Manganese-based materials as cathode for rechargeable aqueous zinc-ion batteries

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Abstract
Rechargeable aqueous zinc-ion batteries (ZIBs) are promising candidates for advanced electrical energy storage systems owing to low cost, intrinsic safety, environmental benignity, and decent energy densities. Currently, significant research efforts are being made to develop high-performance positive electrodes for ZIBs. Nevertheless, there are still many obstacles to be overcome in pursuit of the comprehensive performance of cathode materials, including specific capacity, structural stability, rate performance, and so forth. Many manganese-based compounds have become the hotspots in the study of ZIB cathodes due to their advantages of natural abundance, less toxicity, and high operating voltage. Here, different energy storage mechanisms of various kinds of manganese-based compounds are summarized. Electrochemical results of manganese-based cathodes are compared and analyzed. Moreover, optimization strategies for addressing existing issues of these materials and improving ZIBs are discussed in detail.

KEYWORDS
cathode, manganese-based materials, mechanism, optimization strategies, zinc-ion battery

1 | INTRODUCTION

In the face of energy crisis and climate change derived from the use of traditional fossil fuel, the past decades have witnessed an ongoing revolution for advanced energy, targeting energy sources with more efficiency, higher cleanness, and better renewability.1,2 Developing energy storage systems to meet the rapid technological advances and requirements for sustainable development has become most urgent. Lithium-ion batteries (LIBs) become dominant in the current energy market of secondary batteries due to their high energy densities and maturity of manufacture.3,4 However, the rising cost of battery assembly and the intrinsic harmfulness of organic electrolytes hinder the application of LIBs in large-scale energy storage.5–7

Compared with nonaqueous secondary batteries, rechargeable batteries using aqueous solutions as electrolytes have the advantages of low cost, high safety, high ionic conductivity, and facile processing.8,9 Among many aqueous batteries, zinc-ion batteries (ZIBs) with zinc metal as anode and electrolyte-containing Zn2+ are becoming increasingly favored, owing to ample resources of zinc metal, low redox potential (−0.76 V vs. standard

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hydrogen electrode), and high theoretical specific capacity of Zn anode (820 mAh g\(^{-1}\)).\(^{10,11}\) The much higher cost-effectiveness compared with LIBs makes ZIBs highly competitive in industrial applications. Reviews covering current advances and prospects of ZIBs have sprung up in recent years. Wan et al. revealed the chemical nature of ZIBs by summarizing electrochemical reactions on the electrodes and discussed the remaining challenges facing the practical applications of ZIBs.\(^{12}\) Jia et al. comprehensively discussed the research progress and possible solutions to existing limitations of active materials for ZIB anodes and cathodes.\(^{13}\)

Generally, the overall performance of ZIBs depends on the cathode materials to a great extent.\(^{14,15}\) To date, ZIB cathode materials, mainly including manganese-based compounds, vanadium-based compounds, Prussian Blue Analogs (PBA), and organic compounds, are summarized in many reviews. For instance, Heng et al. commented on the research progress of vanadium-based cathode materials.\(^{16}\) Mathew et al. focused on manganese and vanadium oxides for ZIB cathodes and discussed their performance, mechanisms, and development.\(^{17}\) Zampardi and La Mantia\(^{18}\) presented an overview of PBA for ZIB cathodes. Among these materials, the low-cost, nontoxic manganese-based compounds are favored in the commercial application of ZIBs owing to their high capacities and high operating voltage.\(^{19–23}\) Nonetheless, the development of manganese-based cathodes still faces some critical issues, including sluggish kinetics and poor stability.\(^{24,25}\) The quest for developing manganese-based materials for ZIB cathodes has sped up during the past few years and delivered many promising results. Still, systematical reviews are needed to comprehensively summarize the development in the study of manganese-based materials for ZIB cathodes.

This article reviews in detail the crystal structures of different manganese-based compounds and different energy storage mechanisms of manganese-based ZIBs (Figure 1). Moreover, the existing issues hindering the commercialization of manganese-based ZIBs are discussed and some optimization strategies are mentioned with corresponding electrochemical performance. Also, future research directions of ZIB cathodes are proposed. By discussing these issues, this review intends to help guide the development of manganese-based materials for ZIB cathodes.

2 | MANGANESE-BASED COMPOUNDS

Different valence states and crystal structures will endow manganese-based compounds with different electrochemical behaviors and properties. In the past few

![Figure 1](overview_of_manganese-based_materials_for_zib_cathodes_zib_zinc-ion_batteries.png)
years, many manganese-based compounds have been used in the study of ZIB cathode materials. Here, various manganese-based compounds for ZIB cathodes are summarized and their crystal structures are displayed in Figure 2.

2.1 MnO₂

Due to the high redox potential and high theoretical capacity combined with low cost, MnO₂ has become a common cathode material for many sorts of batteries. Generally, the basic unit of MnO₆ octahedra can construct MnO₂ structures with different corner- and/or edges-sharing manners, resulting in different crystal types of MnO₂, which can be categorized into tunnel structures, layered structures, and three-dimensional (3D) structures. The tunnel type MnO₂ has multiple crystal forms with different tunnel sizes, including α-MnO₂, β-MnO₂, γ-MnO₂, R-MnO₂, T-MnO₂, and so forth. α-MnO₂ has become a widely studied MnO₂ cathode due to the large size of its (2 × 2) tunnel structure, which contributes to better diffusion ability for Zn²⁺ and structural stability. β-MnO₂ with (1 × 1) tunnel is unfavorable for Zn²⁺ diffusion due to its original narrow tunnel but can undergo a phase transition to layered structure and allow Zn²⁺ insertion. With a mixed (1 × 1) tunnel structure of β-MnO₂ and (1 × 2) tunnel structure of R-MnO₂, γ-MnO₂ has better diffusion capacity for Zn²⁺ than β-MnO₂. T-MnO₂ has large (3 × 3) tunnel similar to the medium-sized (2 × 2) tunnel of α-MnO₂, which can facilitate fast Zn²⁺ diffusion. Generally, MnO₂ structures with larger tunnels lead to faster Zn²⁺ diffusion. Although tunnel-type MnO₂ exhibits excellent Zn²⁺ diffusion capacity, the tunnel structure limits the zinc storage capacity of MnO₂, and phase transition during the electrochemical process usually leads to inevitable structural collapsing.

Layer-type MnO₂, that is, δ-MnO₂, has large interlayer spacing, which is conducive to the storage and transportation of Zn²⁺, making it a highly ideal MnO₂ cathode material. However, δ-MnO₂ suffers from unsatisfactory stability as an irreversible phase transition of the layered structure easily occurs during the electrochemical reaction, followed by structural collapse and manganese dissolution. Therefore, it is important to find effective methods to strengthen the layered structure of δ-MnO₂ and increase cycling stability. For instance, Liu et al. reported a 1D–3D hybrid network with interconnected δ-MnO₂ nanowires, which improves the cathode performance in multiple ways, including enhanced contact between electrode and electrolyte.

FIGURE 2 Crystallographic representation of (A) α-MnO₂, (B) β-MnO₂, (C) R-MnO₂, (D) T-MnO₂, (E) γ-MnO₂, (F) δ-MnO₂, (G) ε-MnO₂, (H) Mn₃O₅, (I) MnO, (J) Mn₃O₄, (K) K₁.₆Mn₁.₂Fe(CN)₆. Reproduced with permission. Copyright 2020, Elsevier.
increased active sites, rapid ion transport routes, and optimized layer spacing.\textsuperscript{45} 

3D-type MnO\textsubscript{2} include $\lambda$-MnO\textsubscript{2} and $\epsilon$-MnO\textsubscript{2}. As it is difficult for cations to insert the densely packed structure without tunnel or interlayer space, $\lambda$-MnO\textsubscript{2} and $\epsilon$-MnO\textsubscript{2} deliver limited zinc storage capacity. However, the dissolution/deposition mechanism opens the door to energy storage and high specific capacity for these materials.

2.2 Other manganese-based oxides

Mn\textsubscript{2}O\textsubscript{3} belongs to the orthorhombic crystal system with a basic unit of MnO\textsubscript{6} octahedron. With the insertion of Zn\textsuperscript{2+}, Mn\textsubscript{2}O\textsubscript{3} will undergo a structural phase change from the orthorhombic system to the lamellar phase, corresponding to the reduction of Mn\textsuperscript{3+} to Mn\textsuperscript{2+}, and vice versa for the charging process.\textsuperscript{46} This enables Mn\textsubscript{2}O\textsubscript{3}, whose intrinsic structure is unfavorable for Zn\textsuperscript{2+} storage, to have a good Zn\textsuperscript{2+} diffusion rate and zinc storage capacity. However, the manganese dissolution caused by structural transformation is still inevitable.

Mn\textsubscript{3}O\textsubscript{4}, which can be written as Mn(II)Mn(III)O\textsubscript{4}, is generally considered as a mixture of MnO and Mn\textsubscript{2}O\textsubscript{3}. Mn\textsubscript{3}O\textsubscript{4} presents a spinel phase where Mn\textsuperscript{3+} and Mn\textsuperscript{2+} occupy the sites of the octahedron and tetrahedron, respectively. When used as cathode in ZIB, Mn\textsubscript{3}O\textsubscript{4} converts to Mn\textsubscript{2}O\textsubscript{4} and birnessite phases during the first charge/discharge cycle, which enables the following reversible insertion/extraction of Zn\textsuperscript{2+}.\textsuperscript{47} The composite of Mn\textsubscript{3}O\textsubscript{4} and carbon material was also reported to deliver excellent performance for ZIB cathode.\textsuperscript{48,49}

MnO has a typical NaCl-type face-centered cubic crystal structure, which is theoretically unsuitable for the insertion of cations. However, the initial charge process tends to induce the formation of manganese defects in MnO, which can activate the electrochemical properties of MnO. The formation of manganese defects will provide a lower energy barrier for the migration of Zn\textsuperscript{2+}, thereby promoting the reversible insertion/extraction of Zn\textsuperscript{2+} from the MnO host.\textsuperscript{50,51}

2.3 Manganese-based PBA

PBAs are considered as an ideal host for metal ions due to their 3D open framework with abundant ion insertion sites. Although limited by relatively lower specific capacity than other ZIB cathodes, PBAs exhibit outstanding cycle life and operating voltage. Generally, PBAs can be nominally written as $A\text{M}_1\{M_2(CN)_6\}_{\gamma-y}nH_2O$, where $A$ is an alkaline cation, $M_1$ and $M_2$ nitrogen-coordinated and carbon-coordinated transition metal ion, $\gamma M_2(CN)_6$ vacancies occupied by coordinating water.\textsuperscript{18} Manganese can occupy $M_1$ or $M_2$ to form manganese-based PBA. Li et al. prepared $K_x\text{Mn}_1\text{Fe(CN)}_6$ (MnHCF) and used it as cathode material in nonaqueous ZIB, which shows almost no capacity attenuation over an extremely long duration of 6180 h.\textsuperscript{27} A reversible bi-phase transition between monoclinic and cubic phase of the cathode material during charge/discharge process was also elucidated by the authors.

3 MECHANISMS

Different from the energy storage mechanism of LIBs, the reaction mechanism of manganese-based ZIBs is far more complex and controversial. Four possible energy storage mechanisms in the charge/discharge process have been proposed for manganese-based ZIB cathodes, including Zn\textsuperscript{2+} insertion/extraction, chemical conversion reaction, $H^+/Zn^2+$ co-insertion/extraction, and dissolution/deposition reaction.

3.1 Zn\textsuperscript{2+} insertion/extraction mechanism

It can be inferred that during discharge/charge process, the ZIB cathode undergoes Zn\textsuperscript{2+} insertion/extraction in the cathode material, which is similar to other ion batteries such as LIBs. Lee et al. studied the insertion/extraction mechanism of $\alpha$-MnO\textsubscript{2} for the first time, proposing that layered Zn-birnessite is formed due to Zn\textsuperscript{2+} insertion during the discharge process, and the original tunnel structure is restored during the charge process as Mn\textsuperscript{2+} in the electrolyte disproportionated from Mn\textsuperscript{3+} can reversibly insert Zn-birnessite.\textsuperscript{52} Alfaruqi et al. observed the ZnMn\textsubscript{1.5}O\textsubscript{4} phase in the discharged electrode of $\alpha$-MnO\textsubscript{2} using in situ XRD, elucidating that Zn\textsuperscript{2+} insertion into $\alpha$-MnO\textsubscript{2} leads to the formation of ZnMn\textsubscript{2}O\textsubscript{4}, which can reversibly return to the initial $\alpha$-MnO\textsubscript{2} during the charge process (Figure 3A,B).\textsuperscript{53} The insertion/extraction mechanism of Zn\textsuperscript{2+} in $\gamma$-MnO\textsubscript{2} was also confirmed by Alfaruqi et al.\textsuperscript{59} During the discharge process, phases of ZnMn\textsubscript{1.5}O\textsubscript{4}, $\gamma$-ZnMn\textsubscript{2}O\textsubscript{4}, and $\iota$-ZnMn\textsubscript{2}O\textsubscript{4} are formed successively, which all return to the parent $\gamma$-MnO\textsubscript{2} structure in the subsequent charging process (Figure 3C). For $\delta$-MnO\textsubscript{2}, Alfaruqi et al. reported that during the initial cycles Zn\textsuperscript{2+} insertion results in the reversible formation of mixed phase of $\iota$-ZnMn\textsubscript{2}O\textsubscript{4}, spinel ZnMn\textsubscript{2}O\textsubscript{4}, and Zn-inserted phases, and the layered structure is maintained.\textsuperscript{54} However, after 50 cycles, all phases turn into irreversible spinel ZnMn\textsubscript{2}O\textsubscript{4}, leading to decay of capacity (Figure 3D). Zn\textsuperscript{2+} insertion/extraction
mechanism in other manganese-based cathode materials, such as α-Mn₂O₃ and β-MnO₂, were also found in additional research.⁴⁶,⁵⁴ For manganese-based Prussian analogs, Li et al. described a simple mechanism for Zn storage in MnHCF. When K⁺ ions, which occupies most of the tunnels in pristine MnHCF, are extracted, the material changes from monoclinic phase to cubic phase. And a reversible incomplete co-insertion/extraction of Zn²⁺ and K⁺ follows during the next cycles.²⁷

As Zn²⁺ insertion/extraction is essentially responsible for the poor kinetics and poor stability of manganese-based cathodes due to the strong electrostatic interactions between Zn²⁺ and host material and volume change during the insertion/extraction process, the study on Zn²⁺ insertion/extraction mechanism will enlighten new effective strategies to address the problems.

### 3.2 | H⁺/Zn²⁺ co-insertion/extraction

H⁺/Zn²⁺ co-insertion/extraction furthers the understanding of cation insertion/extraction mechanism for manganese-based ZIB cathodes. A schematic illustration of the H⁺/Zn²⁺ co-insertion mechanism in the discharge progress is shown in Figure 4E. During the discharge process, H⁺ first inserts MnO₂, leading to the formation of MnOOH. Subsequently, Zn²⁺ insertion makes MnOOH transform to ZnMn₂O₄. In addition, due to H⁺ insertion into MnO₂, pH of the electrolyte will rise, leading to precipitation of Zn₄(OH)₆SO₄·5H₂O on the electrode.⁵⁵ Sun et al. first proposed the H⁺/Zn²⁺ co-insertion/extraction mechanism while studying the ε-MnO₂ cathode.⁷⁶ GITT curves usually serve as typical evidence of H⁺/Zn²⁺ co-insertion/extraction. As shown in Figure 4A, two discharge plateaus are present in the GITT curve of the ε-MnO₂ electrode, while the overpotential of the second discharge platform (0.6 V) is one magnitude higher than that of the first discharge platform (0.08 V), which can be attributed to insertion of different ions. Regions I and II are assigned to the insertion of H⁺ and Zn²⁺, respectively, as the strong electrostatic interaction between the bivalent Zn²⁺ and the host lattice lead to the slow insertion of Zn²⁺. The hypothesis is further confirmed by substituting ZnSO₄ + MnSO₄ electrolyte with MnSO₄ electrolyte without ZnSO₄ as in bare MnSO₄ electrolyte, the second discharge platform disappears (Figure 4B), while the MnOOH phase occurs when the electrode is discharged to 1.3 V due to H⁺ insertion according to XRD test (Figure 4C).
A similar cation storage mechanism is also found with $\alpha$-MnO$_2$ by Gao et al.\textsuperscript{57} Calculation derived from GITT results also shows that H$^+$ insertion/extraction delivers much higher diffusion coefficients than Zn$^{2+}$, which ultimately lead to better reversibility (Figure 4D).

As a supplement to the Zn$^{2+}$ insertion/extraction mechanism, the H$^+$/Zn$^{2+}$ co-insertion/extraction mechanism explains the generation of species, including [Zn(OH)$_2$]$_2$ZnSO$_4$·5H$_2$O, MnOOH, and ZnMn$_2$O$_4$. In comparison with H$^+$, greater irreversibility is shown by Zn$^{2+}$ insertion/extraction, which leads to the capacity decay, therefore it is important to find ways to optimize its electrochemical reversibility.

### 3.3 | Conversion reaction

Pan et al. revealed the conversion reaction mechanism, which occurs between the two phases of $\alpha$-MnO$_2$ and MnOOH. In the state of discharge, MnO$_2$ and H$^+$ in water solvent react to produce MnOOH, and the exceeded OH$^-$ reacts with ZnSO$_4$ and H$_2$O to form [Zn(OH)$_2$]$_2$ZnSO$_4$·5H$_2$O.\textsuperscript{58} The reaction also exhibits reversibility as the original $\alpha$-MnO$_2$ can be restored from MnOOH during the charge process. Furthermore, it is found that the capacity of the cathode in organic electrolyte drops significantly, and is recovered when water is added. It implies that the energy storage reaction entails
the reaction of H\(^+\) and cathode material, further proving the conversion reaction.

In the conversion reaction mechanism, only H\(^+\) contributes to energy storage by inserting cathode material, while Zn\(^{2+}\) converts to a basic complex to consume OH\(^-\) and balance the charges. The mechanism reveals another important task of promoting H\(^+\) insertion/extraction for a better electrochemical performance of the cathode.

### 3.4 Dissolution/deposition reaction

The dissolution/deposition reaction mechanism breaks through the conventional opinion that ion insertion/extraction in a stable crystal structure is indispensable for energy storage in ZIBs. By studying the charge/discharge process of \(\alpha\)-MnO\(_2\), Lee et al. found that after the discharge process, Zn\(^{2+}\) is mainly deposited on the surface of the cathode in form of Zn\(_4\)(OH)\(_6\)SO\(_4\)·5H\(_2\)O (ZHS), rather than intercalated in the tunnels of the \(\alpha\)-MnO\(_2\) cathode.\(^{59}\) During the discharge process, MnO\(_2\) is electrochemically reduced to Mn\(^{3+}\). The unstable Mn\(^{3+}\) undergoes disproportionation to generate Mn\(^{2+}\), which dissolves into the aqueous solution. The MnO\(_2\) dissolution can be described with the following reaction

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

According to the reaction, the pH value of the electrolyte will increase with the dissolution of manganese, which leads to the precipitation of ZHS on the cathode.

\[
\text{Zn}^{2+} + 6\text{OH}^- + 5\text{H}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{Zn}_4(\text{OH})_6\text{SO}_4\cdot5\text{H}_2\text{O}.
\]

With the combination of the two reactions, the cathode reaction during the discharge process can thus be described as follows:

\[
\text{MnO}_2 + 8\text{Zn}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{Mn}^{2+} + 2\text{Zn}_4(\text{OH})_6\text{SO}_4\cdot5\text{H}_2\text{O}.
\]

During the charge process, Mn\(^{2+}\) is deposited on the electrode to restore MnO\(_2\) and ZHS dissolves in the electrolyte, which reflexes good reversibility.

Guo et al. put forward a new point of view that energy storage of MnO\(_2\)-ZIB is a hybrid mechanism, which is dominated by dissolution/deposition mechanism and accompanied with cation insertion/extraction.\(^{60}\) Figures 5D,E illustrate the complete scheme of dissolution/deposition reaction mechanism during the charge/discharge process.

In the first discharge process of \(\alpha\)-MnO\(_2\) or \(\delta\)-MnO\(_2\) cathode, MnO\(_2\) reacts with water to form Mn\(^{2+}\) and OH\(^-\), and the surrounding ZnSO\(_4\) reacts with the generated OH\(^-\) immediately to form ZHS, which can be confirmed by XRD tests (Figure 5A–C). The lack of active water inhibits the continuing dissolution of MnO\(_2\), resulting in the decrease of Mn\(^{2+}\) content in the electrolyte. In the subsequent charge process, ZHS reacts with Mn\(^{2+}\) to produce birnessite-MnO\(_2\). A similar dissolution/deposition mechanism reappears in the subsequent cycles, where birnessite-MnO\(_2\) becomes host material instead of the original MnO\(_2\). Meanwhile, cation also inserts MnO\(_2\) to exhibit the H\(^+\)/Zn\(^{2+}\) co-insertion/extraction mechanism. The deposition/dissolution mechanism dominates the entire energy storage process and contributes most of the specific capacity, while cation insertion/extraction is insignificant as H\(^+\)/Zn\(^{2+}\) can only insert into the remaining undissolved MnO\(_2\).

Dissolution/deposition mechanism and its hybrid with other mechanisms complicate the mechanism study of manganese-based cathodes, but at the same time reveal the possibility for energy storage of cathode materials with unsatisfactory structures unconducive to ion insertion.

### 4 OPTIMIZATION STRATEGIES

As one of the most promising cathode materials for ZIBs, most manganese-based materials still fall short of satisfactory electrochemical performance, especially rate performance and cycle stability, due to poor conductivity, poor structural stability and sluggish Zn\(^{2+}\) diffusion, and so forth. To address these issues, researchers have proposed various corresponding optimization strategies for manganese-based materials. The electrochemical performance of the cathode with different optimization strategies are summarized in Table 1.

#### 4.1 Crystal lattice modulation

The crystal structure of the cathode material can be modulated by ion intercalation, defect construction and pillar effect, thus improving the electrode performance, including conductivity, ion diffusion rate, structural stability, and capacity.

##### 4.1.1 Ionic intercalation

Generally speaking, the doping of cations (such as V,\(^{76}\) K,\(^{77}\) Ce,\(^{78}\) Na,\(^{79}\) Ni,\(^{62}\) and Al\(^{61}\)) into the lattice of manganese-based oxides will lead to lattice expansion
due to the larger diameter of these cations than Mn$^{4+}$, which will directly promote the diffusion rate of zinc ions in the lattice. Meanwhile, the presence of heteroatoms will further enhance the electrochemical activity of the cathode material. For example, Chen et al. reported Al-intercalation engineering of MnO$_2$ cathode that delivers high capacity and ultra-long cycle life. The study of the cathode structure shows that the Al-intercalation leads to the formation of strong Al–O bonds in the tunnel-type MnO$_2$ framework (Figure 6A). This structure mitigates Mn dissolution and facilitates Zn$^{2+}$ storage properties. Zhang et al. prepared Ni-doped Mn$_2$O$_3$ with an NiMn-layered double hydroxide. The intercalation of Ni$^{2+}$ increases the conductivity, improves the reaction kinetics of the cathode and greatly increases the capacity of the Mn$_2$O$_3$ cathode. Meanwhile, the intercalation of Ni can reduce the formation energy of Mn$_2$O$_3$ (Figure 6B), which effectively stabilizes the Mn-O bond of Mn$_2$O$_3$ and inhibits the dissolution of manganese.

Recently, the doping of fluorine anions into MnO$_2$ has also been investigated. On the one hand, the high electronegativity of fluorine can promote the diffusion of zinc ions and stabilize the cathode framework. On the other hand, fluorine has a significant “pegging effect” in the manganese dioxide lattice, which can ensure the reversible electrochemical behavior during charge and discharge (Figure 6C), thus greatly improving the cycle life and energy efficiency of the battery.

Besides, the performance of manganese-based PBAs can also be improved by doping heteroatoms. According to the study of Lou, Co doping into manganese-rich PBA hollow spheres effectively stabilized the crystal structure and improved the cycle life of CoMn-PBA hollow spheres.

### 4.1.2 Defect construction

According to the difference of defective elements, defects can be divided into oxygen vacancies ($V_O$) and cationic vacancies. Among them, $V_O$ occupies an important position in regulating the surface chemistry and geometry of oxides.
Density functional theory (DFT) calculations show that the MnO$_2$ lattice near V$_{O}$ exhibits high reversibility for Zn$^{2+}$ adsorption/desorption. In contrast, for pure MnO$_2$, once Zn is adsorbed onto the MnO$_2$ surface, the strong chemical bond between Zn and O will hinder the subsequent Zn$^{2+}$ desorption process. These inserted Zn$^{2+}$ eventually act as a physical barrier and reduce the effective electrochemically active surface area of MnO$_2$ (Figure 7A). Ding et al. synthesized β-MnO$_2$ wrapped by graphene oxide (GO) with abundant oxygen vacancies. The oxygen vacancies accelerate the reaction kinetics and the graphene oxide inhibits Mn$^{2+}$ dissolution. The synergistic effect of the two results in a high-rate and long-life cathode.

Cation vacancies can also be introduced in manganese-based cathodes (Figure 7B). For perfect spinel ZnMn$_2$O$_4$, Zn$^{2+}$ is subject to great electrostatic repulsion from adjacent Mn cations during migration, which leads to slow Zn$^{2+}$ diffusion (Figure 7C). Zhang et al. introduced Mn vacancies into ZnMn$_2$O$_4$ by a two steps method of NH$_3$–H$_2$O–assisted oxidation precipitation and spinel crystallization. The abundant Mn vacancies lowered the electrostatic potential barrier, accelerated the Zn$^{2+}$ diffusion, and enhanced the electrode reaction kinetics.

4.1.3 | Pillar effect

In response to the problem of lattice collapse and poor cycling performance of manganese-based cathodes, some researchers have proposed the introduction of guest molecules as “pillars” between crystal layers, which can help stabilize the host structure during the cycling process.

Nam et al. reported a layered manganese oxide containing a high content of crystalline water. The crystalline water is inserted into the crystal interlayer, which effectively shields the electrostatic interaction between Zn$^{2+}$ ions and the MnO$_2$ skeleton and promotes Zn$^{2+}$ diffusion. Meanwhile, after Zn$^{2+}$ is intercalated in the interlayer, it will be coordinated with water and subsequently form a Zn–Mn dumbbell structure to maintain the stability of the main skeleton structure (Figure 7D). Due to the pillars effect of the crystalline water, the material exhibits high reversible capacity as well as good cycling and rate performance.

Conductive polymers can also play the role of “pillars.” Intercalation of polyaniline (PANI) between the layers of δ-MnO$_2$ can effectively eliminate the phase transition and subsequent structural collapse caused by ion insertion/extraction.

4.2 | Surface modification

Surface modification is a common method for material protection. Carbon materials such as graphene and CNT are widely used to coat the manganese-based cathode. For instance, graphene scrolls are uniformly coated on

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**Table 1** Electrochemical performance of manganese cathode with different optimization strategies

| Materials          | Specific capacity (mAh g$^{-1}$) | Area capacity (mAh cm$^{-2}$) | Circle number | Capacity retention (%) | References |
|--------------------|----------------------------------|-------------------------------|---------------|------------------------|------------|
| AMO                | 401.7                            | 2000                          | 94.5          | 61                     |
| NM                 | 252                              | 2500                          | 85.6          | 62                     |
| F-MnO$_2$          | 300                              | 1200                          | ~70           | 63                     |
| CoMn-PBA           | 128.6                            | 1000                          | 76.4          | 64                     |
| Od-MnO$_2$         | 345                              | 2000                          | 84            | 65                     |
| β-MnO$_2$@GO       | 278.2                            | 2000                          | 77.6          | 66                     |
| ZMO/C              | 150                              | 500                           | 94            | 67                     |
| cw-MnO$_2$         | 350                              | 200                           | 75.3          | 68                     |
| PANI-MnO$_2$       | 280                              | 5000                          | ~90           | 69                     |
| MGS                | 382.2                            | 3000                          | 94            | 70                     |
| MnO$_2$/rGO/PANI   | 241.1                            | 600                           | 82.7          | 71                     |
| MnO$_2$@Ni-C       | 305                              | 1600                          | 100           | 72                     |
| MnO$_2$(H$^+$)     | 2                                | 2000                          | 92            | 73                     |
| MnO$_2$(AC$^-$)    | 1                                | 4000                          | 100           | 74                     |
| MnO$_2$(AC$^-$+I$^-$) | 18                                | 400                           | 80            | 75                     |
MnO$_2$ nanowires with an average width of 5 nm by rolling coating (Figure 8A,B), which improves the conductivity of the MnO$_2$ nanowires and mitigates the dissolution of the cathode material. In addition, conductive polymers can also be used as modified coatings. Improved rate performance and cycle stability are also achieved with MnO$_2$ coated with rGO and PANI.

4.3 | Activation of deposition/dissolution mechanisms

Since the capacity decay of manganese-based cathode is mainly due to lattice collapse and Mn dissolution, some researchers propose to completely activate the mechanism of deposition/dissolution reaction of MnO$_2$ resorting to the design of electrolyte and regulation of charge/discharge intervals. The avail of dissolution/deposition reaction
completely avoids the problem of structural collapse compared with ion insertion/extraction mechanism, thus solving the problem of capacity decay from the root.

Chao et al. activated the deposition-dissolution conversion of the manganese-based cathode by using an acidic electrolyte at high voltage (1.95 V) (Figure 9A).73 During the charge process, Zn\(^{2+}\) is deposited on the graphite foam, and Mn\(^{2+}\) is deposited on carbon fiber cloth to form MnO\(_2\). During the discharge process, Zn and MnO\(_2\) are dissolved in the electrolyte, and the whole process is completely reversible. Such a two-electron process doubles the theoretical capacity of the manganese-based cathode while achieving high area capacity and long cycle life.

However, oxygen evolution reaction and hydrogen evolution reaction are difficult to avoid at high voltages and acidic environments, which will cause the loss of electrolyte and coulombic efficiency. Therefore, Xie et al. proposed to reduce the redox potential of Mn\(^{2+}/\text{MnO}_2\) by 530 mV resorting to the coordination effect of acetate (Figure 9C), thus achieving the two-electron reaction process of Mn\(^{2+}/\text{MnO}_2\) at a relatively low voltage (1.55 V) with a neutral electrolyte.81 This strategy effectively avoids the problem of zinc dendrite while contributing to high capacity, high reversibility, and excellent stability with low cost.

Based on this strategy, Zeng et al. constructed a high-load, long-cycle swagelok-type Zn/MnO\(_2\) cell with a
stable lifetime of 1000 cycles at the area capacity of 1 mA h cm$^{-2}$ (Figure 9D).74 After that, Lei et al. introduced iodide ions as redox mediators into this system to promote the dissolution of MnO$_2$ (Figure 9B) and further increase the area capacity to 18 mA h cm$^{-2}$.75

5 | SUMMARY AND OUTLOOK

In conclusion, ZIBs have become a promising candidate for the next generation of energy storage systems beyond LIBs owing to their high safety, low cost, and environmental friendliness. This review includes the research for manganese-based ZIB cathode materials by describing several kinds of common manganese-based compounds for ZIB cathodes, possible working mechanisms of manganese-based ZIBs and various optimization strategies to improve their electrochemical performance. Nevertheless, there is still a long way ahead for the study of manganese-based ZIBs until the realization of their practical applications and commercialization. Thereby, we propose some perspectives on the directions for the future research of manganese-based ZIBs.

Regarding the study of energy storage mechanisms of manganese-based ZIBs, the novel dissolution/deposition reaction mechanism is worth more in-depth study as it can stimulate the energy storage potential for many new manganese-based materials for ZIB cathodes. In the H$^+$/Zn$^{2+}$ co-insertion/extraction mechanism, due to the small ionic radius and monovalence of H$^+$, the cathode delivers better kinetic performance compared with single Zn$^{2+}$ insertion. Therefore, increasing the contribution of H$^+$ insertion could be a possible approach toward improved rate performance and coulombic efficiency of manganese-based ZIBs.

Meanwhile, the current optimization strategies for manganese-based cathodes are still limited. On the one hand, the experimental attempts are far from comprehensive. For instance, the lattice modulation by anion intercalation is still limited to fluorine, which is still in the primary stage. On the other hand, the cathode materials should not be limited to manganese-based oxides. Examining the properties of other manganese-based compounds (e.g., carbides, nitrides, sulfides, etc.) may lead to new progress. Besides, the barrier for the performance of manganese-based cathodes is not only attributed to the cathode but also relates to various aspects, such as electrolyte, separator, and anode design. Problems should be considered from a whole battery level to realize the applications of...
manganese-based cathodes. However, research containing the design of a whole ZIB is still scarce and calls for more effort.

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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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