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

Henghan Dai¹,², Ruicong Zhou¹,², Zhao Zhang³,², Jinyuan Zhou³, Jinyuan Zhou, 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.

*Authors 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

How to cite this article: Dai H, Zhou R, Zhang Z, Zhou J, Sun G. Design of manganese dioxide for supercapacitors and zinc-ion batteries: similarities and differences. Energy Mater 2022;2:200040. https://dx.doi.org/10.20517/energymater.2022.56

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

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\cite{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\cite{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\cite{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\cite{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\cite{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\cite{30-33}. 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\cite{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\cite{37-41}. 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\cite{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\cite{46}. A $\delta$-MnO$_2$-based cathode for ZIBs showed a capacity of 200 mAh g$^{-1}$ at 0.1 A g$^{-1}$ after full electrochemical activation\cite{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\cite{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$_2$,
Figure 1. Schematic illustrations of (A) SC and (B) ZIB devices. (C) publication numbers of different materials, including MXenes, TMDs, carbon, polymers and TMOs (MnO$_2$ and RuO$_2$), for SCs in the period from 2011 to 2022. (D) publication numbers of different cathode materials, such as TMOs (VO$_x$ and MnO$_2$), PBA, 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.

δ-MnO$_2$, γ-MnO$_2$ and amorphous MnO$_2$ [Figure 2] by arranging the MnO$_6$ octahedral units either via edge-sharing, corner-sharing or a combination of two[26]. In particular, in α-MnO$_2$ [Figure 2A], MnO$_6$ octahedral double chains are connected in a corner-sharing manner to form $2 \times 2$ tunnels ($4.6 \times 4.6$ Å). In β-MnO$_2$ [Figure 2B], single chains assembled by MnO$_6$ octahedra are interlinked in a corner-sharing manner to form $1 \times 1$ tunnels ($2.3 \times 2.3$ Å). In γ-MnO$_2$, both $1 \times 1$ and $1 \times 2$ tunnels coexist and distribute randomly [Figure 2C]. Alternatively, in δ-MnO$_2$, two-dimensional (2D) sheets are built by sharing MnO$_6$ 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 MnO$_2$ 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
MnO$_2$ is considered a pseudocapacitive material[57]. Traditionally, it is believed that the capacitance of MnO$_2$ originates from surface redox reactions with a theoretical value of ~110 μF cm$^{-2}$ based on a
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 reactions⁵⁹. 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):

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

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 decay⁶⁴,⁶⁵. Furthermore, MnO₂ structures experience volume expansion, thereby loosening the electrical contacts between MnO₂ particles, increasing the series resistance and lowering the capacitance over time⁶⁶,⁶⁷. These issues compromise the power density and cycle life of MnO₂ directly⁶⁸,⁶⁹. In an acidic electrolyte, except for the redox reaction between H⁺ and MnO₂, excessive H⁺ induces the further reduction of MnOOH to Mn⁺, leading to the irreversible dissolution of MnO₂ Equations (3) and (4)⁷⁰. 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 V⁷¹.
In a neutral electrolyte:

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

In an acidic electrolyte:

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

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

In an alkaline electrolyte:

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

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

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

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

Overall, two main charge storage mechanisms are involved for MnO\textsubscript{2} when adopted in aqueous SCs: (i) surface redox reactions Equation (10); and (ii) intercalation/deintercalation of cations Equation (11):

\[
(\text{MnO}_2)_\text{surface} + \text{M}^+ + \text{e}^- \leftrightarrow (\text{MnOOM})_{\text{surface}} \quad (10)
\]

\[
(\text{MnO}_2)_\text{bulk} + \text{M}^+ + \text{e}^- \leftrightarrow (\text{MnOOM})_{\text{bulk}} \quad (11)
\]

**Performance enhancements**

**Nanostructure design**

Enhancing the ion diffusion kinetics *via* nanostructural design is considered a feasible method to improve the capacitance of MnO\textsubscript{2} \[70-77\]. Xiong *et al.* prepared interlayer expanded MnO\textsubscript{2} (0.93 nm) with intercalated tetramethylammonium ions (TMA\textsuperscript{+}), 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 MnO\textsubscript{2} and K\textsuperscript{+} due to the decreased diffusion energy barrier, thereby accelerating ion diffusion during charge/discharge. A specific capacitance of 160 F g\textsuperscript{-1} was obtained for the restacked MnO\textsubscript{2} in aqueous K\textsubscript{2}SO\textsubscript{4} electrolytes at 0.2 A g\textsuperscript{-1}, while at 10 A g\textsuperscript{-1}, 70% capacitance was retained (110 F g\textsuperscript{-1}). In contrast, in the cases of K- and H-MnO\textsubscript{2} nanobelts, only 50% and 55% capacitance retentions were obtained, respectively, as the current density increased from 0.2 to 10 A g\textsuperscript{-1} [Figure 4B]. Moreover, the long-term cycling performance of the restacked MnO\textsubscript{2} nanosheets was evaluated at 5 A g\textsuperscript{-1} for 5000 cycles with 100% retention.

**Foreign ion/molecular pre-insertion**

Since the charge storage capacity of MnO\textsubscript{2} can be enhanced by the Mn\textsuperscript{4+}/Mn\textsuperscript{3+} redox pair with cation adsorption (or intercalation) \[79-81\], it is speculated that the pre-insertion of cations in MnO\textsubscript{2} could improve the specific capacitance by enhancing ion diffusion \[81-83\]. Following this guidance, Jabeen *et al.* prepared birnessite Na\textsubscript{0.5}MnO\textsubscript{2} arrays on a carbon cloth by the electrochemical conversion of Mn\textsubscript{3}O\textsubscript{4} in 10 M Na\textsubscript{2}SO\textsubscript{4} via cyclic scanning at 10 mV s\textsuperscript{-1} within the potential window of 0 and 1.3 V (vs. Ag/AgCl) for 500 cycles [Figure 4C] \[84\]. The incorporation of Na\textsuperscript{+} not only upgraded the specific capacitance but also widened the workable potential window to 1.3 V. The redox reaction of the Mn\textsuperscript{3+}/Mn\textsuperscript{4+} 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\textsuperscript{+}. The obtained Na\textsubscript{0.5}MnO\textsubscript{2} electrode showed an obviously improved capacitance of 366 F g\textsuperscript{-1} without compromising its cycling stability [Figure 4D]. Asymmetric SCs were constructed using Na\textsubscript{0.5}MnO\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4} as the cathode and anode, respectively. The asymmetric SC using 1 M Na\textsubscript{2}SO\textsubscript{4} as the electrolyte exhibited a cell voltage of 2.6 V, a capacitance of 88 F g\textsuperscript{-1} and an energy density of 81 Wh kg\textsuperscript{-1}.

**Defect engineering**

In addition to ion diffusion, the high electrical resistance of MnO\textsubscript{2} 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 MnO\textsubscript{2} \[88-96\]. Kang *et al.* designed a thick Au-doped MnO\textsubscript{2} film (1.35 μm) by electrochemically depositing MnO\textsubscript{2} and sputtering Au alternately to adjust the electronic structure of MnO\textsubscript{2} [Figure 5A] \[97\]. Au atoms distributed in the lattice of MnO\textsubscript{2} 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 MnO₂ is much higher than that of pristine MnO₂ (2.5 eV). With increasing Au-doping level, the specific capacitance first increases and then decreases slightly. As a result, the Au-doped MnO₂ 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 MnO₂ tends to change the electronic structure of MnO₂ via electron donation. For example, Wang et al. synthesized a series of interlinked Fe-doped MnO₂ nanostructures via a hydrothermal method\(^{[98]}\). It was confirmed that the incorporation of Fe atoms effectively prevented the collapse of MnO₂ 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\(_{2-x}\)/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 MnO₂ 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 MnO₂ 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 MnO₂.
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$^{-2}$. 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$^{-2}$ with the calculated contribution of MnO$_2$ as high as 615.2 F g$^{-1}$ and excellent rate performance retaining 44.1 F cm$^{-3}$ at 20 A cm$^{-2}$ [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$^{-2}$ and retained 6.9 F cm$^{-3}$ at 5 A cm$^{-2}$, 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
interaction forming Mn$^{3+}$-O-Mn$^{4+}$. The as-prepared MnO$_2$ with a Mn$^{3+}$/Mn$^{4+}$ 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 MnO$_2$/polyaniline (PANI) networks via the top-down exfoliation of δ-MnO$_2$, the electrostatic attraction between the MnO$_2$ nanosheets and aniline monomer and the chemical polymerization in the presence of (NH$_4$)$_2$S$_2$O$_8$ [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 MnO$_2$/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 (Ti$_3$C$_2$T$_x$) nanosheets and MnO$_2$ nanowires [Figure 6C][107]. The high conductivity of the 2D MXene sheets (over 8000 S cm$^{-1}$) facilitated the electron transport of MnO$_2$ during charge/discharge and prevented the aggregation of MnO$_2$, thus ensuring the accessibility of the electrolyte ions. The optimized performance was obtained with a Ti$_3$C$_2$T$_x$/MnO$_2$ 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 MnO$_2$ electrodes[89,108-112]. Jia et al. reported that graphene quantum dots (GQDs) were adopted using a plasma
enhanced chemical vapor deposition process for the modification of MnO₂ nanosheets via Mn-O-C bonds [Figure 6D][113]. An electric field was generated at the interface between the GQDs (~5.2 eV) and MnO₂ (~4.4 eV) owing to their different work functions, thereby providing a barrier for electronic transmission and enabling the extraction of free electrons from MnO₂, and the subsequent accumulation at the edges of the GQDs until the Fermi levels were aligned. Consequently, the MnO₂/GQD heterostructures demonstrated an expanded potential window of 1.3 V (vs. Hg/HgCl₂) in 1 M Na₂SO₄, a Cₑ 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 MnO₂ 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⁺[50]. 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 (ZnMnO₄) 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⁺, Mn³⁺ is reduced to Mn²⁺ Equation (14) and the gray bridge-like double chains of the Mn⁴⁺ units are gradually destroyed because of Mn²⁺ dissolution Equation (15), thereby forming a Zn-birnessite structure. Upon recharging, the dissolved Mn²⁺ can intercalate back and bridge the layers to tunnels with α-MnO₂ completely recovered Equation (16)[118]:

\[
\text{Mn}^{4+}(s) + e^- \rightarrow \text{Mn}^{3+}(s) \quad (14)
\]

\[
2\text{Mn}^{3+}(s) \rightarrow \text{Mn}^{2+}(s) + \text{Mn}^{2+}(\text{aq}) \quad (15)
\]

\[
\text{Mn}^{2+}(\text{aq}) \rightarrow \text{Mn}^{3+}(s) + 2e^- \quad (16)
\]

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)[119]. 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 Mn³⁺ phase to a spinel-type Mn²⁺ phase (ZnMn₂O₄) and two intermediary soluble Mn²⁺ phases, namely, γ-Zn₂MnO₄ (tunnel type) and L-Zn₄MnO₄ (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-Zn₄MnO₄ 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 (20 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.

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

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

\(\delta\)-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 a \(\delta\)-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 \(\text{Zn}_{x+y}\text{MnO}_2\) was formed during the intercalation of \(\text{Zn}^{2+}\) into \(\delta\)-MnO\(_2\) and then some \(\text{Zn}^{2+}\) ions were retained in the MnO\(_2\) interlayer channel (\(\text{Zn}_n\text{MnO}_2\)) 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 \(\text{H}^+\) 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 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 \(\beta\)-Mn\(_2\)O\(_4\) upon electrochemical charge/discharge in 3 M ZnSO\(_4\) and 0.2 M MnSO\(_4\)\([123]\). Ex-situ XRD suggested that the intercalation of H\(^+\) retained the crystal structure of \(\beta\)-Mn\(_2\)O\(_4\) with the formation of Zn\(_4\)(OH)\(_4\)(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\(_3\)O\(_4\) after long-term cycling resulted in capacity fade for the \(\beta\)-Mn\(_2\)O\(_4\) cathode. Li et al. revealed the storage mechanism of birnessite-type Mn\(_2\)O\(_4\) 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 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\(_2\)Mn\(_2\)O\(_4\)_\(_x\)_\(_y\)H\(_2\)\(_y\). Finally, MnOOH and Zn\(_2\)Mn\(_2\)O\(_4\)_\(_x\)_\(_y\)H\(_2\)\(_y\) completely converted into Mn\(^{3+}\) and Zn\(_4\)(OH)\(_4\)_\(_x\)_\(_y\)_\(_x\)_\(_y\)H\(_2\)\(_y\) with a Mn\(^{3+}\)/Mn\(^{4+}\) two-electron pathway achieved Equations (21) and (22):

\[
\text{MnO}_2 + H^+ + e^{-} \rightarrow \text{MnOOH} \tag{19}
\]

\[
4\text{MnO}_2 + 2Zn^{2+} + 4e + H_2O \rightarrow Zn_2\text{Mn}_2\text{O}_4\cdot H_2O \tag{20}
\]

\[
2\text{MnOOH} + SO_4^{2-} + 4Zn^{2+} + 7H_2O + 2e \rightarrow Zn_2SO_4(OH)\cdot 5H_2O + 2Mn^{3+} \tag{21}
\]

\[
3Zn_2\text{Mn}_2\text{O}_4\cdot H_2O + 8SO_4^{2-} + 61H_2O + 26Zn^{2+} + 12e \rightarrow 8Zn_2SO_4(OH)\cdot 5H_2O + 12Mn^{3+} \tag{22}
\]

In contrast, Jin et al. unveiled the successive intercalation of Zn\(^{2+}\) and H\(^+\), respectively, corresponding to the high and low voltage plateaus by exploring the electrochemical behavior of \(\delta\)-Mn\(_2\)O\(_4\) 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 \(\delta\)-Mn\(_2\)O\(_4\) without a significant phase transition Equation (23), while the diffusion-controlled conversion reaction between H\(^+\) and Mn\(_2\)O\(_4\) dominates the following step reactions Equations (24)-(26):

\[
\text{MnO}_2 + xZn^{2+} + 2xe^{-} \leftrightarrow \text{Zn}_x\text{MnO}_2 \text{ (non-diffusion controlled)} \tag{23}
\]

\[
H_2O \leftrightarrow H^+ + OH^{-} \tag{24}
\]

\[
\text{MnO}_2 + H^+ + e^{-} \leftrightarrow \text{MnOOH \text{ (diffusion controlled)}} \tag{25}
\]

\[
3Zn^{2+} + 6OH^- + \text{Zn(TFSI)}_2 + xH_2O \leftrightarrow \text{Zn(TFSI)}_2[Zn(OH)]_x\cdot xH_2O \tag{26}
\]

Typically, the dissolution of Mn\(^{3+}\) and the generation/decomposition of Zn\(_4\)(OH)\(_4\)_\(_x\)_\(_y\)_\(_x\)_\(_y\)H\(_2\)\(_y\) (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//Mn\(_2\)O\(_4\) battery Equations (27)-(30) and confirmed the capacity contribution from the reversibly formed ZSH\([125]\). As shown in Figure 8G, \(\alpha\)-Mn\(_2\)O\(_4\) (or -MnO\(_2\)) reacted with H\(_2\)O to produce ZSH and Mn\(^{3+}\) in the first discharge process and then ZSH reacted with Mn\(^{3+}\) to form birnessite-Mn\(_2\)O\(_4\) 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$^+$/Zn$^{2+}$ in residual undissolved MnO$_2$ is considered to contribute negligible capacity.

\[
3\text{MnO}_2 + 6\text{H}_2\text{O} + 6e^- \rightarrow 3\text{Mn}^{2+} + 12\text{OH}^- \quad (27)
\]

\[
3\text{Mn}^{2+} + 12\text{OH}^- + 6e^- \rightarrow 3\text{birnessite-MnO}_2 + 6\text{H}_2\text{O} \quad (28)
\]

\[
3\text{birnessite-MnO}_2 + 6\text{H}_2\text{O} + 6e^- \leftrightarrow 3\text{Mn}^{2+} + 12\text{OH}^- \quad (29)
\]

\[
12\text{OH}^- + 2\text{SO}_4^{2-} + 8\text{Zn}^{2+} + 8\text{H}_2\text{O} \leftrightarrow 2\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot 4\text{H}_2\text{O} \quad (30)
\]

**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 Zn$^{2+}$ migration due to the strong electrostatic interactions with the host material, as well as the serious structural transformation during cycling\(^\text{[64]}\). The incorporation of cations (e.g., K$^+$, Na$^+$, Zn$^{2+}$, and 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{41,121,126,127}. Fang et al. synthesized potassium manganate (K$_x$Mn$_3$O$_{4-x}$, KMO) nanorods via the intercalation of K$^+$ into the tunnel cavities and used them as cathode materials for ZIBs\cite{128}. 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{129}. Zhang et al. employed crosslinked vertical multilayer graphene (VMG) arrays as the skeleton for the uniform growth of MnO$_2$ nanosheets\cite{130}. 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$_{2-x}$e@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$_{2-x}$e@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]\cite{131}. The oxidation-induced polymerization of aniline (in CCl$_4$) and the reduction of MnO$_2$$^{2+}$ (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{132}. In addition, the strong electrostatic interaction between Zn$^{2+}$ and the host frameworks leads to the sluggish diffusion of Zn$^{2+}$\cite{133}. 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{134}. Layered MnO$_2$ containing crystal water in the interlayer space (cw-MnO$_2$) was prepared through electrochemical transformation from spinel-Mn$_3$O$_4$ 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$_{0.66}$Mn$_3$O$_4$·1.5H$_2$O) but also promote the intercalation of Zn$^{2+}$ during discharge in ZIBs\cite{135}.

**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{136,137}. 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 [131]. 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 (V₀-MnO₂) as cathode materials for ZIBs[136]. The storage mechanisms of Zn²⁺ in V₀-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 V₀ 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 V₀-MnO₂ rather than pristine MnO₂. As a result, V₀-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 Ni₀.₀₂K₀.₁₁Mn₀.₉₈O₂·0.20₈H₂O (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 Grothuss 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.
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 MnO₂ nanorod-like electrode material synthesized by a hydrothermal method[139]. Cerium doping induced a structural transformation of MnO₂ from its original β-phase to the α-phase, along with the appearance of a [2 × 2] tunnel structure. Its electrochemical properties were investigated using zinc as an anode, 2 M ZnSO₄ and 0.1 M MnSO₄ as an electrolyte, glass fiber as a separator and the prepared materials as the cathode. Compared to β-MnO₂, 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-MnO₂ 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 Zn$^{2+}$ in the two electrode materials. The diffusion coefficient of Zn$^{2+}$ was improved by one to two orders of magnitude for the 0.1 mmol Ce-doped cathode than the β-MnO$_2$ cathode. Moreover, Zhang et al. simultaneously introduced oxygen vacancies and heteroatom doping into MnO$_2$ to form a Ndoped MnO$_{2-x}$ (NMnO$_{2-x}$) branch on the surface TiC/C nanorod array (NMnO$_{2-x}$/TiC/C) for ZIBs [Figure 10F][146]. DFT calculations indicated that the combination of oxygen vacancies and N doping greatly improved the conductivity of MnO$_2$ with a much narrower bandgap (0.1 eV). The electrochemical performance of N-MnO$_{2-x}$/TiC/C was studied in an aqueous solution of 2 M ZnSO$_4$ and 0.2 M MnSO$_4$. The designed NMnO$_{2-x}$/TiC/C electrode showed improved 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-MnO$_{2-x}$/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 MnO$_2$/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 ZIBs[55,60]. Cai et al. demonstrated the feasibility of amorphous MnO$_2$ (A-MnO$_{2-δ}$, δ was estimated to be 0.12) in ZIBs and studied the structural evolution of A-MnO$_{2-δ}$ in 2 M ZnSO$_4$ and 0.2 M MnSO$_4$[141]. In-situ XRD profiles were collected at different states in the second discharge/charge cycle [Figure 10H]. Accordingly, the Zn$^{2+}$ storage in A-MnO$_{2-δ}$ 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-MnO$_{2-δ}$ did not change the amorphous structure or generate a new crystalline structure; (II: 1.3-1.0 V) layered Zn$_2$SO$_4$(OH)$_2$·5H$_2$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 Zn$_2$SO$_4$(OH)$_2$·5H$_2$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-MnO$_{2-δ}$ 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 MnO$_2$ in ZIBs[142-146]. Li et al. anchored MnO$_2$ particles on N-doped hollow carbon spheres (NHCSs@MnO$_2$) via a direct reaction between carbon and KMnO$_4$ [Figure 11A][147]. The hollow porous carbon nanospheres provided large interfaces, thus ensuring the fast transport of ions/electrons. The obtained NHCSs@MnO$_2$ exhibited improved performance for Zn$^{2+}$ storage in 2 M ZnSO$_4$ and 0.1 M MnSO$_4$, with an excellent reversible capacity of ~206 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 conformable MnO$_2$ sheath and rough poly(3, 4-ethylenedioxythiophene) (PEDOT) protective layers were deposited sequentially to form a binder-free CNT/MnO$_2$/PEDOT (CMOP) electrode [Figure 11C][148]. CNT/MnO$_2$ (CMO) was also prepared as a control sample. The PEDOT layers prevented MnO$_2$ from dissolution, which effectively boosted the cycling life of the battery. The electrochemical behavior of MnO$_2$, MnO$_2$/PEDOT, CMO and CMOP was evaluated in 2 M ZnCl$_2$ and 0.4 M 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 MnO$_2$ nanosheets with a V$_4$C$_x$ MXene (K-V$_4$C@MnO$_2$) by K$^+$ intercalation, followed by a hydrothermal growth strategy [Figure 11E][149]. It was found that the adsorbed K$^+$ on the V$_4$C surface facilitated the growth of K-birnessite MnO$_2$, hydrogen bonds existed between
MnO$_2$ (O) and K-V$_2$C (H from functional groups), and the Gibbs free energy of Zn$^{2+}$ adsorption in V,C@MnO$_2$ was lower in comparison with pristine $\delta$-MnO$_2$. The performance of K-V$_2$C@MnO$_2$ was evaluated in 2.0 M ZnSO$_4$ and 0.25 M MnSO$_4$. 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 MnO$_2$ [Figure 11F] \cite{150}. Interestingly, strong Mn-N bonds were found at the interface of MnO$_2$ 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 MnO$_2$ and MnO$_2$/PPy was tested in 2 M ZnSO$_4$ and 0.1 M MnSO$_4$. In comparison with MnO$_2$ (133 mAh g$^{-1}$), MnO$_2$/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 MnO₂ 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 MnO₂. 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 Mn³⁺. In an alkaline solution, a passivation layer of Mn(OH)₂ is generated as a result of the reaction between MnO₂ and \( OH^- \). In a neutral electrolyte, the disproportionation of Mn³⁺ to dissoluble Mn²⁺ is usually observed. Considering the chemical stability of the zinc metal anode, a near-neutral electrolyte is usually selected (e.g., ZnSO₄ aqueous solution) for ZIBs. Three possible mechanisms are proposed: (i) intercalation/deintercalation of Zn²⁺; (ii) co-insertion/extraction of \( H^+ / Zn²⁺ \); and (iii) dissolution-deposition of MnO₂/MnO₄. Although it is still under debate, the charge storage mechanism generally involves the insertion of \( H^+ \) (fast kinetics) to generate MnOOH, the insertion of Zn²⁺ (slow kinetics) to generate Zn,MnO₄, and the irreversible deposition of ZSH on the surface of electrodes. Indeed, the existing works on designing MnO₂ cathodes for ZIBs are very similar to the explorations of MnO₂-based SCs using near-neutral electrolytes (zinc salt-based aqueous electrolyte, e.g., ZnSO₄, ZnCl₂, ZnTFSI or Zn(CF₃SO₃)₂). However, different from the monovalent cations mostly investigated in SCs, Zn²⁺ has a larger hydrated ionic radius, higher desolvation energy barrier and stronger electrostatic interaction with MnO₂, all of which induce complex electrode reactions and structural instability in MnO₂ cathodes for ZIBs.

MnO₂ modification methods
Low electrical conductivity, structural instability and slow electrode reaction kinetics are common issues of MnO₂ as electrodes for energy storage. Based on our summary, similar strategies have been adopted for MnO₂ 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 MnO₂ facilitate the ion intercalation/deintercalation by expanding the interlayer spaces, shield the strong electrostatic interaction between intercalated ions and MnO₂, and stabilize the crystal structure of MnO₂ during ion intercalation/deintercalation. The introduction of oxygen vacancies and heteroatom doping (defect engineering) are effective methods to regulate the electron structure of MnO₂, 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 MnO₂, thus boosting the kinetics of the electrode reaction.

Outlook
Although significant efforts have been devoted to the investigation of MnO₂ for potential applications in SCs and ZIBs and there are several prospective aspects that need to be considered:

(1) MnO₂ 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 MnO₂ 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

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

(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
Preparing 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.

Copyright
© The Author(s) 2022.

REFERENCES
1. Gerard O, Numan A, Krishnan S, Khalid M, Subramaniam R, Kasi R. A review on the recent advances in binder-free electrodes for electrochemical energy storage application. *J Energy Storage* 2022;50:104283. DOI
2. Yu C, Gong Y, Chen R, et al. A solid-state fibriform supercapacitor boosted by host-guest hybridization between the carbon nanotube scaffold and MXene nanosheets. *Small* 2018; e1801203. DOI PubMed
3. Xiao J, Han J, Zhang C, Ling G, Kang F, Yang Q. Dimensionality, function and performance of carbon materials in energy storage devices. *Adv Energy Mater* 2012;12:2100775. DOI
4. Liu Y, Xu J, Li J, et al. Pre-intercalation chemistry of electrode materials in aqueous energy storage systems. *Coord Chem Rev* 2022;460:214477. DOI
5. Shin J, Lee J, Park Y, Choi JW. Aqueous zinc ion batteries: focus on zinc metal anodes. *Chem Sci* 2020;11:2028-44. DOI PubMed PMC
6. Dai H, Zhou J, Qin G, Sun G. Enhanced Jahn-Teller distortion boosts molybdenum trioxide’s superior lithium ion storage capability. *Dalton Trans* 2022;51:524-31. DOI PubMed
7. Dai H, Wang L, Zhao Y, et al. Recent advances in molybdenum-based materials for lithium-sulfur batteries. *Research* 2021;2021:5130420. DOI PubMed PMC
8. Zhang X, Li Z, Luo L, Fan Y, Du Z. A review on thermal management of lithium-ion batteries for electric vehicles. *Energy* 2022;238:121652. DOI
9. Rivera-barrera J, Muñoz-galeano N, Sarmiento-maldonado H. SoC estimation for lithium-ion batteries: review and future challenges. *Electronics* 2017;6:102. DOI
10. Muralidharan N, Self EC, Dixit M, et al. Next-generation cobalt-free cathodes - a prospective solution to the battery industry’s cobalt problem. *Adv Energy Mater* 2022;12:2103050. DOI
11. Li J, Fleetwood J, Hawley WB, Kays W. From materials to cell: state-of-the-art and prospective technologies for lithium-ion battery electrode processing. *Chem Rev* 2022;122:903-56. DOI PubMed
12. Chao D, Zhou W, Xie F, et al. Roadmap for advanced aqueous batteries: from design of materials to applications. *Sci Adv* 2020;6:eaba4098. DOI PubMed PMC
13. Sui Y, Ji X. Anticatalytic strategies to suppress water electrolysis in aqueous batteries. *Chem Rev* 2021;121:6654-95. DOI PubMed
14. Bin D, Wen Y, Wang Y, Xia Y. The development in aqueous lithium-ion batteries. *J Energy Chem* 2018;27:1521-35. DOI
15. Jiang X, Chen Y, Meng X, et al. The impact of electrode with carbon materials on safety performance of lithium-ion batteries: a review. *Carbon* 2022;191:448-70. DOI PubMed PMC
16. Liu K, Liu Y, Lin D, Pei A, Cui Y. Materials for lithium-ion battery safety. *Sci Adv* 2018;4:eaa8920. DOI PubMed PMC
17. Su X, Wu Q, Li J, et al. Silicon-based nanomaterials for lithium-ion batteries: a review. *Adv Energy Mater* 2014;4:1300882. DOI
18. Xie J, Lu YC. A retrogressive on lithium-ion batteries. *Nat Commun* 2020;11:2499. DOI PubMed PMC
19. Yang Z, Zhang J, Kintner-Meyer MC, et al. Electrochemical energy storage for green grid. *Chem Rev* 2011;111:3577-613. DOI PubMed
20. Yong B, Ma D, Wang Y, Mi H, He C, Zhang P. Understanding the design principles of advanced aqueous zinc-ion battery cathodes: from transport kinetics to structural engineering, and future perspectives. *Adv Energy Mater* 2020;10:2002354. DOI
21. Peng J, Zhang W, Wang S, et al. The emerging electrochemical activation tactic for aqueous energy storage: fundamentals, applications, and future. *Adv Funct Mater* 2022;32:2111720. DOI
22. Lee B, Lee HR, Kim H, Chung KY, Cho BW, Oh SH. Elucidating the intercalation mechanism of zinc ions into α-MnO2 for rechargeable zinc batteries. *Chem Commun* 2015;51:9265-8. DOI PubMed
23. Tang Y, Zheng S, Xu Y, Xiao X, Xue H, Pang H. Advanced batteries based on manganese dioxide and its composites. *Energy Stor Mater* 2018;12:284-309. DOI
24. Qian J, Jin H, Chen B, et al. Aqueous manganese dioxide ink for paper-based capacitive energy storage devices. *Angew Chem Int Ed Engl* 2015;54:6800-3. DOI PubMed
25. Pan H, Shao Y, Yan P, et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat Energy 2016;1. DOI
26. Tang B, Shan L, Liang S, Zhou J. Issues and opportunities facing aqueous Zinc-ion batteries. Energy Environ Sci 2019;12:3288-304. DOI
27. Ming J, Guo J, Xia C, Wang W, Alshareef HN. Zinc-ion batteries: materials, mechanisms, and applications. Mater Sci Eng R Rep 2019;135:58-84. DOI
28. Fang G, Zhou J, Pan A, Liang S. Recent advances in aqueous Zinc-ion batteries. ACS Energy Lett 2018;3:2480-501. DOI
29. Dong C, Xu F, Chen L, Chen Z, Cao Y. Design strategies for high-voltage aqueous batteries. Small Struct 2021;2:2100001. DOI
30. Wang F, Wu X, Yuan X, et al. Latest advances in supercapacitors: from new electrode materials to novel device designs. Chem Soc Rev 2017;46:6816-54. DOI PubMed
31. Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ Sci 2014;7:1597. DOI
32. Huang J, Yuan K, Chen Y. Wide voltage aqueous asymmetric supercapacitors: advances, strategies, and challenges. Adv Environ Sci 2022;32:2108107. DOI
33. Wang S, Li T, Yin Y, Chang N, Zhang H, Li X. High-energy-density aqueous zinc-based hybrid supercapacitor-battery with uniform zinc deposition achieved by multifunctional decoupled additive. Nano Energy 2022;96:107120. DOI
34. Li H, Ma L, Han C, et al. Advanced rechargeable zinc-based batteries: recent progress and future perspectives. Nano Energy 2019;62:550-87. DOI
35. Zhang K, Han X, Hu Z, Zhang X, Tao Z, Chen J. Nanostructured Mn-based oxides for electrochemical energy storage and conversion. Chem Soc Rev 2015;44:699-728. DOI PubMed
36. Zhong C, Deng Y, Hu W, Qiao J, Zhang L, Zhang J. A review of electrolyte materials and compositions for electrochemical supercapacitors. Chem Soc Rev 2015;44:7484-539. DOI PubMed
37. He P, Chen Q, Yan M, et al. Building better Zinc-ion batteries: a materials perspective. Energy Chem 2019;1:100022. DOI
38. Lv Y, Xiao Y, Ma L, Zhi C, Chen S. Recent advances in electrolytes for “beyond aqueous” Zinc-ion batteries. Adv Mater 2022;34:e2106409. DOI PubMed
39. Zhou T, Zhu L, Xie L, et al. Cathode materials for aqueous Zinc-ion batteries: a mini review. J Colloid Interface Sci 2022;605:828-50. DOI
40. Gao Y, Zhao L. Review on recent advances in nanostructured transition-metal-sulfide-based electrode materials for cathode materials of asymmetric supercapacitors. Chem Eng J 2022;430:132745. DOI
41. Kumar S, Saeed G, Zhu L, Hui KN, Kim NH, Lee JH. 0D to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: a review. Chem Eng J 2021;403:126352. DOI
42. Hu Y, Wu Y, Wang J. Manganese-oxide-based electrode materials for energy storage applications: how close are we to the theoretical capacitance? Adv Mater 2018;30:e1802569. DOI PubMed
43. Kumar A, Sanger A, Kumar A, Mishra YK, Chandra R. Performance of high energy density symmetric supercapacitor based on sputtered MnO nanorods. ChemistrySelect 2016;1:3885-91. DOI
44. Yu N, Yin H, Zhang W, Liu Y, Tang Z, Zhu M. High-performance fiber-shaped all-solid-state asymmetric supercapacitors based on ultrathin MnO nanosheet/carbon fiber cathodes for wearable electronics. Adv Energy Mater 2016;6:1501458. DOI
45. Radhamani AV, Shareef KM, Rao MS. ZnO@MnO core-shell nanofiber cathodes for high performance asymmetric supercapacitors. ACS Appl Mater Interfaces 2016;8:30531-42. DOI PubMed
46. Zhou D, Lin H, Zhang F, et al. Freestanding MnO nanoflakes/porous carbon nanofibers for high-performance flexible supercapacitor electrodes. Electrochim Acta 2015;161:427-35. DOI
47. Cai K, Luo SH, Feng J, et al. Recent advances on spinel zinc manganate cathode materials for Zinc-ion batteries. Chem Rec 2022;22:e202100169. DOI PubMed
48. Davoglio RA, Cabello G, Marco JF, Biaggio SR. Synthesis and characterization of α-MnO 2 nanoneedles for electrochemical supercapacitors. Electrochim Acta 2018;261:428-35. DOI
49. Guo C, Liu H, Li J, et al. Ultrathin 5-MnO 2 nanosheets as cathode for aqueous rechargeable zinc ion battery. Electrochim Acta 2019;304:370-7. DOI
50. Li Y, Zhang D, Huang S, Yang HY. Guest-species-incorporation in manganese/vanadium-based oxides: towards high performance aqueous Zinc-ion batteries. Nano Energy 2021;85:105969. DOI
51. Zhang Z, Li W, Shen Y, et al. Issues and opportunities of manganese-based materials for enhanced Zn-ion storage performances. J Energy Storage 2022;45:103729. DOI
52. Xie Q, Cheng G, Xue T, et al. Alkali ions pre-intercalation of 5-MnO 2 nanosheets for high-capacity and stable Zn-ion battery. Mater Today Energy 2022;24:100934. DOI
53. Wang M, Zheng X, Zhang X, et al. Opportunities of aqueous manganese-based batteries with deposition and stripping chemistry. Adv Energy Mater 2021;11:2002904. DOI
54. Nam KW, Kim H, Choi JH, Choi JW. Crystal water for high performance layered manganese oxide cathodes in aqueous rechargeable zinc batteries. Energy Environ Sci 2019;12:1999-2009. DOI
55. Wu Y, Fee J, Tobin Z, et al. Amorphous manganese oxides: an approach for reversible aqueous Zinc-ion batteries. ACS Appl Energy Mater 2020;3:1627-33. DOI
supercapacitors. *Electrochim Acta* 2018;290:695–703. DOI
86. Chi HZ, Li Y, Xin Y, Qin H. Boron-doped manganese dioxide for supercapacitors. *Chem Commun* 2014;50:13349–52. DOI PubMed
87. Choi C, Sim HJ, Spinks GM, Lepré X, Baughman RH, Kim SJ. Elasticomeric and dynamic MnO2/CNT core-shell structure coiled yarn supercapacitor. *Adv Energy Mater* 2016;6:1502119. DOI
88. Wang Y, Zhang Y, Gao Y, Sheng G, ten Elshof JE. Defect engineering of MnO2 nanosheets by substitutional doping for printable solid-state micro-supercapacitors. *Nano Energy* 2020;68:104306. DOI
89. Wang J, Wang J, Liu H, et al. A highly flexible and lightweight MnO2/graphene membrane for superior Zinc-ion batteries. *Adv Funct Mater* 2021;31:2007397. DOI
90. Tong H, Li T, Liu J, et al. Fabrication of the oxygen vacancy amorphous MnO2/Carbon nanotube as cathode for advanced aqueous Zinc-ion batteries. *Energy Technol* 2021;9:2000769. DOI
91. Shi J, Wang S, Wang Q, et al. A new flexible Zinc-ion capacitor based on β-MnO2@Carbon cloth battery-type cathode and MXene@Cotton cloth capacitor-type anode. *J Power Sources* 2020;446:227345. DOI
92. Zhao L, Wang W, Zhao H, et al. Controlling oxygen vacancies through gas-assisted hydrothermal method and improving the capacitive properties of MnO2 nanowires. *Appl Surf Sci* 2019;491:24–31. DOI
93. Yan L, Shen C, Niu L, et al. Experimental and theoretical investigation of the effect of oxygen vacancies on the electronic structure and pseudocapacitance of MnO2. *ChemSusChem* 2019;12:3571–81. DOI PubMed
94. Zhai T, Xie S, Yu M, et al. Oxygen vacancies enhancing capacitive properties of MnO2 nanorods for wearable asymmetric supercapacitors. *Nano Energy* 2014;8:255–63. DOI
95. Ou T, Hus C, Hu C. Synthesis and characterization of sodium-doped MnO2 for the aqueous asymmetric supercapacitor application. *J Electrochem Soc* 2015;162:A5124–32. DOI
96. Li J, Ren Y, Wang S, Ren Z, Yu J. Transition metal doped MnO2 nanosheets grown on internal surface of macroporous carbon for supercapacitors and oxygen reduction reaction electrocatalysts. *Appl Mater Today* 2016;3:63–72. DOI
97. Kang J, Hirata A, Kang L, et al. Enhanced supercapacitor performance of MnO2 by atomic doping. *Angew Chem Int Ed Engl* 2013;52:1664–7. DOI PubMed
98. Wang Z, Wang F, Li Y, Hu J, Lu Y, Xu M. Interlinked multiphase Fe-doped MnO2 nanostructures: a novel design for enhanced pseudocapacitive performance. *Nanoscale* 2016;8:7309–17. DOI PubMed
99. Peng R, Wang H, Wei X, Wu Z, Yu P, Luo Y. One-step synthesis of vacancy-rich MnO2-x/reduced graphene oxide composite film for high electrochemical performance. *ChemElectroChem* 2019;6:1122–8. DOI
100. Shi P, Li L, Hua L, et al. Design of amorphous manganese oxide@multiwalled carbon nanotube fiber for robust solid-state supercapacitor. *ACS Nano* 2017;11:444–52. DOI
101. Gou L, Xue D, Mou K, et al. α-MnO2/In2O3 nanotubes as cathode material for aqueous rechargeable Zn-ion battery with high electrochemical performance. *J Electrochem Soc* 2019;166:A3362-8. DOI
102. Zhang J, Li Y, Zhang Y, et al. The enhanced adhesion between overlong TiN/MnO2 nanorays and Ti substrate: towards flexible supercapacitors with high energy density and long service life. *Nano Energy* 2018;43:91–102. DOI
103. Xu J, Sun Y, Lu M, et al. Fabrication of hierarchical MnMoO2·H2O/MnO2 core-shell nanosheet arrays on nickel foam as an advanced electrode for asymmetric supercapacitors. *ChemEng J* 2018;334:1466–76. DOI
104. Shinde PA, Lokhande VC, Patil AM, Ji T, Lokhande CD. Single-step hydrothermal synthesis of WO3–MnO2 composite as an active material for all-solid-state flexible asymmetric supercapacitors. *Int J Hydrog Energy* 2018;43:2869-80. DOI
105. Zhu S, Li L, Liu J, et al. Structural directed growth of ultrathin parallel birnessite on β-MnO2 for high-performance asymmetric supercapacitors. *ACS Nano* 2018;12:1033–42. DOI PubMed
106. Liu N, Su Y, Wang Z, et al. Electrostatic-interaction-assisted construction of 3D networks of manganese dioxide nanosheets for flexible high-performance solid-state asymmetric supercapacitors. *ACS Nano* 2017;11:7879-88. DOI PubMed
107. Zhou J, Yu J, Shi L, et al. A conductive and highly deformable all-pseudocapacitive composite paper as supercapacitor electrode with improved areal and volumetric capacitance. *Small* 2018;14:e1803786. DOI PubMed
108. Chen Q, Meng Y, Hu C, et al. MnO2-modified hierarchical graphene fiber electrochemical supercapacitor. *J Power Sources* 2014;247:32-9. DOI
109. Tan X, Liu S, Guo Q, et al. Synthesis and characterisation of amorphous MnO2/CNT via solid-state microwave for high-performance supercapacitors. *Int J Energy Res* 2020;44:4556-67. DOI
110. Chen Y, Zhang X, Xu C, Xu H. The fabrication of asymmetry supercapacitor based on MWCNT/MnO2/PPy composites. *Electrochim Acta* 2019;28:1025157. DOI
111. Zhang QZ, Zhang D, Miao ZC, Zhang XL, Chou SL. Research progress in MnO2-carbon based supercapacitor electrode materials. *Small* 2018;14:e1702883. DOI PubMed
112. Yu G, Hu L, Vosgueritchian M, et al. Solution-processed graphene/MnO2 nanostructured textiles for high-performance electrochemical capacitors. *Nano Lett* 2011;11:2905–11. DOI PubMed
113. Jia H, Cai Y, Lin J, et al. Heterostructural graphene quantum dot/MnO2 nanosheets toward high-potential window electrodes for high-performance supercapacitors. *Adv Sci* 2018;5:1700887. DOI PubMed PMC
114. Song M, Tan H, Chao D, Fan HJ. Recent advances in Zn-ion batteries. *Adv Funct Mater* 2018;28:1802564. DOI
115. Jia X, Liu C, Neale ZG, Yang J, Cao G. Active materials for aqueous Zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. *Chem Rev* 2020;120:7795-866. DOI PubMed
116. Alfaruqi MH, Gim J, Kim S, et al. Enhanced reversible divalent zinc storage in a structurally stable α-MnO₂ nanorod electrode. J Power Sources 2015;288:320-9. DOI

117. Lee B, Yoon CS, Lee HR, Chung KY, Cho BW, Oh SH. Electrochemically-induced reversible transition from the tunneled to layered polymorphs of manganese dioxide. Sci Rep 2014;4:6066. DOI PubMed PMC

118. Alfaruqi MH, Mathew V, Gim J, et al. Electrochemically induced structural transformation in a γ-MnO₂ cathode of a high capacity zinc-ion battery system. Chem Mater 2015;27:3609-20. DOI

119. Deng Y, Wan L, Xie Y, Qin X, Chen G. Recent advances in Mn-based oxides as anode materials for lithium ion batteries. RSC Adv 2014;4:23914-35. DOI

120. Li F, Liu Y, Wang G, et al. The design of flower-like C-MnO₂ nanosheets on carbon cloth toward high-performance flexible Zinc-ion batteries. J Mater Chem A 2021;9:9675-84. DOI

121. Liu G, Huang H, Bi R, Xiao X, Ma T, Zhang L. K⁺ pre-intercalated manganese dioxide with enhanced Zn²⁺ diffusion for high rate and durable aqueous Zinc-ion batteries. J Mater Chem A 2019;7:20806-12. DOI

122. Liu M, Zhao Q, Liu H, et al. Tuning phase evolution of β-MnO₂ during microwave hydrothermal synthesis for high-performance aqueous Zn ion battery. Nano Energy 2019;64:103942. DOI

123. Li G, Huang Z, Chen J, et al. Rechargeable Zn-ion batteries with high power and energy densities: a two-electron reaction pathway in birmesite MnO₂ cathode materials. J Mater Chem A 2020;8:1975-85. DOI

124. Jin Y, Zou L, Liu L, et al. Joint charge storage for high-rate aqueous zinc-manganese dioxide batteries. Adv Mater 2019;31:e1900567. DOI PubMed

125. Guo X, Zhou J, Bai C, Li X, Fang G, Liang S. Zn/MnO₂ battery chemistry with dissolution-deposition mechanism. Mater Today Energy 2020;16:100396. DOI

126. Peng H, Fan H, Yang C, Tian Y, Wang C, Sui J. Ultrathin δ-MnO₂ nanoflakes with Na⁺ intercalation as a high-capacity cathode for aqueous Zinc-ion batteries. RSC Adv 2020;10:17702-12. DOI

127. Sun T, Nian Q, Zheng S, Shi J, Tao Z. Layered Ca₀.₃₉MnO₂·0.₅H₂O as a high performance cathode for aqueous Zinc-ion battery. Small 2020;16:e2000597. DOI

128. Fang G, Zhu C, Chen M, et al. Suppressing manganese dissolution in potassium manganate with rich oxygen defects engaged high-energy-density and durable aqueous Zinc-ion battery. Adv Funct Mater 2019;29:1808375. DOI

129. Zhai T, Wan L, Sun S, et al. Phosphate ion functionalized Co₃O₄ ultrathin nanosheets with greatly improved surface reactivity for high performance pseudocapacitors. Adv Mater 2017;29:1604167. DOI

130. Zhang Y, Deng S, Pan G, et al. Introducing oxygen defects into phosphate ions intercalated manganese dioxide/virtual multilayer graphene arrays to boost flexible Zinc ion storage. Small Methods 2020;4:1900828. DOI

131. Huang J, Wang Z, Hou M, et al. Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous Zinc-ion battery. Nat Commun 2018;9:2906. DOI PubMed PMC

132. Zhang Q, Yang Z, Ji H, et al. Issues and rational design of aqueous electrolyte for Zn-ion batteries. SusMat 2021;1:432-47. DOI

133. Wang D, Wang L, Liang G, et al. A superior δ-MnO₂ cathode and a self-healing Zn-δ-MnO₂ battery. ACS Nano 2019;13:10643-52. DOI

134. Han M, Huang J, Liang S, et al. Oxygen defects in β-MnO₂ enabling high-performance rechargeable aqueous zinc/manganese dioxide battery. SciAdv 2020;23:100797. DOI PubMed PMC

135. Zhao J, Xu Z, Zhou Z, et al. A safe flexible self-powered wristband system by integrating defective MnO₂₄ nanosheet-based Zinc-ion batteries with perovskite solar cells. ACS Nano 2021;15:10597-608. DOI PubMed

136. Xiong T, Yu ZG, Wu H, et al. Defect engineering of oxygen-deficient manganese oxide to achieve high-performing aqueous Zinc ion battery. Adv Energy Mater 2019;9:1803815. DOI

137. Xiong T, Lee WSV, Xue J. K⁺-intercalated MnO₂ electrode for high performance aqueous supercapacitor. ACS Appl Energy Mater 2018. DOI

138. Zhao Q, Song A, Zhao W, et al. Boosting the energy density of aqueous batteries via facile gravthuss proton transport. Angew Chem Int Ed Engl 2021;60:4169-74. DOI

139. Wang J, Sun X, Zhao H, et al. Superior-performance aqueous Zinc ion battery based on structural transformation of MnO₂ by rare earth doping. J Phys Chem C 2019;123:22735-41. DOI

140. Zhang Y, Deng S, Luo M, et al. Defect promoted capacity and durability of N-MnO₂₄ branch arrays via low-temperature NH₃ treatment for advanced aqueous Zinc ion batteries. Small 2019;15:e1905452. DOI

141. Cai Y, Chua R, Huang S, Ren H, Srinivasan M. Amorphous manganese dioxide with the enhanced pseudocapacitive performance for aqueous rechargeable Zinc-ion battery. Chem Eng J 2020;396:125221. DOI

142. Chen X, Li W, Zeng Z, Reed D, Li X, Liu X. Engineering stable Zn-MnO₂ batteries by synergistic stabilization between the carbon nanofiber core and birmesite-MnO₂ nanosheets shell. Chem Eng J 2021;405:126969. DOI

143. Wu F, Gao X, Xu X, et al. MnO₂ nanosheet-assembled hollow polyhedron grown on carbon cloth for flexible aqueous Zinc-ion batteries. ChemSusChem 2020;13:1537-45. DOI PubMed

144. Long J, Yang F, Cuan J, et al. Boosted charge transfer in twinborn α-(Mn₂O₃·MnO₂) heterostructures: toward high-rate and ultralong-life Zinc-ion batteries. ACS Appl Mater Interfaces 2020;12:32526-35. DOI

145. Chen J, Cheng F. Combination of lightweight elements and nanostructured materials for batteries. ACC Chem Res 2009;42:713-23. DOI PubMed
146. Ling W, Wang P, Chen Z, et al. Nanostructure design strategies for aqueous Zinc-ion batteries. *ChemElectroChem* 2020;7:2957-78. DOI

147. Li D, Gao Q, Zhang H, et al. MnO₂ particles grown on the surface of N-doped hollow porous carbon nanospheres for aqueous rechargeable zinc ion batteries. *Appl Surf Sci* 2020;510:145458. DOI

148. Zhang X, Wu S, Deng S, et al. 3D CNTs networks enable MnO₂ cathodes with high capacity and superior rate capability for flexible rechargeable Zn-MnO₂ batteries. *Small Methods* 2019;3:1900525. DOI

149. Zhu X, Cao Z, Wang W, et al. Superior-performance aqueous zinc-ion batteries based on the in situ growth of MnO₂ nanosheets on V₃CT, MXene. *ACS Nano* 2021;15:2971-83. DOI

150. Huang J, Tang X, Liu K, Fang G, He Z, Li Z. Interfacial chemical binding and improved kinetics assisting stable aqueous Zn-MnO₂ batteries. *Mater Today Energy* 2020;17:100475. DOI