Review

Design of manganese dioxide for supercapacitors and zinc-ion batteries: similarities and differences

Henghan Dai1,4, Ruicong Zhou1,4, Zhao Zhang2,4, Jinyuan Zhou3,*, Gengzhi Sun1,∗

1School of Flexible Electronics (Future Technologies), Nanjing Technology University, Nanjing 211816, Jiangsu, China.
2College of Intelligent Science and Control Engineering, Jinling Institute of Technology, Nanjing 211169, Jiangsu, China.
3School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, Gansu, China.
4Authors contributed equally.

Correspondence to: Prof./Dr. Jinyuan Zhou, School of Physical Science and Technology, Lanzhou University, 222 Tianshui South Road, Lanzhou 730000, Gansu, China. E-mail: zhoujy@lzu.edu.cn; Prof./Dr. Gengzhi Sun, School of Flexible Electronics (Future Technologies), Nanjing Technology University, 5 Xin Mofan Road, Nanjing 211816, Jiangsu, China. E-mail: iamgzsun@njtech.edu.cn


Received: 22 Sep 2022 First Decision: 26 Oct 2022 Revised: 16 Nov 2022 Accepted: 29 Nov 2022 Published: 12 Dec 2022

Academic Editors: Yuping Wu, Bin Wang Copy Editor: Ke-Cui Yang Production Editor: Ke-Cui Yang

Abstract

Energy storage devices, e.g., supercapacitors (SCs) and zinc-ion batteries (ZIBs), based on aqueous electrolytes, have the advantages of rapid ion diffusion, environmental benignness, high safety and low cost. Generally, SCs provide excellent power density with the capability of fast charge/discharge, while ZIBs offer high energy density by storing more charge per unit weight/volume. Although the charge storage mechanisms are considered different, manganese dioxide (MnO₂) has proven to be an appropriate electrode material for both SCs and ZIBs because of its unique characteristics, including polymorphic forms, tunable structures and designable morphologies. Herein, the design of MnO₂-based materials for SCs and ZIBs is comprehensively reviewed. In particular, we compare the similarities and differences in utilizing MnO₂-based materials as active materials for SCs and ZIBs by highlighting their corresponding charge storage mechanisms. We then introduce a few commonly adopted strategies for tuning the physicochemical properties of MnO₂ and their specific merits. Finally, we discuss the future perspectives of MnO₂ for SC and ZIB applications regarding the investigation of charge storage mechanisms, materials design and the enhancement of electrochemical performance.

Keywords: Aqueous energy storage devices, manganese dioxide, zinc-ion batteries, supercapacitors, mechanisms
INTRODUCTION

In recent decades, electrochemical energy storage devices have been widely applied as power systems for a variety of applications ranging from portable electronics and electric vehicles to smart electric grids\(^{1-5}\). Due to their advantages of high energy density and long cycling lifespan without a memory effect, lithium-ion batteries (LIBs) are the most successful products, with the 2019 Nobel Prize in Chemistry awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino\(^{6-13}\). However, safety issues, such as fires and explosions, are always major concerns regarding the utilization of LIBs since their lithium salt-containing organic electrolytes are highly flammable\(^{12-13}\). To address this issue, one viable strategy is to develop aqueous-based devices, which are considered as promising alternatives due to their high safety and low cost\(^{16-22}\).

Presently, two types of aqueous-based devices, namely, supercapacitors (SCs) and zinc-ion batteries (ZIBs), as schematically illustrated in Figure 1A and B, have attracted tremendous attention owing to their unique features\(^{20,23-29}\). Typically, SCs exhibit ultralong cyclic stability, fast charge/discharge rates and high power density, thus explaining their broad applications in urban public transportation, aerospace, the military, and so on\(^{30-35}\). The charges are stored in SC materials based on two mechanisms: (1) adsorption/desorption of electrolyte ions on the electrode surface, excluding any redox reactions (electrochemical double-layer capacitance, EDLC); and (2) fast and reversible redox reactions on the electrode materials (pseudocapacitance). In contrast, ZIBs are considered promising candidates for grid-scale safe energy storage due to their low redox potential (-0.76 V vs. NHE), high theoretical capacity (820 mAh g\(^{-1}\)) due to the metal Zn anode, intrinsic nonflammability, non-toxicity and high ionic conductivity of the aqueous electrolytes and low cost\(^{34-36}\).

In contrast to SCs, electrolyte ions (Zn\(^{2+}\)) are inserted and extracted from the electrode materials, usually accompanied with phase transitions. Undoubtedly, the performance of both devices severely relies on their electrode materials\(^{36-41}\). Based on the statistics summarized in Figure 1C and D, it is very interesting to find that the commonly used electrode materials for SCs, including nanocarbon, conducting polymers, transition metal oxides (RuO\(_2\) and MnO\(_2\)), transition metal dichalcogenides (TMDs) and transition metal carbides/nitrides (MXenes), are also suitable for ZIBs. Among these materials, the most studied one is manganese dioxide (MnO\(_2\)) because of its natural abundance, non-toxicity, wide potential window and high theoretical capacitance/capacity\(^{42-47}\). For example, \(\alpha\)-MnO\(_2\) nanoneedles synthesized by a microwave-assisted method were used as SC materials and delivered 289 F g\(^{-1}\) at 0.5 A g\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) and maintained 88% after cycling 10,000 times\(^{48}\). A \(\beta\)-MnO\(_2\)-based cathode for ZIBs showed a capacity of 200 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) after full electrochemical activation\(^{49}\). However, when utilized as electrode materials for SCs and ZIBs, MnO\(_2\) typically faces similar problems, including high electrical resistance, cycling instability, slow electrode kinetics, and so on. Moreover, the charge storage mechanisms of MnO\(_2\) in SCs and ZIBs are still under debate. In particular, based on the literature, complicated processes are involved when MnO\(_2\) is applied in ZIBs, whereas pseudocapacitive behavior is understood in SCs. Although several articles have been published summarizing the applications of MnO\(_2\) either in SCs or ZIBs, a comprehensive and comparative review to elucidate the similarity and difference in materials design for both devices is essential\(^{50-53}\). Herein, we focus on the recent advances in the design and utilization of MnO\(_2\) in aqueous-based SCs and ZIBs. In particular, we describe the respective charge storage mechanisms, highlight the materials design principles and provide a direct comparison and perspectives for future endeavors regarding MnO\(_2\)-based SCs and ZIBs.

CRYSTAL STRUCTURE

The commonly utilized MnO\(_2\) polymorphs in SCs and ZIBs can be classified into \(\alpha\)-MnO\(_2\), \(\beta\)-MnO\(_2\),
δ-MnO₂, γ-MnO₂ and amorphous MnO₂ [Figure 2] by arranging the MnO₆ octahedral units either via edge-sharing, corner-sharing or a combination of two[26]. In particular, in α-MnO₂ [Figure 2A], MnO₆ octahedral double chains are connected in a corner-sharing manner to form 2 × 2 tunnels (4.6 × 4.6 Å). In β-MnO₂ [Figure 2B], single chains assembled by MnO₆ octahedra are interlinked in a corner-sharing manner to form 1 × 1 tunnels (2.3 × 2.3 Å). In γ-MnO₂, both 1 × 1 and 1 × 2 tunnels coexist and distribute randomly [Figure 2C]. Alternatively, in δ-MnO₂, two-dimensional (2D) sheets are built by sharing MnO₆ octahedral edges [Figure 2D] and then stacked into laminar structures with an interlayer spacing of ~7 Å[23]. It is known that the intercalated cations or water molecules between the sheets play a critical role in stabilizing the layered structure[54]. In comparison, amorphous MnO₂ possesses a highly disordered structure [Figure 2E] with higher strength, lower hardness, larger surface area and even superior structural stability[55,56].

SUPERCAPACITORS
Charge storage mechanisms
MnO₂ is considered a pseudocapacitive material[57]. Traditionally, it is believed that the capacitance of MnO₂ originates from surface redox reactions with a theoretical value of ~110 μF cm⁻² based on a

Figure 1. Schematic illustrations of (A) SC and (B) ZIB devices. (C) publication numbers of different materials, including MXenes, TMDs, carbon, polymers and TMOs (MnO₂ and RuO₂), for SCs in the period from 2011 to 2022. (D) publication numbers of different cathode materials, such as TMOs (VOₓ and MnO₂), PBAs, polymers and other materials (including carbonaceous materials, TMDs and MXenes), for ZIBs in the period from 2013 to 2022. All data were obtained from the Web of Science. EDLC: electrochemical double-layer capacitance; SCs: supercapacitors; ZIBs: zinc-ion batteries.
Figure 2. Crystal structures of (A) α-, (B) β-, (C) γ-, (D) δ- and (E) amorphous MnO₂. Reproduced with permission[26]. Copyright 2019, Royal Society of Chemistry.

Brunauer-Emmett-Teller surface (10 to 180 m² g⁻¹)[58]. Nevertheless, a much higher capacitance (over 300 F g⁻¹) was obtained experimentally in a neutral electrolyte, suggesting extra contributions from other electrochemical mechanisms beyond the surface redox reactions[59]. Zhang et al. confirmed the capacitance from the insertion/extraction of Na⁺ in δ-MnO₂ by assembling a sodium-ion capacitor [Figure 3A][60]. The interlayer spacing of layered δ-MnO₂ was expanded to ~7 Å after activation during the first discharge. Moreover, the contribution of diffusion-controlled capacitance was determined to be as high as 64.4% of the total charge storage at 0.1 mV s⁻¹ (0-1.2 V vs. SCE), indicating that the dominant charge storage depends on Na⁺ insertion/extraction. In another work, Chen et al. investigated the charge storage mechanism of Zn₂⁺ pre-intercalated α-MnO₂ (ZnₓMnO₂) nanowires in a blended aqueous electrolyte (2 M ZnSO₄ and 0.4 M MnSO₄)[61]. Ex-situ Inductive Coupled Plasma (ICP) analysis showed that the Zn/Mn molar ratio in ZnₓMnO₂ varied from 0.029 to 0.596 during the first three discharge processes, corresponding to the reversible insertion/extraction of Zn₂⁺ [Figure 3B]. The reaction mechanism follows Equation (1):

\[
\text{Zn}_x\text{MnO}_2 - 2(x-y)e^- \leftrightarrow \text{Zn}_y\text{MnO}_2 + (x-y)\text{Zn}^{2+}
\]  

(1)

The electrochemical behavior of MnO₂ is found to be heavily dependent on the pH of the electrolyte [Figure 3C][62,63]. In a neutral electrolyte, the generated Mn³⁺ ions involve a slow process of disproportionation following Equation (2), leading to Mn²⁺ loss and continuous capacity decay[64,65]. Furthermore, MnO₂ structures experience volume expansion, thereby loosening the electrical contacts between MnO₂ particles, increasing the series resistance and lowering the capacitance over time[66,67]. These issues compromise the power density and cycle life of MnO₂ directly[62,63]. In an acidic electrolyte, except for the redox reaction between H⁺ and MnO₂, excessive H⁺ induces the further reduction of MnOOH to Mn²⁺, leading to the irreversible dissolution of MnO₂. Equations (3) and (4)[63]. In an alkaline electrolyte, hydroxyl ions (OH⁻) react with MnO₂ at the surface, generating a layer of insulative Mn(OH)₂, which prevents the inner active materials from being exposed to the electrolyte ions. The overall electrochemical reactions in an alkaline electrolyte follow Equations (5)-(9) with a narrow voltage window of < 0.7 V[69].
Figure 3. (A) Intercalation/deintercalation of Na$^+$ using NaClO$_4$ as the electrolyte. Reproduced with permission[60]. Copyright 2018, Elsevier. (B) Charge storage mechanism of α-MnO$_2$-based SC using ZnSO$_4$ and MnSO$_4$ as the electrolyte. Reproduced with permission[61]. Copyright 2020, Wiley-VCH. (C) Redox reactions of MnO$_2$ in acidic, neutral and alkaline electrolytes, respectively. Reproduced with permission[63]. Copyright 2019, Elsevier.

In a neutral electrolyte:

\[ 2\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+} + \text{Mn}^{2+} \text{(aq)} \quad (2) \]

In an acidic electrolyte:

\[ \text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnOOH} \quad (3) \]

\[ \text{MnOOH} + 3\text{H}^+ + e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (4) \]

In an alkaline electrolyte:

\[ \text{MnO}_2 + \text{H}_2\text{O} + e^- \rightarrow \text{MnOOH} + \text{OH}^- \quad (5) \]

\[ \text{MnOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Mn(OH)}_2 + \text{OH}^- \quad (6) \]

\[ 3\text{Mn(OH)}_2 \leftrightarrow \text{Mn}_3\text{O}_4·2\text{H}_2\text{O} + 2\text{H}^+ + 2e^- \quad (7) \]

\[ \text{Mn}_3\text{O}_4·2\text{H}_2\text{O} + \text{OH}^- \leftrightarrow 2\text{MnOOH} + \text{Mn(OH)}_3 + e^- \quad (8) \]
4MnOOH + 2Mn(OH)₃ + 6OH⁻ ↔ 6MnO₂·5H₂O + 3H₂O + 6e⁻ (9)

Overall, two main charge storage mechanisms are involved for MnO₂ when adopted in aqueous SCs: (i) surface redox reactions Equation (10); and (ii) intercalation/deintercalation of cations Equation (11):

(MnO₂)_{surface} + M⁺ + e⁻ ↔ (MnOOM)_{surface} (10)

(MnO₂)_{bulk} + M⁺ + e⁻ ↔ (MnOOM)_{bulk} (11)

Performance enhancements

Nanostructure design

Enhancing the ion diffusion kinetics via nanostructural design is considered a feasible method to improve the capacitance of MnO₂ [70-77]. Xiong et al. prepared interlayer expanded MnO₂ (0.93 nm) with intercalated tetramethylammonium ions (TMA⁺), following a two-step cation exchange [Figure 4A] [78]. Density functional theory (DFT) calculations suggested that the expanded interlayer can weaken the interactions between the negatively charged MnO₂ and K⁺ due to the decreased diffusion energy barrier, thereby accelerating ion diffusion during charge/discharge. A specific capacitance of 160 F g⁻¹ was obtained for the restacked MnO₂ in aqueous K₂SO₄ electrolytes at 0.2 A g⁻¹, while at 10 A g⁻¹, 70% capacitance was retained (110 F g⁻¹). In contrast, in the cases of K- and H-MnO₂ nanobelts, only 50% and 55% capacitance retentions were obtained, respectively, as the current density increased from 0.2 to 10 A g⁻¹ [Figure 4B]. Moreover, the long-term cycling performance of the restacked MnO₂ nanosheets was evaluated at 5 A g⁻¹ for 5000 cycles with 100% retention.

Foreign ion/molecular pre-insertion

Since the charge storage capacity of MnO₂ can be enhanced by the Mn⁴⁺/Mn³⁺ redox pair with cation adsorption (or intercalation) [79-81], it is speculated that the pre-insertion of cations in MnO₂ could improve the specific capacitance by enhancing ion diffusion [81-83]. Following this guidance, Jabeen et al. prepared birnessite Na₀.₅MnO₂ arrays on a carbon cloth by the electrochemical conversion of Mn₃O₄ in 10 M Na₂SO₄ via cyclic scanning at 10 mV s⁻¹ within the potential window of 0 and 1.3 V (vs. Ag/AgCl) for 500 cycles [Figure 4C] [84]. The incorporation of Na⁺ not only upgraded the specific capacitance but also widened the workable potential window to 1.3 V. The redox reaction of the Mn³⁺/Mn⁴⁺ couple was verified by ex-situ X-ray photoelectron spectroscopy, while the newly emerged peaks at 0.96 V were attributed to the insertion and extraction of residual Na⁺. The obtained Na₀.₅MnO₂ electrode showed an obviously improved capacitance of 366 F g⁻¹ without compromising its cycling stability [Figure 4D]. Asymmetric SCs were constructed using Na₀.₅MnO₂ and Fe₃O₄ as the cathode and anode, respectively. The asymmetric SC using 1 M Na₂SO₄ as the electrolyte exhibited a cell voltage of 2.6 V, a capacitance of 88 F g⁻¹ and an energy density of 81 Wh kg⁻¹.

Defect engineering

In addition to ion diffusion, the high electrical resistance of MnO₂ needs to be lowered to achieve rapid electron transport during the redox reactions [85-87]. Defect engineering (heteroatom doping and the introduction of oxygen vacancies) has been demonstrated to be an effective strategy for improving the conductivity of MnO₂ [88-96]. Kang et al. designed a thick Au-doped MnO₂ film (1.35 μm) by electrochemically depositing MnO₂ and sputtering Au alternately to adjust the electronic structure of MnO₂ [Figure 5A] [97]. Au atoms distributed in the lattice of MnO₂ with a total doping level of 9.9 at.% act as electron donors to induce a new state in the bandgap (~1.0 eV), thereby enhancing the overall conductivity, which is beneficial to the kinetics of the electrode reaction [Figure 5B]. As shown in Figure 5C, the specific capacitance of the
Au-doped MnO$_2$ is much higher than that of pristine MnO$_2$ (2.5 eV). With increasing Au-doping level, the specific capacitance first increases and then decreases slightly. As a result, the Au-doped MnO$_2$ film achieved a gravimetric capacitance ($C_g$) as high as 626 F g$^{-1}$ tested in 2 M Li$_2$SO$_4$ at 5 mV s$^{-1}$ and superior stability over 15000 charge/discharge cycles [Figure 5D]. In addition, substituting Mn with heterogeneous atoms (such as Co, Ni, Al, Fe, Ag and Au) in MnO$_2$ tends to change the electronic structure of MnO$_2$ via electron donation. For example, Wang et al. synthesized a series of interlinked Fe-doped MnO$_2$ nanostructures via a hydrothermal method[98]. It was confirmed that the incorporation of Fe atoms effectively prevented the collapse of MnO$_2$ crystals during protonation, thereby prolonging the service life of the device. The optimized sample with a mass loading of ~5 mg cm$^{-2}$ exhibited a specific capacitance of 267.0 F g$^{-1}$ at 0.1 A g$^{-1}$ with 68.6% retention at 1 A g$^{-1}$ and excellent cycling stability over 2000 cycles at 2 A g$^{-1}$ (~100% retention).

Alternatively, Peng et al. hydrothermally built an oxygen vacancy-rich MnO$_{2-x}$/reduced graphene oxide (rGO) composite in tetrahydrofuran using manganese carbonyl (Mn(CO)$_5$) and GO as the precursors[99]. Benefiting from the good electronic conduction in the interconnected rGO networks and high redox activity of the partially reduced MnO$_2$ nanoparticles, the vacancy-rich MnO$_{2-x}$/rGO film showed a high specific capacitance of 675.5 F g$^{-1}$ (0.5 A g$^{-1}$) in a 0.5 mol L$^{-1}$ Na$_2$SO$_4$ solution and retained 96.1% of the capacitance after 10,000 cycles. Amorphous MnO$_2$ with abundant vacancies and ion transport channels has also been considered as a promising electrode material for SCs. As a typical work, Shi et al. fabricated hybrid fiber electrodes by anchoring amorphous MnO$_2$ on well-aligned multiwall carbon nanotube (MWCNT) sheets, followed by twisting [Figure 5E][100]. The MWCNT sheets, which were drawn from a spinnable array, showed excellent electron conductivity that facilitated the redox reaction of amorphous MnO$_2$. The direct
Figure 5. (A) Fabrication and (B) first-principle calculations of Au-doped MnO$_2$. Differential charge densities of (left) Au-substituted and (right) Au-interstitial MnO$_2$. Green indicates a loss of electrons and pink represents a gain of electrons. (C) Specific capacitance of Au/MnO$_2$ at different Au sputtering times. (D) Cycling stability of pure MnO$_2$ and Au-doped MnO$_2$ electrodes with the same thickness of ~1.35 μm. Reproduced with permission [97]. Copyright 2013, Wiley-VCH. (E) Fabrication of amorphous MnO$_2$@MWCNT fibers. (F) CV of amorphous MnO$_2$@MWCNT fiber electrode. (G) Cycling and bending stability of fiber SC at 1 A cm$^{-3}$. Reproduced with permission [100]. Copyright 2017, American Chemical Society.

Chemical deposition of amorphous MnO$_2$ was carried out at 80 °C using acidic KMnO$_4$ and MWCNTs as the precursors via Equations (12) and (13):

\[
4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{CO}_3^{2-} + 2\text{HCO}_3^- \quad (12)
\]

\[
4\text{MnO}_4^- + 4\text{H}^+ \rightarrow 4\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} \quad (13)
\]

Benefiting from the abundant ion transport channels and the fast electron transport of the MWCNTs, the as-prepared amorphous MnO$_2$@MWCNT fibers exhibited a capacitance of 60.8 F cm$^{-3}$ at 0.2 A cm$^{-3}$ with the calculated contribution of MnO$_2$ as high as 615.2 F g$^{-1}$ and excellent rate performance retaining 44.1 F cm$^{-3}$ [Figure 5F]. The symmetric SC made of amorphous MnO$_2$@MWCNT fibers delivered a volumetric capacitance ($C_v$) of 10.9 F cm$^{-3}$ at 0.1 A cm$^{-3}$ and retained 6.9 F cm$^{-3}$ at 5 A cm$^{-3}$, together with an $E_V$ of 1.5 mWh cm$^{-3}$ at the $P_V$ of 0.05 W cm$^{-3}$. In addition, the fiber SC also presented outstanding stability over 15,000 charge/discharge cycles and mechanical robustness for 5000 bending/unbending cycles [Figure 5G].

Hybridization

Combining the merits of two materials via hybridization is highly desired for improving the performance of MnO$_2$ [103-104]. Zhu et al. developed a core-shell structure by depositing δ-MnO$_2$ nanosheets on the outer surface of β-MnO$_2$ via two-step hydrothermal reactions using MnOOH nanowires as the self-sacrificial template and KMnO$_4$ as the oxidant [Figure 6A] [105]. It was found from their experiments that the content of Mn$^{3+}$ played a critical role in improving the electrical conductivity of MnO$_2$ due to the double-exchange

\[
\text{MnO}_2 + \text{MnO}_3 \rightarrow 2\text{MnO}_2^-
\]
Figure 6. (A) Synthesis of β-MnO₂/parallel birnessite core/shell nanorod and a diagram illustrating the enhanced utilization of Mn. Reproduced with permission[105]. Copyright 2018, American Chemical Society. (B) preparation of 3D network composed of MnO₂ sheets and PANI chains. Reproduced with permission[106]. Copyright 2017, American Chemical Society. (C) fabrication of Ti₃C₂Tx/MnO₂ NW composite paper. Reproduced with permission[107]. Copyright 2018, Wiley-VCH. (D) fabrication of GQD/MnO₂ heterostructures. Reproduced with permission[113]. Copyright 2018, Wiley-VCH. GQDs: graphene quantum dots.

interaction forming Mn³⁺-O-Mn⁴⁺. The as-prepared MnO₂ with a Mn³⁺/Mn⁴⁺ ratio of 0.69 exhibited a $C_a$ of 306 F g⁻¹ at 0.25 A g⁻¹, retaining 226 F g⁻¹ at 64 A g⁻¹ and 207 F g⁻¹ after cycling at 2 A g⁻¹ for 3000 times. Liu et al. prepared a three-dimensional (3D) mesoporous architecture composed of MnO₂/polyaniline (PANI) networks via the top-down exfoliation of δ-MnO₂, the electrostatic attraction between the MnO₂ nanosheets and aniline monomer and the chemical polymerization in the presence of (NH₄)₂S₂O₈[Figure 6B][106]. The hybrid exhibited a high conductivity of 0.08 S cm⁻¹, which was slightly lower than that of neat PANI (0.09 S cm⁻¹), due to the electrical interconnections formed by PANI. The as-obtained MnO₂/PANI composite presented a high $C_a$ of 762 F g⁻¹ at 1 A g⁻¹, retaining 587 F g⁻¹ at 10 A g⁻¹ and 578 F g⁻¹ at 5 A g⁻¹ over 8000 charge/discharge cycles.

Recently, a hybrid paper electrode with high flexibility was proposed by Zhou et al. through vacuum infiltrating a homogeneous suspension of MXene (Ti₃C₂Tx) nanosheets and MnO₂ nanowires[Figure 6C][107]. The high conductivity of the 2D MXene sheets (over 8000 S cm⁻¹) facilitated the electron transport of MnO₂ during charge/discharge and prevented the aggregation of MnO₂, thus ensuring the accessibility of the electrolyte ions. The optimized performance was obtained with a Ti₃C₂Tx/MnO₂ mass ratio of six, delivering a $C_a$ (areal capacitance) of 205 mF cm⁻² (corresponding to a $C_a$ of 1025 F cm⁻³), 98% retention after cycling at 0.2 mA cm⁻² for 10000 times and good bending/unbending robustness. Carbonaceous materials were also adopted to improve the electrochemical performance of MnO₂ electrodes[108-112]. Jia et al. reported that graphene quantum dots (GQDs) were adopted using a plasma
enhanced chemical vapor deposition process for the modification of MnO, nanosheets via Mn-O-C bonds [Figure 6D][113]. An electric field was generated at the interface between the GQDs (~5.2 eV) and MnO, (~4.4 eV) owing to their different work functions, thereby providing a barrier for electronic transmission and enabling the extraction of free electrons from MnO, and the subsequent accumulation at the edges of the GQDs until the Fermi levels were aligned. Consequently, the MnO/GQD heterostructures demonstrated an expanded potential window of 1.3 V (vs. Hg/HgCl) in 1 M Na₂SO₄, a Cₓ of 1170 F g⁻¹ at 5 mV s⁻¹ and good stability with 92.7% capacitance retained after 10,000 cycles.

**ZINC-ION BATTERIES**

**Charge storage mechanisms**

Distinct from those described for SCs above, the charge storage mechanisms of MnO, in aqueous ZIBs are relatively complicated, possibly involving the insertion/extraction of Zn²⁺, the co-insertion/extraction of H⁺ and Zn²⁺ and the reversible dissolution-deposition of MnO₂/Mn₂⁻[116]. Typically, although MnO₂ with tunnel structures that can accommodate Zn²⁺, such as α-MnO₂ (2 × 2 tunnels), β-MnO₂ (1 × 1 tunnels) and γ-MnO₂ (1 × 2 and 1 × 1 tunnels), are considered as promising cathodes for ZIBs, they suffer from irreversible phase conversions to layered structure, spinel structure (ZnMn₂O₄) or both during discharge/charge, as shown in Figure 7A[114,115]. Alfaruqi et al. reported the application of a hydrothermally synthesized α-MnO₂ cathode for rechargeable ZIBs using a ZnSO₄ aqueous solution as the electrolyte within a cell voltage of 1.0-1.8 V[116].

X-ray diffraction (XRD) and ex-situ synchrotron X-ray absorption spectroscopy measurements confirmed the reversible insertion and extraction of Zn²⁺ accompanied by the formation and decomposition of ZnMn₂O₄. Alternatively, Lee et al. proposed a reversible and electrochemically triggered phase conversion between α-MnO₂ and layered Zn-birnessite (or Zn-buserite) upon the intercalation/deintercalation of Zn²⁺[117]. The phase conversion mechanism during Zn²⁺ insertion was ascribed to the partial dissolution of MnO₂ in the electrolyte because of the Jahn-Teller effect. With the insertion of Zn²⁺, Mn²⁺ is reduced to Mn⁴⁺ Equation (14) and the gray bridge-like double chains of the MnO₄ units are gradually destroyed because of Mn²⁺ dissolution Equation (15), thereby forming a Zn-birnessite structure. Upon recharging, the dissolved Mn⁴⁺ can intercalate back and bridge the layers to tunnels with α-MnO₂ completely recovered Equation (16)[114]:

\[ \text{Mn}^{2+}(s) + e^{-} \rightarrow \text{Mn}^{4+}(s) \]  \hspace{1cm} (14)

\[ 2\text{Mn}^{4+}(s) \rightarrow \text{Mn}^{2+}(s) + \text{Mn}^{2+}(aq) \]  \hspace{1cm} (15)

\[ \text{Mn}^{2+}(aq) \rightarrow \text{Mn}^{2+}(s) + 2e^{-} \]  \hspace{1cm} (16)

Distinctly, using ex-situ and synchrotron XRD and in-situ X-ray absorption near edge structure, Alfaruqi et al. unveiled that orthorhombic γ-MnO₂ underwent a phase transformation upon the insertion of Zn²⁺ [Figure 7B] following Equations (17) and (18)[118]. During discharge, the oxidation state of Mn in γ-MnO₂ was reduced from Mn⁴⁺ to Mn³⁺/Mn²⁺, accompanied with a structural transformation from an orthorhombic Mn⁴⁺ phase to a spinel-type Mn²⁺ phase (ZnMn₂O₄) and two intermediary soluble Mn²⁺ phases, namely, γ-Zn,MnO₂ (tunnel type) and L-Zn₂MnO₄ (layered type), as a result of the electrochemical Zn intercalation [Figure 7C]. In fact, γ-MnO₂ is composed of R-MnO₂ (ramsdellite) and β-MnO₂ (pyrolusite) phases in a slightly distorted hcp array of the oxygen anion sublattice. In contrast, the ZnMn₂O₄ and L-Zn₂MnO₄ phases share a cubic close-packing (ccp) array of the oxygen network. The intercalation of Zn²⁺ in γ-MnO₂ led to an anisotropic expansion of the orthorhombic unit cell, transforming the hcp oxygen sublattice to a ccp structure[119]. It was noted that a small hump corresponding to the high intensity line of the spinel-type ZnMn₂O₄ phase (2θ of ~32°) appeared to be retained even after complete charging. This
behavior clearly suggests that the spinel phase may not completely revert to the orthorhombic phase and most likely may contribute to some of the capacity loss observed during extended cycling.

\[
\text{Zn}^{2+} + 2e^- + 2\text{MnO}_2 \rightarrow \text{Zn}_2\text{MnO}_4 \quad (17)
\]

\[
n\text{Zn}^{2+} + 2xe^- + \text{MnO}_2 \rightarrow \text{Zn}_n\text{MnO}_2 \quad (18)
\]

\(\delta\)-MnO\(_2\) with a typical layered structure has also been directly utilized as a cathode material for ZIBs. Li et al. investigated the electrochemical storage mechanism of \(\alpha\)-MnO\(_2\) cathode using ex-situ XRD, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy\(^{[120]}\). The results, as schematically shown in Figure 7D, indicated that at the first discharge stage, birnessite \(\text{Zn}_x\text{MnO}_2\) was formed during the intercalation of \(\text{Zn}^{2+}\) into \(\alpha\)-MnO\(_2\) and then some \(\text{Zn}^{2+}\) ions were retained in the MnO\(_2\) interlayer channel (\(\text{Zn}_x\text{MnO}_2\)) in the subsequent charge/discharge. Therefore, the storage behavior was described as the interlayer diffusion of \(\text{Zn}^{2+}\) without any observations regarding the changes in crystal structure.

The co-intercalation of H\(^+\) and \(\text{Zn}^{2+}\) is also an important mechanism for MnO\(_2\) cathodes in ZIBs. Liu et al. investigated the charge storage process of tunnel-structured MnO\(_2\) nanotubes pre-intercalated by K\(^+\) (\(\alpha\)-K\(_{0.19}\)MnO\(_2\)) in 3 M Zn(CF\(_3\)SO\(_3\))\(_2\) and 0.2 M Mn(CF\(_3\)SO\(_3\))\(_2\)\(^{[121]}\). It was found that \(\alpha\)-K\(_{0.19}\)MnO\(_2\) underwent
chemical conversion and cation interaction, as schematically shown in Figure 8A. The ex-situ XRD results demonstrated the reversible formation/decomposition of the Zn-buserite phase during the insertion/extraction of $\text{H}^+$ and Zn$^{2+}$ [Figure 8B and C], corresponding to the two platforms in the discharge/charge curve. Liu et al. studied the phase evolution of $\beta$-MnO$_2$ upon electrochemical charge/discharge in 3 M ZnSO$_4$ and 0.2 M MnSO$_4$.[123] Ex-situ XRD suggested that the intercalation of $\text{H}^+$ retained the crystal structure of $\beta$-MnO$_2$ with the formation of Zn$_4$((OH)$_2$)(SO$_4$)(H$_2$O)$_x$, while the subsequent insertion of Zn$^{2+}$ resulted in a partial phase transformation to spinel ZnMn$_2$O$_4$ [Figure 8D]. Taking the evidence from high-resolution transmission electron microscopy (HRTEM) and TEM [Figure 8E] into consideration, it was concluded that the irreversible formation of ZnMn$_2$O$_4$ after long-term cycling resulted in capacity fade for the $\beta$-MnO$_2$ cathode. Li et al. revealed the storage mechanism of birnessite-type MnO$_2$ in 2.0 M ZnSO$_4$ and 0.5 M MnSO$_4$ [Figure 8F].[123] When discharged from 1.9 to 1.5 V, the $\text{H}^+$ intercalation reaction produced MnOOH Equation (19). Subsequently, with further discharge to 1.41 V, the Zn$^{2+}$ insertion reaction Equation (20) led to the formation of Zn$_2$MnO$_4$·H$_2$O. Finally, MnOOH and Zn$_2$MnO$_4$·H$_2$O completely converted into Mn$^{4+}$ and Zn$_2$SO$_4$(OH)$_2$·5H$_2$O with a Mn$^{4+}$/Mn$^{2+}$ two-electron pathway achieved Equations (21) and (22):

$$\text{MnO}_2 + \text{H}^+ + e \rightarrow \text{MnOOH}$$  \hspace{1cm} (19)

$$4\text{MnO}_2 + 2\text{Zn}^{2+} + 4e + \text{H}_2\text{O} \rightarrow 2\text{Zn}_2\text{MnO}_4 \cdot \text{H}_2\text{O}$$  \hspace{1cm} (20)

$$2\text{MnOOH} + \text{SO}_4^{2-} + 4\text{Zn}^{2+} + 7\text{H}_2\text{O} + 2e \rightarrow 2\text{Zn}_2\text{SO}_4\text{(OH)}_2 \cdot 5\text{H}_2\text{O} + 2\text{Mn}^{2+}$$  \hspace{1cm} (21)

$$3\text{Zn}_2\text{MnO}_4 \cdot \text{H}_2\text{O} + 8\text{SO}_4^{2-} + 61\text{H}_2\text{O} + 26\text{Zn}^{2+} + 12e \rightarrow 8\text{Zn}_2\text{SO}_4\text{(OH)}_2 \cdot 5\text{H}_2\text{O} + 12\text{Mn}^{2+}$$  \hspace{1cm} (22)

In contrast, Jin et al. unveiled the successive intercalation of Zn$^{2+}$ and $\text{H}^+$, respectively, corresponding to the high and low voltage plateaus by exploring the electrochemical behavior of $\delta$-MnO$_2$ in a Zn(TFSI)$_2$-based aqueous electrolyte.[124] Bulky TFSI (vs. SO$_4$$^{2-}$) can decrease the number of water molecules surrounding the Zn$^{2+}$ cation and reduce the solvation effect, thus facilitating Zn$^{2+}$ transport and charge transfer. Therefore, in the Zn(TFSI)$_2$-based electrolyte, the non-diffusion-controlled mechanism dominates the first step of fast Zn$^{2+}$ storage in bulk $\delta$-MnO$_2$ without a significant phase transition Equation (23), while the diffusion-controlled conversion reaction between $\text{H}^+$ and MnO$_2$ dominates the following step reactions Equations (24)-(26):

$$\text{MnO}_2 + x\text{Zn}^{2+} + 2xe^- \leftrightarrow 2x\text{ZnMnO}_2 \text{ (non-diffusion controlled)}$$  \hspace{1cm} (23)

$$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$$  \hspace{1cm} (24)

$$\text{MnO}_2 + \text{H}^+ + e^- \leftrightarrow \text{MnOOH} \text{ (diffusion controlled)}$$  \hspace{1cm} (25)

$$3\text{Zn}^{2+} + 6\text{OH}^- + \text{Zn(TFSI)}_2 + x\text{H}_2\text{O} \leftrightarrow \text{Zn(TFSI)}_2[(\text{Zn(OH)})_x]_x\cdot x\text{H}_2\text{O}$$  \hspace{1cm} (26)

Typically, the dissolution of Mn$^{4+}$ and the generation/decomposition of Zn$_2$SO$_4$(OH)$_2$·H$_2$O (ZSH) observed in ZnSO$_4$ electrolytes are regarded as side reactions for capacity fade. However, a recent study performed by Guo et al. proposed a dissolution-deposition mechanism in a Zn//MnO$_2$ battery Equations (27)-(30) and confirmed the capacity contribution from the reversibly formed ZSH.[125] As shown in Figure 8G, $\alpha$-MnO$_2$ (or -MnO$_x$) reacted with H$_2$O to produce ZSH and Mn$^{2+}$ in the first discharge process and then ZSH reacted with Mn$^{2+}$ to form birnessite-MnO$_2$ in the first charge process. Such a dissolution-deposition mechanism
dominated the subsequent energy storage processes, with the newly formed birnessite-MnO$_2$ as a host material contributing most of the specific capacity. In contrast, the intercalation/deintercalation of H$^+$/$\text{Zn}^{2+}$ in residual undissolved MnO$_2$ is considered to contribute negligible capacity.

$$3\text{MnO}_2 + 6\text{H}_2\text{O} + 6e^- \rightarrow 3\text{Mn}^{2+} + 12\text{OH}^- \hspace{1cm} (27)$$

$$3\text{Mn}^{2+} + 12\text{OH}^- + 6e^- \rightarrow 3\text{birnessite-MnO}_2 + 6\text{H}_2\text{O} \hspace{1cm} (28)$$

$$3\text{birnessite-MnO}_2 + 6\text{H}_2\text{O} + 6e^- \leftrightarrow 3\text{Mn}^{2+} + 12\text{OH}^- \hspace{1cm} (29)$$

$$12\text{OH}^- + 2\text{SO}_4^{2-} + 8\text{Zn}^{2+} + 8\text{H}_2\text{O} \leftrightarrow 2\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot 4\text{H}_2\text{O} \hspace{1cm} (30)$$

**Performance enhancements**

*Foreign ion/molecular pre-insertion*

One of the current issues for the development of Mn-based cathodes is the sluggish reaction kinetics caused by a high-energy barrier for $\text{Zn}^{2+}$ migration due to the strong electrostatic interactions with the host material, as well as the serious structural transformation during cycling$^{[64]}$. The incorporation of cations (e.g., $\text{K}^+$, $\text{Na}^+$, $\text{Zn}^{2+}$ and $\text{Ca}^{2+}$) in MnO$_2$ *via* surface coordination has been proven to be an effective strategy for...
accelerating ion diffusion in tunnels or interlayer corridors, improving electrical conductivity and stabilizing the host structures \cite{126,127}. Fang et al. synthesized potassium manganate (K$_{x}$Mn$_{2}$O$_{4-x}$, KMO) nanorods via the intercalation of K$^{+}$ into the tunnel cavities and used them as cathode materials for ZIBs. It is reported that the steadily intercalated K$^{+}$ via the K-O bonds in the tunnels of KMO can effectively suppress the dissolution of Mn [Figure 9A]. As a result, the KMO-based ZIB exhibited a capacity of over 300 mAh g$^{-1}$ at 100 mA g$^{-1}$, an energy density of 398 Wh kg$^{-1}$ (based on the mass of the cathode) and impressive durability over 1000 cycles at 1 A g$^{-1}$ (154 mAh g$^{-1}$). In contrast, pristine α-MnO$_{2}$ exhibited a significant capacity fade with only 50 mAh g$^{-1}$ after 200 cycles. Anions (e.g., PO$_{4}^{3-}$) can also be inserted into host materials, leading to structural defects, narrow bandgaps and enhanced electrical conductivity \cite{126}. Zhang et al. employed crosslinked vertical multilayer graphene (VMG) arrays as the skeleton for the uniform growth of MnO$_{2}$ nanosheets \cite{129}. The obtained MnO$_{2}$@VMG shell/core arrays were subsequently phosphorized under an Ar flow at 200 °C in the presence of NaH$_{2}$PO$_{4}$H$_{2}$O to form P-MnO$_{2}$@VMG [Figure 9B]. It was found that the phosphorization induced the intercalation of PO$_{4}^{3-}$ and oxygen defects in MnO$_{2}$ simultaneously and expanded the interlayer spacing of (001) (from 0.68 to 0.70 nm), which facilitated ion transfer. The obtained P-MnO$_{2}$@VMG cathode exhibited enhanced electrochemical performance in an aqueous electrolyte of 2 M ZnSO$_{4}$ and 0.2 M MnSO$_{4}$ delivering a capacity of 302.8 mAh g$^{-1}$ at 0.5 A g$^{-1}$, a high energy density of 369.5 Wh kg$^{-1}$ and > 90% capacity retention after 1000 cycles at 2.0 A g$^{-1}$. In comparison, MnO$_{2}$@VMG provided 261.1 mAh g$^{-1}$ at 0.5 A g$^{-1}$ and 79.4% capacity retention after 1000 cycles at 2.0 A g$^{-1}$.

Alternatively, Huang et al. prepared mesoporous PANI-intercalated MnO$_{2}$ nanosheets with a thickness of ~10 nm and expanded interlayer space of ~1.0 nm through the polymerization at the interface of the organic and aqueous phases [Figure 9C]. The oxidation-induced polymerization of aniline (in CCL) and the reduction of MnO$_{2}^{4-}$ (in H$_{2}$O) occurred simultaneously, thereby restricting the growth of MnO$_{2}$ anisotropically and facilitating the layer-by-layer assembly of the 2D MnO$_{2}$ and PANI. Since the guest polymer in the interlayer of the MnO$_{2}$ nanosheets efficiently prevented phase transformation and strengthened the layered structure during repeated insertion/extraction of hydrated cations, a reversible discharge capacity of 280 mAh g$^{-1}$ at 200 mA g$^{-1}$ was achieved with 110 mAh g$^{-1}$ retained even at 3 A g$^{-1}$. Compared to its monovalent counterparts, Zn$^{2+}$ requires high energy for desolvation at the electrode-electrolyte interface, thereby imposing an additional energy penalty for its facile intercalation \cite{130}. In addition, the strong electrostatic interaction between Zn$^{2+}$ and the host frameworks leads to the sluggish diffusion of Zn$^{2+}$ \cite{131}. Nam et al. demonstrated that the interlayer crystal water can effectively screen the electrostatic interactions between Zn$^{2+}$ and the host, thus facilitating Zn$^{2+}$ diffusion \cite{130}. Layered MnO$_{2}$ containing crystal water in the interlayer space (cw-MnO$_{2}$) was prepared through electrochemical transformation from spinel-MnO$_{2}$ in a 1 M MgSO$_{4}$ solution because the insertion of H$_{2}$O$^{+}$ is far more favorable over Mg$^{2+}$. DFT calculations revealed that Zn$^{2+}$ prefers octahedrally coordinated triple-corner-sharing (TCS) sites with three H$_{2}$O molecules by forming a tridentate bond with a Zn-Mn dumbbell structure [Figure 9D]. Therefore, upon intercalation, Zn$^{2+}$ ions tend to migrate together with the coordinate water molecules because of the strong Zn-H$_{2}$O coordination bond, which effectively weakens the electrostatic interaction between Zn$^{2+}$ and MnO$_{2}$. As a result, cw-MnO$_{2}$ exhibited high reversible capacities of 350 mAh g$^{-1}$ at 100 mA g$^{-1}$, 154 mAh g$^{-1}$ at 3 A g$^{-1}$ and 116 mAh g$^{-1}$ after 200 cycles at 3 A g$^{-1}$. A similar observation was reported by Wang et al., where H$_{2}$O molecules not only stabilize the intercalated Na$^{+}$ in the structure (Na$_{0.4}$Mn$_{2}$O$_{4}$·1.5H$_{2}$O) but also promote the intercalation of Zn$^{2+}$ during discharge in ZIBs \cite{132}.

**Defect engineering**

Defect engineering is another widely adopted method to enhance the performance of MnO$_{2}$ by tuning the electronic structure, enhancing the structural robustness and adjusting the interaction between the host and Zn$^{2+}$ \cite{134,135}. Oxygen vacancies (V$_{O}$) have proven their capability in gauging the adsorption/desorption of
Figure 9. (A) Tunnel structure stabilized by K⁺ and cycling performance of KMO and α-MnO₂ at 1 A g⁻¹. Reproduced with permission [128]. Copyright 2019, Wiley-VCH. (B) synthesis of P-MnO₂@VMG shell/core arrays. Reproduced with permission [130]. Copyright 2020, Wiley-VCH. (C) preparation and structural advantage of PANI-intercalated MnO₂ nanolayers. Reproduced with permission [131]. Copyright 2018, Nature. (D) optimized structure of cw-MnO₂ for Zn²⁺ intercalation and the corresponding relative energies. Reproduced with permission [54]. Copyright 2019, Royal Society of Chemistry. HT: hydrothermal method; TCS: triple-corner-sharing; KMO: K₀.₈Mn₈O₁₆; PP: phosphorization; VMG: vertical multilayer graphene.

Zn²⁺ [93]. For example, Xiong et al. proposed the use of oxygen-deficient δ-MnO₂ (V₉-MnO₂) as cathode materials for ZIBs [136]. The storage mechanisms of Zn²⁺ in V₉-MnO₂ involve the insertion/extraction of Zn²⁺ into the interlayer spacing, surface redox reaction of xZn²⁺ + 2xe⁻ + MnO₂ → MnOOZnx, and the formation of electric double layers [Figure 10A]. The calculated Gibbs free energies of Zn²⁺ adsorption at the vicinity sites to V₉ are close to thermoneutral values of ~0.05 eV [Figure 10B], suggesting a weakened bonding strength between Zn and O due to the diminished charge transfer. Therefore, more reversible adsorption/desorption of Zn²⁺ can be achieved for V₉-MnO₂ rather than pristine MnO₂. As a result, V₉-MnO₂ in an aqueous electrolyte of 1 M ZnSO₄ and 0.2 M MnSO₄ delivered a specific capacity of 345 mAh g⁻¹ without any decay after 100 cycles at 0.2 A g⁻¹ [Figure 10C]. The Zn-ion storage capability of MnO₂ can also be improved by heteroatom doping [137]. Zhao et al. hydrothermally synthesized Ni-doped MnO₂ with a stoichiometry of Ni₀.₀₂K₀.₁₄Mn₇.₉₄O₂·0.₂₀₈H₂O (NKMO) [138]. The reference sample prepared without Ni(NO₃)₂ was KMO. The presence of the Ni-induced tetragonal-orthorhombic lattice distortion can mediate the cooperative motion of H⁺ via the formation of hydrogen bonds similar to Groththus proton hopping in water [Figure 10D]. The electrochemical performance of NKMO and KMO cathodes was evaluated using a Zn plate as an anode in a 3 M ZnSO₄ and 0.2 M MnSO₄ aqueous electrolyte. The discharge capacity of the Zn/NKMO cell was ~303 mAh g⁻¹, which was ~29% higher than that of Zn/KMO
Figure 10. (A) Zn$^{2+}$ storage mechanism for V$_x$MnO$_{2-y}$ and V$_x$MnO$_2$. (B) comparison of adsorption energies for Zn$^{2+}$ on δ-MnO$_2$ and V$_x$MnO$_2$. (C) cycling performance of V$_x$MnO$_2$ at 0.2 A g$^{-1}$. Reproduced with permission[136]. Copyright 2019, Wiley-VCH. (D) Zn$^{2+}$ storage in Ni-doped MnO$_2$ regulated by TO distortion. (E) cycling performance of Ni-doped MnO$_2$ at 4 C. Reproduced with permission[139]. Copyright 2021, Wiley-VCH. (F) fabrication of N-MnO$_{2-x}$@TiC/C arrays. (G) cycling capability of MnO$_{2-x}$@TiC/C and N-MnO$_{2-x}$@TiC/C at 1.0 A g$^{-1}$. Reproduced with permission[136]. Copyright 2019, Wiley-VCH. (H) structure of A-MnO$_{2-x}$δ and in-situ XRD patterns during second charge/discharge cycle. (I) cycling performance of A-MnO$_{2-x}$δ at 1 A g$^{-1}$. Reproduced with permission[141]. Copyright 2020, Elsevier. KMO: K$_{0.8}$Mn$_{8}$O$_{16}$; NKMO: Ni$_{0.052}$K$_{0.119}$Mn$_{0.948}$O$_{2-0.208}$H$_2$O. (~235 mAh g$^{-1}$). As shown in Figure 10E, the long-term cycling stability of the Zn/KMO and Zn/NKMO cells examined at 4 C indicated that NKMO showed a slight sacrifice in capacity (73.6% for KMO vs. 71.4% for NKMO after 2000 cycles).

Alternatively, Wang et al. reported a Ce-doped MnO$_2$ nanorod-like electrode material synthesized by a hydrothermal method[139]. Cerium doping induced a structural transformation of MnO$_2$ from its original β-phase to the α-phase, along with the appearance of a [2 x 2] tunnel structure. Its electrochemical properties were investigated using zinc as an anode, 2 M ZnSO$_4$ and 0.1 M MnSO$_4$ as an electrolyte, glass fiber as a separator and the prepared materials as the cathode. Compared to β-MnO$_2$, 0.1 mmol Ce doping displayed a higher initial capacity and Coulombic efficiency of 134 mAh g$^{-1}$ at 5 C and 82%. More importantly, after 100 cycles, the capacity retention of 0.1 mmol Ce doping was almost twice as high as that of β-MnO$_2$ at such a high current density. When the rate was in the range of 1-5 C, the 0.1 mmol Ce-doped electrode had high discharge capacities, indicating a better rate capability (308 mAh g$^{-1}$). Additionally, the galvanostatic intermittent titration technique (GITT) was used to calculate the chemical diffusion
coefficient of \( \text{Zn}^{2+} \) in the two electrode materials. The diffusion coefficient of \( \text{Zn}^{2+} \) was improved by one to two orders of magnitude for the 0.1 mmol Ce-doped cathode than the \( \beta \)-\( \text{MnO}_2 \) cathode. Moreover, Zhang et al. simultaneously introduced oxygen vacancies and heteroatom doping into \( \text{MnO}_2 \) to form a Ndoped \( \text{MnO}_{2-x} \) (\( \text{N MnO}_{2-x} \)) branch on the surface \( \text{TiC/C} \) nanorod array (\( \text{N MnO}_{2-x} @\text{TiC/C} \)) for \( \text{ZIBs} \) [Figure 10F] [142]. DFT calculations indicated that the combination of oxygen vacancies and N doping greatly improved the conductivity of \( \text{MnO}_2 \) with a much narrower bandgap (0.1 eV). The electrochemical performance of N-\( \text{MnO}_{2-x} @\text{TiC/C} \) was studied in an aqueous solution of 2 M \( \text{ZnSO}_4 \) and 0.2 M \( \text{MnSO}_4 \). The designed \( \text{N MnO}_{2-x} @\text{TiC/C} \) electrode showed improved \( \text{Zn}^{2+} \) storage performance with faster reaction kinetics, higher capacity (285 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\)) and excellent cycling performance. After 1000 cycles at 1 A g\(^{-1}\), the N-\( \text{MnO}_{2-x} @\text{TiC/C} \) electrode delivered a reversible capacity of 172.7 mAh g\(^{-1}\) with a capacity retention of 84.7% [Figure 10G], higher than its \( \text{MnO}_2 @\text{TiC/C} \) counterpart with a reversible capacity of 84.8 mAh g\(^{-1}\) (capacity retention of 55.6%).

Amorphous structures with disordered atomic arrangements and abundant structural defects that may lead to enhanced ion diffusion kinetics, improved capacity and alleviated volume expansion are considered to be promising cathode candidates for \( \text{ZIBs} \) [55,56]. Cai et al. demonstrated the feasibility of amorphous \( \text{MnO}_2 \) (A-\( \text{MnO}_{2-\delta} \)) \( \delta \) was estimated to be 0.12) in \( \text{ZIBs} \) and studied the structural evolution of A-\( \text{MnO}_{2-\delta} \) in 2 M \( \text{ZnSO}_4 \) and 0.2 M \( \text{MnSO}_4 \) [143]. In-situ XRD profiles were collected at different states in the second discharge/charge cycle [Figure 10H]. Accordingly, the \( \text{Zn}^{2+} \) storage in A-\( \text{MnO}_{2-\delta} \) can be divided into four stages: (I: 1.85-1.30 V) no observable peak was found, suggesting that the cation insertion in the A-\( \text{MnO}_{2-\delta} \) did not change the amorphous structure or generate a new crystalline structure; (II: 1.3-1.0 V) layered \( \text{ZnSO}_4(\text{OH})_2\cdot\text{SH}_2\)O was generated, as evidenced by a new set of diffraction peaks at 8.1°, 16.2°, 24.4°, 32.7°, 33.5°, 34.9°, 35.3°, 36.3° and 38.6° (JCPDS No. 39-0688); (III: 1.0-1.5 V) the peaks of \( \text{ZnSO}_4(\text{OH})_2\cdot\text{SH}_2\)O became weakened gradually and completely disappeared at a capacity of 157.3 mAh g\(^{-1}\); (IV: 1.50-1.85 V) no other peaks appeared, suggesting ion extraction from the amorphous Mn-based compound. The A-\( \text{MnO}_{2-\delta} \) cathode exhibited a reversible capacity of 147 mAh g\(^{-1}\) at 1 A g\(^{-1}\) with a capacity retention of 78% after 1000 cycles [Figure 10I].

Hybridization

Hybridization has been confirmed as a useful method for improving the performance of \( \text{MnO}_2 \) in \( \text{ZIBs} \) [142-146]. Li et al. anchored \( \text{MnO}_2 \) particles on N-doped hollow carbon spheres (NHCSs@\( \text{MnO}_2 \)) via a direct reaction between carbon and K\( \text{MnO}_2 \) [Figure 11A] [147]. The hollow porous carbon nanospheres provided large interfaces, thus ensuring the fast transport of ions/electrons. The obtained NHCSs@\( \text{MnO}_2 \) exhibited improved performance for \( \text{Zn}^{2+} \) storage in 2 M \( \text{ZnSO}_4 \) and 0.1 M \( \text{MnSO}_4 \) with an excellent reversible capacity of \( \approx 206 \text{ mAh g}^{-1} \) and a retention ratio of 89.5% after 200 cycles at 0.1 A g\(^{-1}\) [Figure 11B]. Zhang et al. used a CNT network as a conductive scaffold on which formable \( \text{MnO}_2 \) sheath and rough poly(3, 4-ethylenedioxythiophene) (PEDOT) protective layers were deposited sequentially to form a binder-free CNT/\( \text{MnO}_2 \)/PEDOT (CMOP) electrode [Figure 11C] [146]. CNT/\( \text{MnO}_2 \) (CMO) was also prepared as a control sample. The PEDOT layers prevented \( \text{MnO}_2 \) from dissolution, which effectively boosted the cycling life of the battery. The electrochemical behavior of \( \text{MnO}_2 \), \( \text{MnO}_2 /\text{PEDOT} \), CMO and CMOP was evaluated in 2 M \( \text{ZnCl}_2 \) and 0.4 M \( \text{MnSO}_4 \). As demonstrated, the CMOP cathode delivered a maximum specific capacity of 306.1 mAh g\(^{-1}\) at 1.1 A g\(^{-1}\) and 176.8 mAh g\(^{-1}\) at 10.8 A g\(^{-1}\) and good long-term stability with a capacity retention of 81.3% after 2000 charge/discharge cycles [Figure 11D].

Alternatively, Zhu et al. hybridized \( \text{MnO}_2 \) nanosheets with a \( \text{V}_x\text{C}_y \) MXene (K-\( \text{V}_x\text{C}@\text{MnO}_2 \)) by K- intercalation, followed by a hydrothermal growth strategy [Figure 11E] [148]. It was found that the adsorbed K\(^+\) on the \( \text{V}_x\text{C} \) surface facilitated the growth of K-birnessite \( \text{MnO}_2 \), hydrogen bonds existed between
Figure 11. (A) Synthesis of SiO₂@phenol-formaldehyde resin (RF), SiO₂@RF@polydopamine (PDA), NHCSs and NHCSs@MnO₂ composites using tetraethoxysilane (TEOS) as Si source. (B) cyclic performance of NHCSs@MnO₂ at 100 mA g⁻¹ for 200 cycles. Reproduced with permission[147]. Copyright 2020, Elsevier. (C) 3D structure of CNT conductive networks and fabrication of CMOP cathodes. (D) long-term cycling performance of CMO and CMOP electrodes. Reproduced with permission[148]. Copyright 2019, Wiley-VCH. (E) synthesis and structural analysis of K-V₂C@MnO₂ and calculated absorption energies for Zn²⁺ on the surfaces of perfect MnO₂-V₂C and δ-MnO₂. Reproduced with permission[149]. Copyright 2021, American Chemical Society. (F) preparation of MnO₂/PPy nanorod. Reproduced with permission[150]. Copyright 2020, Elsevier. CNT: carbon nanotube; CMO: CNT/MnO₂; CMOP: CNT/MnO₂/PEDOT; NHCS: N-doped hollow carbon sphere; PEDOT: poly(3,4-ethylenedioxythiophene).

**MnO₂** (O) and K-V₂C (H from functional groups), and the Gibbs free energy of Zn²⁺ adsorption in V₂C@MnO₂ was lowered in comparison with pristine δ-MnO₂. The performance of K-V₂C@MnO₂ was evaluated in 2.0 M ZnSO₄ and 0.25 M MnSO₄. A remarkable capacity of 408.1 mAh g⁻¹ at 0.3 A g⁻¹ was achieved and 119.2 mAh g⁻¹ was retained after 10,000 cycles at 10 A g⁻¹. Huang et al. attempted to coat a thin layer of polypyrrole (PPy) to slow the interfacial electrochemical kinetics and prevent the dissolution of MnO₂ [Figure 11F][150]. Interestingly, strong Mn-N bonds were found at the interface of MnO₂ and PPy. DFT calculations revealed that the energy barrier for Mn escape was increased to 6.76 eV owing to the Mn-N bond. The performance of MnO₂ and MnO₂/PPy was tested in 2 M ZnSO₄ and 0.1 M MnSO₄. In comparison with MnO₂ (133 mAh g⁻¹), MnO₂/PPy provided 256 mAh g⁻¹ after 50 cycles at 100 mA g⁻¹ without capacity fade.
SUMMARY AND OUTLOOK

Summary
This review focuses on the applications of MnO$_2$ for aqueous energy storage (SCs and ZIBs) and summarizes and compares the similarities and differences of the corresponding charge storage mechanisms and the principles for materials modification [Table 1].

Charge storage mechanisms
In the case of SCs, the surface redox reactions and bulk intercalation of electrolyte ions are the two dominating mechanisms for charge storage in MnO$_2$, Equations (10) and (11). The pH of the electrolyte severely affects the electrochemical reactions during charge/discharge. In an acidic solution, an irreversible reaction occurs between H$^+$ and MnOOH, forming dissoluble Mn$^{2+}$. In an alkaline solution, a passivation layer of Mn(OH)$_2$ is generated as a result of the reaction between MnO$_2$ and OH$^-$. In a neutral electrolyte, the disproportionation of Mn$^{3+}$ to dissoluble Mn$^{2+}$ is usually observed. Considering the chemical stability of the zinc metal anode, a near-neutral electrolyte is usually selected (e.g., ZnSO$_4$ aqueous solution) for ZIBs. Three possible mechanisms are proposed: (i) intercalation/deintercalation of Zn$^{2+}$; (ii) co-insertion/extraction of H$^+$/Zn$^{2+}$; and (iii) dissolution-deposition of MnO$_2$/Mn$^{2+}$. Although it is still under debate, the charge storage mechanism generally involves the insertion of H$^+$ (fast kinetics) to generate MnOOH, the insertion of Zn$^{2+}$ (slow kinetics) to generate Zn$_n$MnO$_4$ and the irreversible deposition of ZSH on the surface of electrodes. Indeed, the existing works on designing MnO$_2$ cathodes for ZIBs are very similar to the explorations of MnO$_2$-based SCs using near-neutral electrolytes (zinc salt-based aqueous electrolyte, e.g., ZnSO$_4$, ZnCl$_2$, ZnTFSI or Zn(CF$_3$SO$_2$)$_2$). However, different from the monovalent cations mostly investigated in SCs, Zn$^{2+}$ has a larger hydrated ionic radius, higher desolvation energy barrier and stronger electrostatic interaction with MnO$_2$, all of which induce complex electrode reactions and structural instability in MnO$_2$ cathodes for ZIBs.

MnO$_2$ modification methods
Low electrical conductivity, structural instability and slow electrode reaction kinetics are common issues of MnO$_2$ as electrodes for energy storage. Based on our summary, similar strategies have been adopted for MnO$_2$ modification in both SCs and ZIBs, including foreign ion/molecular pre-insertion, defect engineering, nanostructural design and hybridization. Typically, the pre-inserted ions/molecules in MnO$_2$ facilitate the ion intercalation/deintercalation by expanding the interlayer spaces, shield the strong electrostatic interaction between intercalated ions and MnO$_2$ and stabilize the crystal structure of MnO$_2$ during ion intercalation/deintercalation. The introduction of oxygen vacancies and heteroatom doping (defect engineering) are effective methods to regulate the electron structure of MnO$_2$, which significantly affect the electron transport during the redox reaction. Rational nanostructural design contributes to the accessibility of electrolyte ions to active sites, thereby improving the capacity of the electrode. Hybridizing with high conductive carbonaceous materials (e.g., CNTs and rGO) can efficiently improve the conductivity of bare MnO$_2$, thus boosting the kinetics of the electrode reaction.

Outlook
Although significant efforts have been devoted to the investigation of MnO$_2$ for potential applications in SCs and ZIBs and there are several prospective aspects that need to be considered:

1. MnO$_2$ is considered as one of the most promising candidates for SCs because of its low cost, earth abundance, high theoretical capacitance and environmental benignness. Nevertheless, the performance of MnO$_2$ in SCs is far from satisfactory. An in-depth understanding of the underlying mechanisms and efficient strategies for performance improvements are highly required.
Table 1. Similarities and differences in using MnO$_2$ as electrode material in SCs and ZIBs

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mechanisms</th>
<th>Modification strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCs</td>
<td>☆ Surface redox reaction</td>
<td>• Nanostructural design</td>
</tr>
<tr>
<td></td>
<td>☆ Bulk intercalation (no phase transition)</td>
<td>• Foreign ion/molecular pre-insertion</td>
</tr>
<tr>
<td>ZIBs</td>
<td>☆ Insertion/extraction of Zn$^{2+}$</td>
<td>• Defect engineering</td>
</tr>
<tr>
<td></td>
<td>☆ Co-insertion of H$^+$ and Zn$^{2+}$</td>
<td>• Hybridization</td>
</tr>
<tr>
<td></td>
<td>☆ Dissolution-deposition (with phase transition)</td>
<td></td>
</tr>
</tbody>
</table>

(2) To date, the mechanism for Zn$^{2+}$ storage is still under debate and severely depends on the testing conditions. More efforts are required by employing advanced characterization techniques.

(3) The introduction of oxygen vacancies and heteroatoms is deemed to be an effective method to regulate the properties of MnO$_2$ for enhancing the charge storage in both SCs and ZIBs. However, since MnO$_2$ crystals are composed of MnO$_6$ octahedral units, it remains necessary to quantitatively identify the concentration and position of oxygen vacancies and heteroatoms that play a critical role in governing MnO$_2$ performance.

(4) The pre-intercalation of cations, water molecules and polymers has been demonstrated to be an effective strategy to enhance the capacitance/capacity and stability of MnO$_2$. The mechanisms for performance enhancement need to be further investigated.

(5) Hybridization with conductive materials (e.g., graphene and MXenes) is considered a feasible method to efficiently improve the electron transfer/transport of MnO$_2$. In addition, the interfacial properties between two materials are believed to contribute to the performance enhancement. However, a detailed explanation of interface-dependent electrochemical behavior is still required.

(6) Finally, more attention should be paid to the performance decay mechanisms of MnO$_2$ in SCs and ZIBs, which are the guidelines for future materials design.

**DECLARATIONS**

**Authors' contributions**
Preparation of the manuscript draft: Dai H, Zhou R
Writing-review: Zhang Z
Editing: Zhou J
Funding acquisition, supervision: Sun G

**Availability of data and materials**
Not applicable.

**Financial support and sponsorship**
This work was supported by the National Natural Science Foundation of China (No. 21975123), Anhui Provincial Key R&D Program (No. 2022i01020021) and Six Talent Peaks Project in Jiangsu Province (No. XCL-024).
Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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