma$-MnO$_2$ [150], $\epsilon$-MnO$_2$ [12], layered Zn-birnessite [36,145], and ZnMn$_2$O$_4$ [39]. Accurately defining the depositional facies of manganese and understanding its influencing factors are crucial for analyzing the subsequent evolution process. However, there is currently a limited number of studies dedicated to investigating this aspect.

3.3.2. Activation process and passivation process

Reversible phase transitions, serving as an energy storage mechanism, can account for capacity retention but are insufficient in explaining capacity changes. The capacity rise observed during the initial cycle is commonly attributed to an activation process, whereas the subsequent capacity decline can be described as a passivation process. It is important to note that the irreversible phase change plays a pivotal role in both of these processes.

The activation process is commonly observed in various types of secondary batteries, and it is generally attributed to multiple factors in the case of aqueous zinc-ion batteries. Firstly, the penetration of electrolyte into the positive electrode material facilitates enhanced contact between the electrode and the electrolyte. Secondly, the presence of Mn$^{2+}$ additives in the electrolyte can lead to additional capacity through Mn$^{2+}$ deposition. Lastly, a portion of manganese oxides often undergo irreversible phase evolution during the initial charge and discharge cycles, resulting in the formation of structures more conducive for cation insertion.

During the cycling process, the structural stability of each active substance may vary, and certain active phases may undergo limited irreversible side reactions during the reversible changes, leading to the loss of active substances and a decline in capacity. Although the exact mechanism behind this decline remains a subject of controversy, it is generally accepted that the dissolution of manganese and the formation
of inactive materials are significant contributing factors.

3.3.3. Evolving structure, mechanisms, and performance throughout the lifecycle

The intricate structural evolution of manganese oxides during long-term cycling is one of the key factors contributing to the ongoing debate surrounding their energy storage mechanisms. Elucidating such co-evolution mechanisms can greatly enhance our understanding of the behavior of zinc-ion batteries throughout their entire life cycle, as well as provide valuable guidance for improving performance at different stages.

Lately, Becknell et al. conducted a study that elucidated the evolving reaction mechanism and offered a plausible explanation for capacity fade (Fig. 21a) [38]. In their investigation, layered δ-MnO₂ was employed as the pristine cathode material in aqueous zinc batteries. During the initial 10 cycles, an appreciable dissolution of δ-MnO₂ was observed in the slightly acidic electrolyte using inductively coupled plasma-mass spectrometry (ICP-MS), while XRD analyses confirmed the electrodeposition of ε-MnO₂. These findings indicated that a significant quantity of δ-MnO₂ dissolved into the electrolyte during the discharge reaction (Eq1), and the dissolved Mn²⁺ ions were subsequently reversibly deposited as ε-MnO₂ during the charge reaction (Eq2). Simultaneously, Zn²⁺ intercalation/deintercalation (Eq3 and Eq4) still contributed to a certain amount of capacity, thereby hindering further dissolution of MnO₂. As the δ-MnO₂ gradually diminished due to its irreversible dissolution, ε-MnO₂ progressively accumulated through electrodeposition from the concentrated MnSO₄ electrolyte. Consequently, the dominant reaction mechanism shifted from Eq1 and Eq3 to Eq2 and Eq4. After 55 cycles, Mn²⁺ ions appeared to decrease due to continued Zn²⁺ intercalation and the growth of the host ZnxMnO₄, which, in turn, inhibited the further dissolution of manganese. Consequently, the main reaction mechanism transitioned to Eq5, allowing tetragonal ZnxMnO₄ with excess Zn²⁺ to convert to cubic Zn₁₋ₓMnO₂.

\[
\begin{align*}
\delta\text{-MnO}_2 & \rightarrow \text{Mn}^{2+} \\
\delta\text{-MnO}_2 + \text{Zn}^{2+} & \rightarrow \text{ZnMn}_2\text{O}_4 \\
\varepsilon\text{-MnO}_2 & \rightarrow \text{Mn}^{2+} \\
\varepsilon\text{-MnO}_2 + \text{Zn}^{2+} & \rightarrow \text{ZnMn}_2\text{O}_4 \\
\text{ZnMn}_2\text{O}_4 + \text{Zn}^{2+} & \rightarrow \text{Zn}_{1+x}\text{Mn}_2\text{O}_4
\end{align*}
\]

In another study, the characteristics of various structures of manganese dioxide, including α-, δ-, ε-, γ-, and γ-MnO₂, were investigated and compared. The general phase transitions occurring in different manganese dioxide structures were identified and summarized (Fig. 21b) [62]. It was found that pristine MnO₂ operates based on the H⁺/Zn²⁺ co-insertion mechanism for energy conversion. During the discharge process, the resulting products MnOOH and ZnOₓMnO₂ undergo Jahn-Teller distortion and experience disproportionation reactions and structural evolution due to the inherent instability of trivalent Mn³⁺. This instability leads to the dissolution of divalent manganese ions into the electrolyte. Subsequently, a portion of the dissolved manganese ions is redeposited as a more reactive layered Birnessite-MnO₂ during the charging phase. As the cycling progresses, Birnessite-MnO₂ gradually replaces the initially present manganese dioxide as the new host material, resulting in an increase in capacity. However, since the layered Birnessite-MnO₂ structure is thermodynamically prone to converting to the inert spinel state (Zn, Mn)MnO₄, prolonged cycling eventually leads to capacity decay.

A recent study suggests that the formation of spinel-type ZnMnO₄ may be closely associated with the presence of Mn³⁺, and accordingly, two potential reaction pathways are identified (Fig. 21c) [39]. By comparing the voltage and total Gibbs free energy differences between these two pathways, it has been determined that the main route for ZnMnO₄ formation is the direct deposition of Mn²⁺ from the liquid

---

**Fig. 21.** (a) Transformation of the electrochemical interface at a dynamic δ-MnO₂ cathode. (b) Schematic illustration of the transformation process and reaction mechanism in each step of MnO₂ during long-term cycling, where the MnO₂ is finally converted to electrochemical inactive (Zn, Mn)MnO₄. (c) The total Gibbs energy differences at 300 K for two possible reaction paths. (d) Mn-oxide competitive capacity evolution protocol: upper is the partition of the cycle profile and pH value at 1.85 V for different stages, the middle is the micromechanism schematic in four different regions, and the bottom is the concentration and contribution ratio of the Mn²⁺. (a) Reproduced from ref. [38] with permission. (b) Reproduced from ref. [62] with permission. (c) Reproduced from ref. [39] with permission.
phase into $\text{ZnMn}_2\text{O}_4$. In this particular study, $\delta$-$\text{MnO}_2$ was employed as the cathode material in ZIBs, and the cycling process was divided into four distinct regions based on capacity fluctuations and the contribution of $\text{Mn}^{2+}$ (Fig. 21d). The first region corresponds to the activation stage, where the capacity increase is primarily attributed to the wetting of the electrode. The second stage is dominated by the reversible $\text{H}^+/\text{Zn}^{2+}$ intercalation mechanism, leading to a maintained capacity level. The third stage is governed by the deposition of $\text{Mn}^{2+}$ and exhibits a capacity increase. Lastly, the fourth stage displays a capacity decrease due to the continuous irreversible deposition of $\text{ZnMn}_2\text{O}_4$. The different reaction mechanisms observed in each phase are closely connected to the structural evolution of the electrode material and the local pH environment at the electrode/electrolyte interface. As the cycling progresses, the pH gradually increases, promoting the deposition reaction of $\text{ZnMn}_2\text{O}_4$ and contributing to the degradation of battery performance. However, the precise mechanism responsible for the irreversible depletion of $\text{H}^+$ and the subsequent rise in pH still requires further research for definitive verification.

4. Strategies for improvement

Mn-oxide materials exhibit a relatively high redox potential and specific capacity, but their fragile chemical structure presents a significant challenge that limits their practical utility. To enhance the structural stability of Mn-oxide materials and improve their cycle life, extensive research has been conducted, yielding significant progress. Scholars have explored six main strategies in recent years: heterogeneous doping, nanostructure engineering, carbon composite engineering, defect engineering, guest ion pre-insertion, and functional electrolyte addition (Fig. 22). In order to provide a clear and comprehensive comparison of various improvement strategies, we reviewed different types of improvement strategies, their functions, cathode materials, electrolytes, and cycling stability in Table 2.

4.1. Doping

Heterogeneous doping is a crucial technique employed to enhance the intrinsic conductivity of electrode materials. For instance, the introduction of $\text{V}^{5+}$ into the lattice of $\text{MnO}_2$ has been shown to effectively elevate its Fermi energy level and reduce the energy band width, thereby improving electronic conductivity [156]. Furthermore, the incorporation of $\text{V}^{5+}$ promotes the formation of layered nanostructures, increases specific surface area, and facilitates ion diffusion and transport. Consequently, compared to pure $\text{MnO}_2$ electrodes, $\text{V}$-doped $\text{MnO}_2$ demonstrates substantial enhancements in specific capacity and cycling performance [157]. In a similar vein, Xu et al. proposed that the doping of $\text{Al}^{3+}$ and the application of lignin coating in the hydrothermal synthesis of $\delta$-$\text{MnO}_2$ can augment the specific surface area of the material and enhance its electrical conductivity [158]. These modifications contribute to improved electrochemical performance.

Overall, heterogeneous doping plays a pivotal role in tailoring the structural and electrochemical properties of Mn-oxide electrode materials, enabling advancements in their conductivity and performance. These findings offer valuable insights for the design and development of next-generation high-performance energy storage systems.

Furthermore, doping elements play a crucial role in facilitating the activation of manganese oxides and maintaining the stability of the active phase. For instance, in their investigation of the phase evolution during the charge-discharge process of $\text{Bi}_2\text{O}_3$ incorporated with $\text{MnO}_2$ nanotubes as cathode materials for ZIBs, Lei et al. discovered that a small amount of bi-doping could form Bi-O bonds [159], leading to changes in bond energy and lattice parameters, thereby reducing the dissolution of $\text{Mn}^{2+}$ and preserving the structural stability of $\text{MnO}_2$. Additionally, the formation of $\text{Bi}_2\text{Mn}_2\text{O}_{10}$ inhibits the formation of the inactive spinel phase $\text{ZnMn}_2\text{O}_4$, while simultaneously serving as a host for $\text{H}^+$ insertion and deinsertion, thus enabling effective charging and discharging capacity. In another study, Fenta et al. designed Cu-MnO nanospheres as cathode materials and demonstrated through electrochemical testing and characterization that [113], during the initial discharge, the spinel-type Cu-MnO is transformed into a layered structure, Cu-MnO$_2$-n$\text{H}_2\text{O}$, which acts as the true host for insertion and deinsertion of $\text{Zn}^{2+}/\text{H}^+$. The doping of Cu contributes significantly to the formation and stabilization of this layered structure. Similarly, Ce was investigated as a doping element in another study [160], where it induces the structural transformation of $\text{MnO}_2$ from the $\beta$-phase to the $\alpha$-phase. This transformation leads to a broadened tunneling structure, promoting the transport and storage of $\text{Zn}^{2+}$ and accelerating surface diffusion rates on the cathode material. Additionally, the Ce ions embedded in the Mn-O framework act as anchors, enhancing the stability of the cathode structure [161]. In yet another exploration by Zhang et al., the doping of Ni elements in $\text{Mn}_2\text{O}_3$ was found to serve a similar purpose [93]. It not only facilitates electron rearrangement, improving conductivity, but also stabilizes the structure by reducing the overall formation energy. The incorporation of these doping elements represents an effective

![Fig. 22. Schematic diagram of the six main modification strategies: (a) doping, (b) nanostructure, (c) pre-insertion, (d) defection, (e) components, and (f) electrolyte additive.](image-url)
<table>
<thead>
<tr>
<th>Strategies</th>
<th>Effect</th>
<th>Cathode materials</th>
<th>Electrolyte</th>
<th>Cycling stability (mAh g⁻¹/cycles/mA g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>2D V doped MnO₂</td>
<td>0.5 M Na₂SO₄</td>
<td>92%/1000/5000</td>
<td>[156]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>V-doped α-MnO₂</td>
<td>1 M ZnSO₄</td>
<td>50%/100/66</td>
<td>[157]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>L α-Al₃O₃ α-MnO₂</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>90%/3000/1500</td>
<td>[158]</td>
</tr>
<tr>
<td>Doping</td>
<td>inducing phase transition</td>
<td>β-MnO₃ α-MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>80/5000/10000</td>
<td>[159]</td>
</tr>
<tr>
<td>Doping</td>
<td>maintaining crystal structure stability</td>
<td>Cu/αMnO</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>70%/100/3 C</td>
<td>[113]</td>
</tr>
<tr>
<td>Doping</td>
<td>inducing phase transition</td>
<td>Ce/β-MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>7%/400/2 C</td>
<td>[160]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>Ce-MnO₂ β/CC</td>
<td>2 M ZnSO₄</td>
<td>202/450/100</td>
<td>[161]</td>
</tr>
<tr>
<td>Doping</td>
<td>maintaining crystal structure stability</td>
<td>Ni-doped MnO₂</td>
<td>2 M ZnSO₄</td>
<td>85.6%/2500/1000</td>
<td>[93]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>Co-MnO₂</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>80%/1100/200</td>
<td>[148]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>N-MnO₂</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>85%/1000/1000</td>
<td>[162]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>F-doped β-MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>85%/150/500</td>
<td>[59]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>F-doped MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>79%/120/5 C</td>
<td>[163]</td>
</tr>
<tr>
<td>Doping</td>
<td>improving the electronic conductivity</td>
<td>α-MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>95%/3000/100</td>
<td>[164]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>enhancing diffusion kinetics</td>
<td>ZnMn₂O₆ nanocrystals</td>
<td>1 M ZnSO₄ + 0.05 M MnSO₄</td>
<td>97.4%/2500/1000</td>
<td>[165]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>enhancing diffusion kinetics</td>
<td>α-MnO₂ nanorod</td>
<td>1 M ZnSO₄</td>
<td>104/75/83</td>
<td>[152]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>enhancing diffusion kinetics</td>
<td>δ-MnO₂ nanosheets</td>
<td>1 M ZnSO₄</td>
<td>133/100/100</td>
<td>[70]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>enhancing diffusion kinetics</td>
<td>hollow MnO₂ nanospheres</td>
<td>1 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>305/100/1 C</td>
<td>[166]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>maintaining crystal structure stability</td>
<td>MnO₂ nanoporous</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>89%/3000/10 C</td>
<td>[116]</td>
</tr>
<tr>
<td>Nanostructures</td>
<td>maintaining crystal structure stability</td>
<td>NiO-plated MnO₂</td>
<td>2 M ZnSO₄</td>
<td>400/300/1000</td>
<td>[167]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>MnO₂/graphite CNT</td>
<td>2 M ZnSO₄ + 0.5 M MnSO₄</td>
<td>40/800/700</td>
<td>[168]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>MnO₂/graphite CNT</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>87.4/800/700</td>
<td>[168]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>ZnMn₂O₆/NG</td>
<td>1 M ZnSO₄ + 0.05 M MnSO₄</td>
<td>94%/500/500</td>
<td>[165]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>MnO@NGS</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>98%/300/500</td>
<td>[91]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>β-MnO₂ @NC</td>
<td>3 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>100/700/2000</td>
<td>[169]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>MnO₂ @NCNrs</td>
<td>3 M ZnSO₄</td>
<td>100/700/1000</td>
<td>[170]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>MnO@N-C</td>
<td>2 M ZnSO₄</td>
<td>176/200/50</td>
<td>[94]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>PVP-MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>8%/850/1000</td>
<td>[171]</td>
</tr>
<tr>
<td>Composite material</td>
<td>improving the electronic conductivity</td>
<td>cation-deficient spinel ZnMn₂O₄</td>
<td>3 M Zn(CF₃SO₃)₂</td>
<td>94%/500/500</td>
<td>[45]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving mechanical performance</td>
<td>hollow porous spinel ZnMn₂O₄</td>
<td>1 M ZnSO₄ + 0.05 M MnSO₄</td>
<td>106/300/100</td>
<td>[172]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving the electronic conductivity</td>
<td>MnO@NC</td>
<td>2 M ZnSO₄</td>
<td>98%/300/500</td>
<td>[91]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving the electronic conductivity</td>
<td>MnO@NC</td>
<td>2 M ZnSO₄</td>
<td>116/1500/1000</td>
<td>[50]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving the electronic conductivity</td>
<td>O₂-defect MnO₂</td>
<td>3 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>154%/1000/1000</td>
<td>[153]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving the electronic conductivity</td>
<td>O₂-defect MnO₂</td>
<td>3 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>94%/300/500</td>
<td>[60]</td>
</tr>
<tr>
<td>Defective engineering</td>
<td>improving the electronic conductivity</td>
<td>O₂-defect MnO₂</td>
<td>1 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>8%/2000/5000</td>
<td>[154]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>improving the electronic conductivity</td>
<td>α-K₀.15MnO₂</td>
<td>3 M Zn(CF₃SO₃)₂</td>
<td>180/400/5 C</td>
<td>[110]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>A1-intercalated MnO₂</td>
<td>1 M ZnSO₄</td>
<td>98%/2000/2000</td>
<td>[109]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>α-Zn,MnO₂</td>
<td>3 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>93%/100/1000</td>
<td>[173]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>PANI-intercalated MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>125/5000/2000</td>
<td>[31]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>δ-Na₀.13MnO₂·1.5 H₂O</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>98%/1000/200</td>
<td>[174]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>Na⁺-intercalated δ-MnO₂</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>93%/100/2000</td>
<td>[175]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>N-doped Na₂MnO₇</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>78.9%/550/2000</td>
<td>[176]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>K₂₀.5MnO₂·0.1 H₂O</td>
<td>3 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>95%/1.000/2000</td>
<td>[177]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>K₂₀.5H₂·δMnO₂·0.28 H₂O</td>
<td>3 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>93.4%/3000/4 C</td>
<td>[178]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>K⁺-intercalated MnO₂</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>77.3%/10000/10 C</td>
<td>[179]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>Cu₀.2MnO₂·0.5 H₂O</td>
<td>1 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>100.9/500/350</td>
<td>[180]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>La⁺⁻intercalated δ-MnO₂</td>
<td>1 M ZnSO₄ + 0.4 M MnSO₄</td>
<td>71%/200/800</td>
<td>[181]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>Sn₂MnO₇/SnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>92.4%/2000/2000</td>
<td>[182]</td>
</tr>
<tr>
<td>Pre-intercalation</td>
<td>maintaining crystal structure stability</td>
<td>Zn⁺⁻-intercalated MnO₂</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>69%/7000/5000</td>
<td>[183]</td>
</tr>
</tbody>
</table>

(continued on next page)
strategy for optimizing the performance and stability of manganese oxide-based cathode materials in ZIB systems. However, further research and investigation are still required to fully understand and optimize the doping effects for improved energy storage performance.

A recent study on Co-doped Mn2O4 cathode materials has garnered attention within the scientific community [148]. This research employed density functional theory calculations and X-ray absorption spectroscopy (XAS) analysis to investigate the effects of Co doping with varying valence states and lattice positions on phase transition products. The study found that Co2+-, located in the interlayer of the phase transition product δ-MnO2, acts as a structural pillar similar to pre-inserted K+. This configuration expands the layer spacing and provides structural support. On the other hand, Co4+ replaces Mn4+ within the layers, effectively improving the electrical conductivity. Additionally, the doping of Co ions, which are more stable than Mn3+4+, effectively suppresses the Jahn-Teller effect of the discharge products, preventing structural collapse and the dissolution of active materials.

In addition to metallic elements, doping with non-metallic elements has also shown potential. For instance, Zhang et al. demonstrated that N-doped N-MnOx, as a cathode material exhibits a narrower band gap, thereby enhancing electronic conductivity and enabling higher discharge capacity and improved long-term cycling stability [162]. Similarly, subsequent reports have indicated that F doping can play a similar role [59]. Furthermore, F in the lattice of MnO2 can reduce the activation energy of surface reactions, improving reversibility and activity [163]. The "peging effect" of F can also enhance framework stability and promote ion diffusion.

Notably, the doping of these exotic elements often contributes to the creation of oxygen vacancies. The synergy between the incorporation of dopant elements and these oxygen vacancies is a crucial factor in their observed effects, which will be further discussed later. These findings highlight the importance of carefully selecting doping elements to optimize the performance and stability of cathode materials for advanced energy storage applications. Future investigations can explore the intricate relationships between dopant incorporation, oxygen vacancies, and electrochemical properties to further enhance the performance of rechargeable battery systems.

### 4.2. Nanostructures

The particle size and morphology of anode materials are critical factors that influence their electrochemical performance. Nanostructured cathode materials with a larger surface area can expand the contact interface between the electrolyte and electrode, exposing more active sites and shortening the diffusion path of active ions, thus enhancing diffusion kinetics. Therefore, researchers have been focusing on developing and designing nanostructured MnO2 cathodes with suitable size and morphology. With advancements in nanotechnology, various morphologies of Mn-based oxides have been reported, including nanospheres, nanorods, nanowires, nanosheets, and nanoflowers. To address the issue of slow migration of Zn ions within the ZnMn2O4 spinel lattice due to their high valence property, Chen et al. reduced the size of ZnMn2O4 to 21 nm, preparing ultrafine nanoparticles [165]. This reduction effectively shortened the diffusion path of Zn ions and enhanced capacitive behavior, including double-layer effect and pseudocapacitive behavior occurring at and near the surface of the active material. Kim et al. successfully synthesized α-MnO2 nanorods with a diameter of approximately 7 nm and a length of about 100 nm using a facile solvent-free synthesis method (Fig. 23a) [152]. Brunauer-Emmett-Teller (BET) measurements revealed a surface area of 153 m2/g and a total pore volume of 0.45 cm3/g for α-MnO2, promoting the diffusion of Zn ions over shorter paths. At a current density of 16 mA g−1, the ZIBs based on these cathodes achieved first and second discharge capacities of 323 and 270 mAh/g, respectively (Fig. 23b). However, the controllability of particle size and dimensions of these one-dimensional nanostructured electrode materials is still limited, restricting their further development and application [79]. In recent studies, two-dimensional nanostructured Mn oxide materials have gained attention [66]. For instance, when ultrathin δ-MnO2 nanosheets with a thickness ranging from 2 to 5 nm are used as ZIB anodes, a higher specific capacity of 200 mAh/g at 100 mA g−1 and improved cycling performance (133 mAh/g retained after 100 cycles) can be achieved [70]. These findings highlight the significance of tailoring the size and morphology of nanostructured Mn-oxide cathode materials to optimize their electrochemical performance in ZIB systems. Further research is required to enhance the controllability and scalability of these nanostructures for practical application in advanced energy storage devices. By contrast, δ-MnO2 microspheres consisting of nanoflakes measuring around 50 nm in thickness and 2–6 µm in diameter display a capacity of only 180 mAh/g under identical current density conditions as the cathode. Additionally, after 100 cycles, the capacity retention is merely 87 mAh/g. The 2D ultrathin structure of the δ-MnO2 nanosheets, with a larger contact surface area for H+ and Zn2+, facilitates ion intercalation. As a result, the activation time is reduced, and the MnO2 materials with this specific crystal structure and morphology exhibit enhanced capacity and improved cycling stability.

Furthermore, when compared to bulk materials, nanostructured Mn-oxide materials possess the ability to expand and contract in response to the structural stress resulting from phase transitions during cycling. This characteristic allows them to avoid structural collapse. Consequently, new structural designs have emerged in recent years, such as porous nanostructures [116] and hollow nanostructures [92,185]. For instance, the cycling performance of MnO2 with a hollow nanosphere structure proves superior to that of nanorod structures when used as cathode material for ZIBs. This improvement can be attributed to the hollow structure’s ability to buffer the stress caused by the insertion and deinsertion processes of Zn2+ [166].

### 4.3. Composite material

Various methods have been employed to address the inherent low electrical conductivity of Mn-based oxides and to mitigate the phase transition stress during cycling [186]. One such approach involves compounding these materials with conductive substrates, including...
carbon nanotubes (CNTs) [28,86,123,167,187,188], graphene [91,165, 168,189], onion-like carbon [190], and stainless-steel welded mesh (SSWM) [191]. These conductive substrates, particularly carbon-based materials, possess larger surface areas and higher electrical conductivity, thereby facilitating ion-material contact and improving the kinetics of intercalation reactions while suppressing side reactions. Among these options, carbon nanotubes exhibit a one-dimensional tubular nanostructure and high aspect ratios. For instance, Kang et al. synthesized MnO2/a-CNT nanocomposites by depositing MnO2 nanorods onto acid-treated carbon nanotubes [167]. The unique architecture of carbon nanotubes allows for tight attachment of MnO2 and provides additional Zn2+ storage sites due to their high surface area and oxidation functional groups. Additionally, the three-dimensional conducting network formed by carbon nanotubes enhances charge transfer efficiency in MnO2 and yields excellent electrochemical performance. Graphene, characterized by superior electrical conductivity, specific surface area, and mechanical properties, has also been extensively studied in this regard. Mai et al., for instance, utilized graphene-coated α-MnO2 as the cathode material for an aqueous zinc-ion battery [168]. Compared to bare MnO2, the graphene-coated composite exhibited significant improvements in discharge capacity, long-cycle stability, and multiplicative performance. Moreover, the incorporation of nitrogen-doped conductive carbon-based composites has proven effective in enhancing electrode material conductivity. Notable examples include ZnMn2O4/N-doped graphene [165], MnO@N-doped graphene spools (MnO@NGS) [91], β-MnO2/N-doped carbon matrix (NCm) [169], Mn2O4 @N-doped carbon matrix composite nanorods (Mn2O4@NCNs) [170], and N-doped carbon-coated manganese oxide (MnO@N-C) composite fibers [94], nanorod-like polyvinylpyrrolidone-manganese dioxide (PVP-MnO2) [171]. Furthermore, the utilization of porous structural supports further increases the material’s surface area and enhances its structural stability [89,114,192].

4.4. Defective Engineering

Defect engineering has emerged as an effective approach to enhance the electrochemical performance of Mn-oxide cathode materials in ZIBs by manipulating the physicochemical properties of the electrode materials [193]. In general, the high channel structure of a host material is crucial for the insertion and extraction process of Zn2+ due to the strong electrostatic interaction between Zn2+ and the cathode material. Mn-oxides with non-tunnel structures or narrow tunnels do not facilitate the diffusion and storage of Zn2+, resulting in sluggish reaction kinetics and low activity. Introducing defect sites offers a solution by reducing electrostatic repulsion and overcoming migration and diffusion barriers, thereby greatly enhancing reaction kinetics. For instance, the perfect spinel structure ZnMn2O4 is intrinsically unsuitable as a host for Zn insertion and extraction due to high electrostatic repulsion within the lattice (Fig. 23c). However, the cation vacancy strategy effectively facilitates the migration of Zn2+ [45,172]. The use of cation-deficient spinel as the cathode material reduces the electrostatic repulsion between adjacent cations when Zn2+ pass through the unoccupied 8c sites, significantly enhancing the diffusion rate of Zn2+ within the crystal. Additionally, higher average Mn valency in ZMO with Mn defects effectively alleviates distortion and disproportionation of the Jahn-Teller structure caused by Mn3+, leading to improved structural stability. As a result, cation-deficient ZMO exhibits high specific capacity (150 mAh/g at a current density of 50 mA g−1) and excellent long-term cycling performance (94% capacity retention after 500 cycles) as a cathode material for ZIBs. Similarly, MnO, considered an inactive material, can also be modified to improve the storage activity of Zn ions through in-situ electrochemical methods that introduce Mn vacancies. Li [91] and Zhu [50] recently demonstrated that MnO, when used as an anode material in ZIBs, induces manganese defects through Mn2+ dissolution during the initial cycle (Fig. 23d). Density functional theory calculations indicate that the presence of Mn defects not only
enhances the electrical conductivity of MnO but also provides sufficient diffusion channels and storage sites for Zn$^{2+}$.

An alternative approach for defect engineering involves the introduction of anionic defects. Fang et al. investigated the influence of oxygen defects in α-MnO$_2$ and found that they not only alter the electronic structure of the material [153], reducing the energy required for electron transport and charge transfer during redox reactions, but they may also create openings in the MnO$_2$ polyhedral wall, facilitating the diffusion of H$^+$ in the ab plane (Fig. 23e). Similar conclusions were drawn for the incorporation of oxygen vacancies in β-MnO$_2$, which has a narrow tunneling space [60]. Density functional theory (DFT) calculations support these findings by illustrating that oxygen defects can lower the energy barrier for H$^+$ insertion (Fig. 23f). Furthermore, Xiong et al. further investigated the effects of oxygen vacancies on the surface properties of oxides [154]. The presence of oxygen vacancies (Vo) in the MnO$_2$ lattice effectively reduces the Gibbs free energy of Zn$^{2+}$ adsorption near the vacancies on the material surface, thereby enhancing the reversibility of the Zn$^{2+}$ adsorption/dissociation process (Fig. 23g).

### 4.5. Pre-intercalation

Interlayer engineering, aimed at enhancing the electrochemical properties of active materials, involves the pre-insertion of guest particles. These guest particles may consist of organic molecules, inorganic cations, or water molecules. The pre-inserted guest particles have several beneficial effects, such as regulating the channel space to improve ion diffusion ability and acting as pillars to enhance the structural stability of Mn-oxide materials.

Previous research has shown that tunnelled MnO$_2$ tends to undergo a phase transformation into a layered structure during initial cycling, despite the presence of pre-inserted guest particles as pillars in the tunneling space [26,109,110,173,194,195]. To address this, δ-MnO$_2$, which has a more stable and spacious layered structure, is commonly used as the host material for pre-insertion. For instance, polyaniline can be pre-inserted into the δ-MnO$_2$ layer (Fig. 24a). This strategy mitigates volume changes during cation insertion/extraction, thus preventing structural collapse and suppressing phase transitions. As a result, diffusion kinetics are improved, enabling long-term stable cycling [31].

Subsequently, extensive research has been conducted in the academic community regarding the pre-insertion of various cations, such as Na$^+$ [174–176], K$^+$ [177–179], Ca$^{2+}$ [180], Mg$^{2+}$, Ba$^{2+}$ [39], Cu$^{2+}$ [196], La$^{3+}$ [181], Sn$^{2+}$ [182], and Zn$^{2+}$ [183], into δ-MnO$_2$. Similar to the role of polyaniline, these pre-inserted cations effectively act as stress buffers during phase transitions, significantly enhancing the structural stability.

Selecting suitable pre-inserted cations also enables the regulation of the layer spacing since different cations vary in ionic radius (Fig. 24b), thus expanding the Zn$^{2+}$/H$^+$ diffusion channel and effectively improving the ionic conductivity [39]. Water molecules are often inserted into the layers alongside other exotic cations to support the crystal structure. Additionally, the polarity of water molecules assists in buffering the electrostatic repulsion between Zn$^{2+}$ and H$^+$ within the crystal structure [174,179].

For a more comprehensive understanding of the interaction mechanism between different cation pre-intercalation, Chomkhunot et al. conducted a study using three cations with varying charge densities: Al$^{3+}$, Ca$^{2+}$, and Li$^+$ [155]. The electrochemical analysis (Fig. 24c) revealed that the highly charged Al$^{3+}$ intercalator resulted in higher capacity and better cycling stability. In situ XRD measurements further supported this finding by showing a strong electrostatic interaction between Li-MnO$_2$ and Zn$^{2+}$, making it susceptible to irreversible spinel phase formation during Zn$^{2+}$ intercalation. Density functional theory (DFT) calculations (Fig. 24d) indicated that cationic intercalators with different charge densities significantly influenced the binding energy of Zn$^{2+}$ insertion into the MnO$_2$ crystal structure (Al$^{3+}$: −0.59 eV; Li$^+$: −2.49 eV; Ca$^{2+}$: −1.85 eV). Even small amounts of highly charged intercalators can reduce the binding energy between Zn$^{2+}$ and MnO$_2$, preventing irreversible phase transitions and improving the structural stability. Furthermore, Li et al. successfully demonstrated that the pre-intercalation process in δ-MnO$_2$ can be utilized to introduce various metal ions, thereby achieving precise modulation of the p-band center (cp) and H intercalation ability of O [198]. Significantly, among the metal-ion-intercalated specimens, Cu-MnO$_2$ emerged as the optimal cathode, exhibiting exceptional electrochemical performance.

### 4.6. Electrolyte additives

As a critical component of ZIBs, the design of electrolytes plays a vital role in promoting electrochemical performance [199]. In terms of the cationic intercalation mechanism, ensuring structural stability of Mn-oxide materials and suppressing phase transitions, particularly the

---

**Fig. 24.** (a) Schematic illustration of expanded intercalated structure of polyaniline (PANI)-intercalated MnO$_2$ nanolayers. (b) Schematic illustration of different cations as pillars of δ-MnO$_2$. (c) Electrochemical performance and (d) binding energy of Zn$^{2+}$ inserted in the (001) plane of MnO$_2$ crystal structures with different pre-intercalated cations.

(a) Reproduced from ref. [31] with permission (b) Reproduced from ref. [39] with permission. (c) Reproduced from ref. [155] with permission.
dissolution of Mn, are important considerations that can be addressed through appropriate electrolyte additives. For instance, the addition of Mn$^{2+}$ to the electrolyte effectively inhibits the dissolution of manganese, leading to significant improvements in cycle life (as discussed in Section 3.2.2). However, the precise mechanism behind this phenomenon remains unclear. Moreover, reducing the activity of water molecules theoretically helps slow down the dissolution of Mn. High-concentration electrolytes can alter the solvation structure of cations, which not only enhances electrode stability but also widens the electrochemical window, enabling high-voltage aqueous batteries [200,201]. However, this design approach relies on large quantities of expensive, highly soluble electrolytes, which may hamper ionic conductivity. To address these challenges, Zhang et al. replaced ZnSO$_4$ with Zn(CP$_4$SO$_3$)$_2$ as the electrolyte for ZIB systems, resulting in higher ionic conductivity [26]. The voluminous CP$_4$SO$_3$ anions help reduce the number of water molecules surrounding Zn$^{2+}$ and limit solvation, thereby facilitating the transport of Zn$^{2+}$ within the MnO$_2$ channels. More recently, Wang et al. proposed the use of chelating agents to modulate the solvation structure of multivalent metal ions [202], bypassing the energetically unfavorable de-solvation process [202]. This approach lowers the overpotential and mitigates irreversible phase transitions.

Regarding the deposition dissolution mechanism, modifying the electrolyte environment is necessary to promote the reversible conversion of Mn$^{3+}$/MnO$_2$. Qiao et al. demonstrated that the dissolution process of MnO$_2$ relies on a continual supply of protons [82]. However, using strong acid solutions can lead to severe corrosion of the zinc anode. On the other hand, weak acidic conditions can result in inadequate dissolution of MnO$_2$ due to pH fluctuations [203]. Therefore, the substitution of strong acids with weak acids, such as acetic acid, has gained attention in recent studies [124,204,205]. Acetic acid acts as a pH buffer, maintaining the electrolyte in a favorable weakly acidic environment [134]. It also facilitates the direct MnO$_2$/Mn$^{2+}$ conversion through coordination with acetate ions, improving the reversibility of the reaction [137]. In electrolyte design, careful consideration should be given to the Mn$^{3+}$ concentration. Higher concentrations of Mn$^{2+}$ inhibit the dissolution of Mn$^{2+}$ and impact the reversibility of the reaction. However, a certain Mn$^{3+}$ concentration must be maintained to achieve higher capacity. To address this challenge, Xie et al. proposed a method of controlling the Mn$^{2+}$ ion concentration using a benontite colloidal (Ben-colloid) electrolyte [184]. During discharge, the Ben-colloid electrolyte absorbs the dissolved Mn$^{2+}$ to balance negative charge fluctuations, while the Zn$^{2+}$ on the positive surface are diluted through the formation of ZHS. This maintains the Mn$^{3+}$ concentration in the electrolyte, facilitating continuous dissolution of MnO$_2$. The Ben-colloid electrolyte also helps maintain a flattened pH in the solution, potentially due to the combined effect of ZHS formation. Additionally, the introduction of strongly electronegative cations like Ni$^{2+}$ and Co$^{2+}$ promotes a more active electronic state and faster charge transfer kinetics for the deposited MnO$_2$ [125,136]. This contributes to the achievement of electrolytic MnO$_2$/Zn batteries with high area capacity.

Furthermore, electrolyte decoupling has emerged as a promising strategy to enhance the output voltage and stability of cathode and anode materials, as discussed in previous sections. However, the practical application of this strategy is hindered by the lack of ion exchange membranes that possess high ionic conductivity, low cost, and stable performance [203]. Researchers are currently addressing this challenge, and progress has been made in recent studies. In a recent report, a low-cost proton-barrier separator induced by the Hofmeister effect was developed [206]. This separator effectively blocks proton migration while allowing fast transport of Zn$^{2+}$. As a result, it enables the realization of an economical and stable MnO$_2$/Zn battery system. This innovative approach shows promise in overcoming the limitations associated with ion exchange membranes and provides a pathway for practical applications.

5. Summary

The inherent intrinsic safety, low cost, and environmental friendly characteristics make aqueous zinc ion batteries highly promising for grid-scale energy storage applications. Among various cathode materials, Mn-oxide materials with high capacity and moderate output voltage have been extensively investigated in aqueous zinc ion batteries. However, the diverse crystal structures and multiple valence states of Mn-oxide materials introduce the potential for complex phase transitions during electrochemical reactions. In earlier studies, the original material was typically considered as the primary insertion host, and the decline in performance was attributed to the dissolution of active species and the formation of inactive species during cation insertion/extraction processes. However, subsequent research revealed that the active phase during cycling often deviates from the initial phase due to structural evolution of the Mn-based oxide. This is because different electrochemical and chemical reactions interweave and compete on the Mn-based oxide cathode in aqueous zinc ion batteries. Moreover, factors such as material particle size, morphology, and testing conditions can significantly influence the evolution path and rate of these reactions. Consequently, uncovering the precise evolution pattern of Mn-oxide materials in aqueous zinc ion batteries remains a significant challenge.

This review provides an introduction to the energy storage mechanisms of aqueous Zn-ionic Mn-oxide materials and the crystalline channel types present in these materials. The electrochemical performance of Mn-oxide materials is highly dependent on the ion diffusion channels within the host material, specifically the three mechanisms of Zn$^{2+}$ insertion/deinsertion, chemical conversion reaction, and Zn$^{2+}$/H$^+$ co-insertion and deinsertion. Therefore, this paper categorizes Mn-oxide materials based on the dimension of their channel structure and briefly describes the research progress on various materials, with a particular focus on the influence of different channel structures on the electrochemical mechanism and performance. The complex phase transition process of Mn-oxide materials is a key focus of this review, and it is divided into three distinct paths: solid phase evolution, liquid phase evolution, and mixed evolution. These paths are determined by the transfer of Mn elements during the phase transition process. Layered Mn-oxide materials demonstrate relatively better performance in terms of multiplicative capability and stability during solid-phase conversion. However, the transformation to inactive phases and rapid capacity decay are still persistent challenges. On the other hand, the liquid phase evolution path, which does not rely on crystal channels and ion intercalation, exhibits higher specific capacity and discharge voltage. Electrolytic MnO$_2$/Zn batteries developed accordingly demonstrate significantly enhanced performance and hold great promise for future applications. However, such batteries require a high electrochemical environment, and researchers are actively exploring strategies for improvement. Given the sensitivity of the phase evolution process to various factors, this review also addresses electrodes, electrolytes, and working conditions as influential parameters. Additionally, several recent studies and reports on cyclic phase characteristics arising from the phase evolution are summarized. Finally, considering the existing challenges in the current research on the structural evolution of Mn-oxide materials for aqueous Zn-ion batteries, this review presents future perspectives and potential directions for further investigation in this area.

1. In-depth research on the mechanism and influencing factors of phase change

The academic community has recognized the significant impact of the phase evolution process of Mn-oxide cathode materials on battery performance, leading to extensive research in this area. However, subtle differences in reaction conditions have resulted in varying experimental results, thereby leaving the mechanism of phase evolution of Mn-oxide materials still unclear. Multiple studies have demonstrated the extreme sensitivity of the evolution process of
Mn-oxide materials to factors such as reaction rate, the chemical environment of the electrode surface, and changes in solution pH. Furthermore, the formation of by-products can obscure the actual phase transition process. Therefore, in order to thoroughly understand the phase transition mechanism, achieving stable control of multiple experimental conditions is necessary, albeit a highly challenging task at present.

2. Clarify phase transition relationships with the assistance of advanced in situ characterization techniques

Despite the application of various characterization techniques in studying the phase transition mechanism of Mn-oxide materials for Zn-ion batteries, certain methods, including X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM), still possess limitations in providing a comprehensive understanding of the mechanism. For instance, due to the intricate transformation of Mn-oxide materials, multiple reaction products with varying degrees of crystallinity and crystal structures may be present experimentally, leading to controversies in confirming the overlapping peaks of different phases using XRD. Furthermore, non-in situ characterization techniques face challenges in capturing the sensitivity of Mn-oxide materials to dynamic changes in conditions such as current and voltage, pH, and ion concentration at different charge and discharge depths. These techniques may not effectively identify intermediate reaction products and thus fail to accurately portray the real phase evolution process. Therefore, greater utilization of advanced in situ characterization techniques is indispensable to elucidate the phase transition relationships of cathode materials under diverse conditions.

3. Novel structural modification strategies

Several effective strategies have been proposed to enhance the structural stability of Mn-oxide materials, including doping, nanoengineering, and pre-insertion of ions. However, some of these strategies introduce new challenges. For instance, the incorporation of composite conductive materials may lead to a reduction in the overall energy density of the system, and there is a risk of the loss of pre-inserted ions during cycling. Moreover, since most experimental results have been obtained at low mass loads, further advancements are required to address issues related to solid-phase ion diffusion and changes in electrolyte environment at large capacity scales, particularly when aiming to achieve grid-scale energy storage.

4. Development of an electrochemical environment conducive to achieving MnO2/Mn4+ deposition dissolution

The recently emerged MnO2/Mn4+ mechanism holds great potential for achieving high capacity and high voltage in aqueous rechargeable zinc ion batteries. Various solutions have been proposed to address the challenges associated with the low electrical conductivity of MnO2 and the electrolyte deposition reaction, which is highly dependent on acidic conditions. However, there are still hurdles to overcome before commercialization can be realized. Since the highly reversible conversion of MnO2/Mn4+ is crucial for maintaining stable battery performance, further detailed discussions and studies on the possible intermediate conversion processes are necessary. This can be achieved through a combination of advanced in situ analysis and density functional calculations. Additionally, it is important to actively explore and develop the electrochemical environment that favors MnO2/Mn4+ deposition and dissolution. Electrolyte decoupling, which involves optimizing the electrolyte environment to meet the different demands of the cathode and anode, is an effective strategy. Hence, the development of low-cost, high ion transport rate, stable, and reliable proton diaphragms shows promise as an area of research.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Fundamental Research Funds for the Central Universities (Grant No. 2042023k0004), the National Key Research and Development Program of China (2022YFA1502902), the National Natural Science Foundation of China (No.22101217).

References

[20] N. Zhang, Insights on rational design and energy storage mechanism of Mn-based cathode materials towards high performance aqueous zinc-ion batteries.
18. X. Ke et al. Next Energy 2 (2024) 100095
H. Chen, S. Cai, Y. Wu, W. Wang, C.-Z. Qiao, Successive electrochemical
X. Ke et al.

L. Wang, X. Cao, L. Xu, J. Chen, J. Zheng, Transformed akhtenskite MnO₂ from

Y. Gao, H. Yang, Y. Bai, C. Wu, Mn-based oxides for aqueous rechargeable metal

F. Tang, J. Gao, Q. Ruan, X. Wu, X. Wu, T. Zhang, Z. Liu, Y. Xiang, Z. He, X. Wu,

D. Zhang, J. Gao, H. Kuang, F. Liu, Y. Wu, S. Cai, M. Xu, S.-J. Bao, A self-healing neutral

H. Chen, F. Liu, Y. Wu, S. Cai, M. Xu, S.-J. Bao, Electrochemical

J. Hwang, Electrochemical transformation reaction of Cu-InO₄ in aqueous rechargeable zinc-ion batteries, Energy Storage


A close look at electrolytic manganese dioxide (EMD) and the γ-MnO₂ & ε-MnO₂ phases using Rietveld modeling, 2004.


Y. Zhao, Y. Zuo, X. Wu, F. Lu, Y. Bai, Perspectives and challenges for manganese-based oxides for advanced aqueous zinc-ion batteries, Electroacta 259 (2018) 170-178.


pre-intercalation and revealing the ions insertion/extraction mechanisms,


