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Application of Manganese-Based Materials in Aqueous Rechargeable Zinc-Ion Batteries

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In recent years, aqueous rechargeable zinc-ion batteries (AZIBs) have attracted more and more attention not only because they use earth-abundant metals but also due to their improved safety and high volumetric energy density. As one type of promising electrode material for AZIBs, manganese-based materials are receiving considerable attention owing to their high theoretical specific capacity, non-toxicity, and low cost. This mini review summarizes the recent advances on the application of manganese-based materials (manganese oxide, manganate, and their composites) in AZIBs. In addition, the methods to enhance their zinc-ion storage properties are summarized and discussed, such as morphology engineering, doping, as well as compositing with other materials. Ultimately, some personal prospects for future research of the manganese-based materials for AZIBs are also proposed.

Keywords: manganese oxide, manganate, cathode materials, zinc-ion batteries, aqueous electrolyte

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INTRODUCTION

In recent years, overconsumption of fossil fuels has caused many problems, such as global warming and environmental deterioration, which have been paid more and more attention by people all over the world (Liu et al., 2016, 2019c,d; He et al., 2017; Ma et al., 2017; Chen et al., 2019a; Guo et al., 2019c; Pan et al., 2020). Renewable energies like solar and wind energy are regarded as clean and sustainable ways to solve these issues. However, the intermittent nature of solar and wind energies greatly hinder their further development (Wang et al., 2019c; Xiao et al., 2019; Yuan et al., 2019; Zhao X. et al., 2019; Cheng et al., 2020; Ma J. Q. et al., 2020). Fortunately, electrochemical energy storage (EES) devices are regarded as a promising solution which could store electric energy obtained from renewable energies (Ding et al., 2018; Chen et al., 2019b; Li Y. et al., 2019; Li J. et al., 2020; Li Y. et al., 2020; Zhang et al., 2019; Ma J. Y. et al., 2020; Wang R. et al., 2020; Wang W. et al., 2020). Among various EES devices, lithium-ion batteries have been intensively investigated and used in many applications such as portable electronics, electrical vehicles, and smart grids due to their high energy density, long cycle life, and environmental benignity (Wang F. et al., 2018; Wang F. et al., 2020; Wang G. et al., 2020; Hao et al., 2019; Liu et al., 2019f; Wu et al., 2019; Zhao Q. et al., 2019; Gao G. J. et al., 2020; Song et al., 2020; Zou et al., 2020). Nevertheless, the increasing concerns about limited lithium resources, high cost, and safety issue strongly limit their further development for large-scale

applications (Liu et al., 2018; Ma X. D. et al., 2019; Wang et al., 2019d; Yixuan et al., 2020; Yu et al., 2020; Zhang et al., 2020). In addition, the other alkali metals, Na and K, are extremely reactive and the introduced organic electrolytes are flammable, which bring great security risks for sodium-ion and potassium-ion batteries (Song et al., 2018; Ding et al., 2019; Hua et al., 2019). Therefore, it is urgent to explore alternative battery systems with low cost, high safety, and long cycle life.

Aqueous rechargeable zinc-ion batteries (AZIBs), in particular, comprise of a zinc metal anode, the aqueous electrolyte in majority, and a cathode for accommodation of Zn ions. Significantly, it differs from the traditional alkaline Zn battery (such as Zn-Mn or Ni-Zn battery) which is based on dissolution/precipitation reactions at the Zn anode and H^+ intercalation/extraction reactions at the cathode. Also, it is also distinguished from other batteries with Zn anode but no intercalation of Zn ions in cathode reactions (Kordesh and Weissenbacher, 1994; Song et al., 2018). Nowadays, AZIBs have attracted more and more attention not only because they use earth-abundant metals but also due to their improved safety and high volumetric energy density (Chen et al., 2017; Song et al., 2018). As a typical type of cathode materials for AZIBs, manganese-based materials are receiving considerable attention in recent years owing to their high theoretical specific capacity, non-toxicity, and low cost (**Figures 1A,B**). For instance, Wu et al. (2018) recently reported an article about α-MnO_2 coated with graphene as a high-performance cathode material for AZIBs. By a simple hydrothermal method, Zhu et al. (2018) fabricated a flower-like Mn_3O_4 and used it as a cathode material of AZIBs. And Wan and Niu (2019) reviewed the design strategies of vanadium-based materials for AZIBs. However, there is still a lack of review to exclusively cover the state-of-the-art developments of manganese-based materials for AZIBs.

Herein, we will give an overview on manganese-based materials, mainly including manganese oxide, manganate, as well as their composite materials, and their application in the field of electrode materials for AZIBs. Their micro/nanostructures and electrochemical properties are systematically summarized. Furthermore, some reasonable suggestions to promote future breakthroughs were also presented.

MANGANESE-BASED MATERIALS FOR AQUEOUS RECHARGEABLE ZINC-ION BATTERIES

The electrochemical performances of manganese-based materials, such as manganese oxide, manganate, and their composites, as cathode materials for AZIBs are summarized in **Table 1**. The zinc-ion storage properties of manganese-based materials combined with carbon-based materials are significantly superior than those of pure manganese-based materials.

Manganese Oxide

Since manganese has a variety of valence states, it could form a series of manganese oxides, such as MnO_2 (Alfaruqi et al., 2016), Mn_3O_4 (Zhu et al., 2018), etc. Due to their special structure, they could be used as cathode materials for AZIBs (Khamsanga et al., 2019; Palaniyandy et al., 2019).

Manganese Dioxide

Manganese dioxide has a variety of crystal structures, such as α-MnO_2 (Wu et al., 2018), β-MnO_2 (Zhang et al., 2017), γ-MnO_2 (Alfaruqi et al., 2015c), δ-MnO_2 (Khamsanga et al., 2019), etc., which are composed of the basic structural unit MnO_6 octahedral into chain/tunnel/layered structure by sharing angle/edge and have been well applied in AZIBs (Song et al., 2018; Tang et al., 2019). However, the low electronic conductivity of MnO_2 and large volume change of electrode during Zn^{2+} insertion/extraction process hinder the further development of MnO_2 as the cathode material for AZIBs (Tang et al., 2019). At present, many researchers are devoted to improve the electronic conductivity of MnO_2 and the cycling stability of MnO_2-based AZIBs (Wu et al., 2018; Tang et al., 2019).

α-MnO_2, which have stable 2 × 2 tunnel structure, has received considerable attention in recent years as a cathode material for AZIBs (**Figure 1C**; Palaniyandy et al., 2019; Gao X. et al., 2020). In 2009, α-MnO_2 was first applied as a cathode material for AZIBs, and specific capacity reached 210 mAh g^{-1} at 0.2 A g^{-1} (Xu et al., 2009). Pan et al. (2016) added $MnSO_4$ into $ZnSO_4$ electrolyte to suppress the dissolution of Mn^{2+} and stabilize the electrode. During the discharging process, Zn^{2+} and H^+ co-inserted into α-MnO_2, generating $ZnSO_4[Zn(OH)_2]_3.xH_2O$ and MnOOH, from which Zn^{2+} and H^+ could reversibly extract in the charging process. And these Zn/α-MnO_2 batteries show excellent rate capability and high capacity retention of 92% after 5,000 cycles. To further enhance the zinc-ion storage properties of α-MnO_2, Wu et al. (2018) fabricated α-MnO_2 nanowires coated with graphene (MGS) by hydrothermal method (**Figure 1D**). The graphene not only increases the electronic conductivity of the material but also effectively inhibits the erosion of the electrolyte to electrode. During discharge and charging, the insertion of Zn^{2+} takes place in two steps, First, Zn^{2+} inserted into water layers and formed zinc-buserite, then continued to be inserted into 2 × 2 tunnels of α-MnO_2 (**Figure 1E**). These detailed studies provide a good theoretical basis for α-MnO_2 in AZIBs.

Compared with other manganese dioxide phases, β-MnO_2 has the narrowest tunnel and minimal channel. The 1 × 1 tunnel (2.3 × 2.3 Å) of the β-MnO_2 hardly incorporates Zn^{2+} inserting (**Figure 1F**; Devaraj and Munichandraiah, 2008; Islam et al., 2017a; Zhang et al., 2017). However, β-MnO_2 has high thermodynamic stability. Therefore, it has also been reported as a cathode material for AZIBs. For instance, Islam et al. (2017a) synthesized β-MnO_2 nanorods exposed to (101) plane by a microwave-assisted hydrothermal method and used them as cathode materials for AZIBs. By a combination of *in situ* synchrotron, *ex situ* X-ray diffraction (XRD), and other techniques, the Zn-ion storage mechanism has revealed that the reaction mechanism of the β-MnO_2 nanorod electrode in the Zn cell proceeded *via* a combination of solid solution and conversion reactions, in which Zn ion intercalated into the β-MnO_2 framework, followed by the formation of Zn-inserted phases along with the precipitation of $ZnSO_4{\cdot}3Zn(OH)_2.5H_2O$

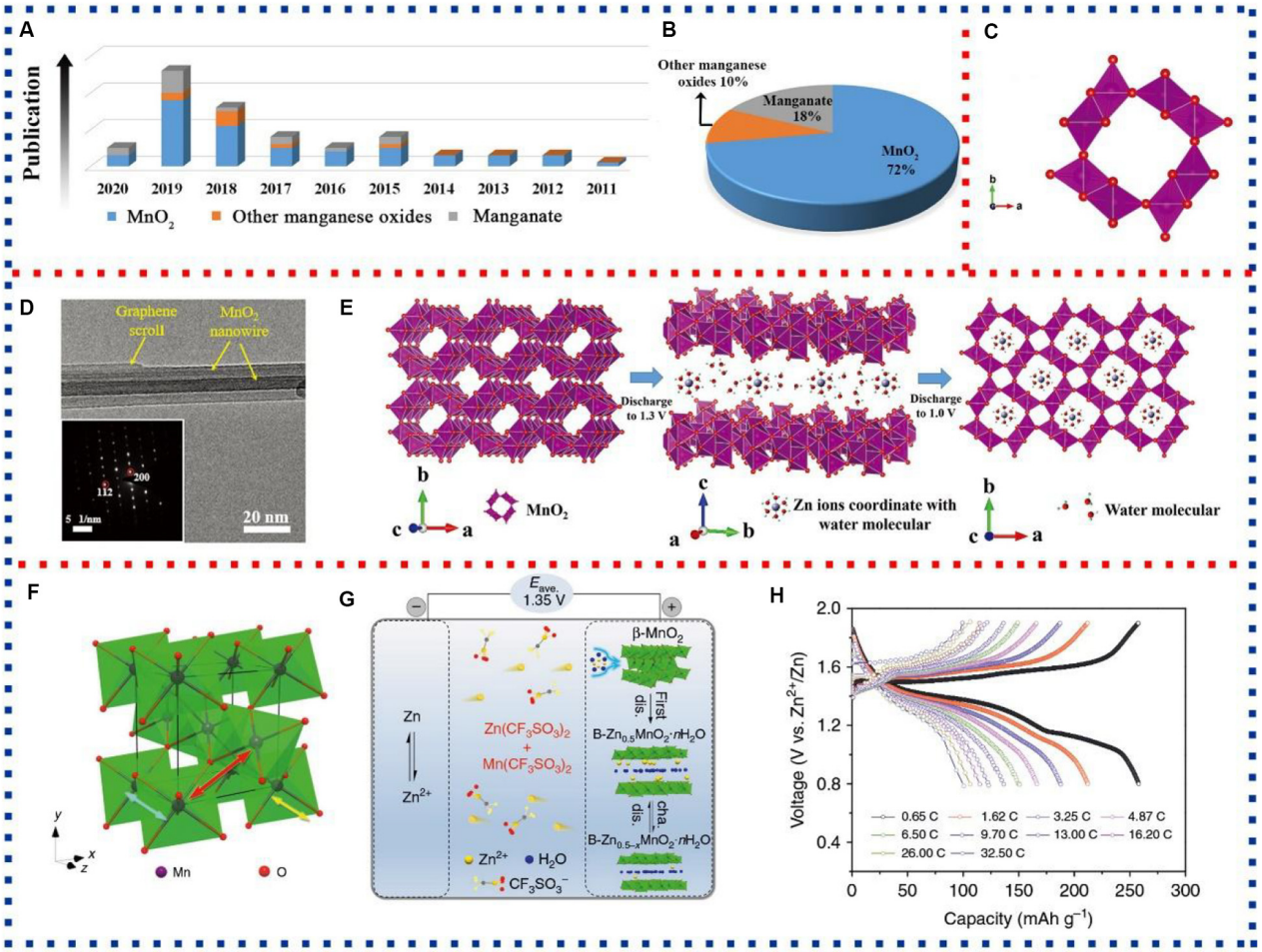

FIGURE 1 | (A) The statistical table of manganese-based materials reported in aqueous rechargeable zinc-ion batteries (AZIBs). **(B)** The percentage of different manganese-based materials reported in AZIBs. **(C)** Schematic diagram of α-MnO_2 crystal structure. **(D)** Transmission electron microscopy (TEM) and corresponding selected area electron diffraction (SAED) of α-MnO_2/graphene scrolls (MGS). **(E)** Schematic diagram of zinc ions inserting into the MGS electrode in two steps. **(F)** Schematic diagram of β-MnO_2 crystal structure. **(G)** Schematic diagram of the Zn/β-MnO_2 batteries with β-MnO_2 as cathode, $Zn(CF_3SO_3)_2$ add $Mn(CF_3SO_3)_2$ as electrolyte. **(H)** Discharge/charge profiles of Zn/β-MnO_2 batteries. **(C)** Reprinted with permission (Gao X. et al., 2020). Copyright 2020, WILEY-VCH. **(D,E)** Reprinted with permission (Wu et al., 2018). Copyright 2018, WILEY-VCH. **(F–H)** Reprinted with permission (Zhang et al., 2017). Copyright 2017, Springer Nature.

on the electrode surface. And the electrode shows a high discharge capacity of 270 mA h g^{-1} at 0.1 A g^{-1}. Similarly, Zhang et al. (2017) synthesized β-MnO_2 nanorods by a hydrothermal method and took 3 M $Zn(CF_3SO_3)_2$ with 0.1 M $Mn(CF_3SO_3)_2$ as electrolyte. As shown in **Figure 1G**, during the initial discharge, a phase transformed from tunneled structure to layered structure (Zn-buserite) and followed by reversible Zn^{2+} (de)intercalation in the H_2O-containing Zn-buserite framework. Mn^{2+} dissolution can be effectively inhibited by the addition of $Mn(CF_3SO_3)_2$ in which the amorphous MnO_x *in situ* generated on the electrode surface. The electrode showed excellent rate performance, which maintained 100 mAh g^{-1}, even the current density reached 32.5 C (**Figure 1H**).

Comprised of randomly arranged 1 × 1 (size ∼ 2.3 × 2.3 Å, pyrolusite) and 1 × 2 (size ∼2.3 × 4.6 Å, ramsdellite) tunnels, γ-MnO_2 is suitable for Zn^{2+} intercalation/deintercalation. In 2003, Kumar and Sampath (2003) first applied γ-MnO_2 as the positive electrode for AZIBs. Subsequently, various γ-MnO_2 were reported and used as cathode materials for AZIBs. For example, Alfaruqi et al. (2015c) prepared tunnel mesoporous γ-MnO_2 by simple redox reaction. As shown in **Supplementary Figure S1C**, during the discharge process, the tunnel-type γ-MnO_2 transformed to three phases ($ZnMn_2O_4$, γ-Zn_xMnO_2, and L-Zn_yMnO_2), which was accompanied that Mn^{4+} was reduced to Mn^{3+} and Mn^{2+}, respectively.

δ-MnO_2 is considered to be a favorable host for Zn^{2+} due to its unique layered structure (the interlayer spacing can reach up to 7.0 Å) (Corpuz et al., 2019; Guo et al., 2019b). Compared with α-MnO_2, β-MnO_2, and γ-MnO_2, another advantage of δ-MnO_2 is that there is no phase transition during Zn^{2+} insertion or extraction, which could prevent the capacity fading effectively. However, unstable structure during the cycling limits its further application. At present, refine grain (Han et al., 2017; Guo et al., 2019a), synthetized special

TABLE 1 | Electrochemical performance of manganese-based materials as cathode materials for AZIBs.

Material	Current density ($A\ g^{-1}$)	Cycle number (n)	Voltage window (V)	Initial capacity ($mAh\ g^{-1}$)	Post-cycle capacity ($mAh\ g^{-1}$)	References
MnO_2 powder	1.0	50	–	~171	~171	Xu et al., 2009
α-MnO_2	1.26	100	1.0–1.9	~135	~100	Xu et al., 2012
α-MnO_2	0.1	50	0.8–1.8	~	96.8	Guo et al., 2020
α-MnO_2 nanorods	0.083	50	1.0–1.8	233	~160	Alfaruqi et al., 2015b
MnO_2/a-CNT	5.0	500	1.0–1.9	~110	~100	Xu et al., 2014
α-MnO_2 nanorods	0.083	75	1.0–1.8	190	104	Alfaruqi et al., 2016
α-MnO_2	1.3	5,000	–	~100	~92	Pan et al., 2016
MnO_2@C	0.066	50	1.0–1.8	~220	189	Islam et al., 2017b
MGS	3.0	3,000	1.0–1.85	154.6	145.3	Wu et al., 2018
MnO_2	1.0	1,000	0.8–1.8	157.6	134	Zhao K. et al., 2018
MnO_2	0.1	50	1.0–1.8	~225	97	Alfaruqi et al., 2018
MnO_2	1.0	100	1.0–1.8	~280	~220	Liu et al., 2019a
α-MnO_2@In_2O_3	3.0	1,300	–	~60	75	Gou et al., 2019
Ti-MnO_2 NWs	1.0	4,000	–	~175	~145	Lian et al., 2019
α-$K_{0.07}MnO_2$	1.54	400	0.8–1.9	~170	180	Liu et al., 2019b
α-MnO_2/OLC	0.246	100	1.0–1.8	181	168	Palaniyandy et al., 2019
α-MnO_2	0.3	100	0.9–1.9	62	103	Poyraz et al., 2019
α-MnO_2	0.1	300	0.9–1.8	240	140	Gao X. et al., 2020
β-MnO_2 nanorods	0.1	50	1.0–1.8	~270	~150	Islam et al., 2017a
β-MnO_2	–	2,000	0.8–1.9	144	135	Zhang et al., 2017
D-β-MnO_2	0.5	300	0.8–1.8	225	200	Han et al., 2020
MnO_2@CC	2.0	700	1.0–1.8	~100	~90	Deng et al., 2019
β-MnO_2	0.1	100	1.0–1.8	100	~105	Guo et al., 2019b
D-β-MnO_2	0.5	300	0.8–1.8	~210	~200	Han et al., 2020
Ce-MnO_2	1.54	100	1.0–1.8	134	~78	Wang et al., 2019a
MnO_2- graphene	10	300	0.8–1.8	~100	~64	Wang C. et al., 2020
γ-MnO_2	–	40	0.8–1.8	~160	~158	Alfaruqi et al., 2015c
δ-MnO_2	0.1	100	1.0–1.8	126	96	Guo et al., 2019b
δ-MnO_2	0.083	100	1.0–1.8	122	112	Alfaruqi et al., 2015a
δ-MnO_2-HN	–	100	1.0–1.8	168	~305	Guo et al., 2018
δ-MnO_2-NS	0.1	100	1.0–1.8	126	133	Guo et al., 2019a
δ-MnO_2	0.1	150	0.4–1.9	–	~45	Kao-ian et al., 2019
δ-MnO_2-NFG	0.4	100	1.0–1.8	230	113.4	Khamsanga et al., 2019
MnO_2@CFP	1.885	10,000	1.0–1.8	50	70	Sun et al., 2017
$Mg_{1.8}Mn_6O_{12}.4.8H_2O$	0.05	50	0.7–2.0	98	~85	Lee et al., 2013
V-MnO_2	0.066	100	1.0–1.8	260	~130	Alfaruqi et al., 2017
P-MnO_2	0.2	200	1.0–1.8	~290	280	Huang et al., 2018
MBC	4.0	2,000	1.0–1.85	~130	~120	Qiu et al., 2018b
MnO_2-birnessite	2.0	2,000	1.0–1.8	164	134	Qiu et al., 2018a
MnO_2/CNT	0.155	100	1.0–1.8	~200	145	Zhao L. et al., 2018
MnO_2 nanospheres	3.0	2,000	1.0–1.85	124	~80	Wang et al., 2019b
α-Mn_2O_3	2.0	1,000	1.0–1.9	73.6	82.2	Jiang et al., 2017
MnO_x@N-C	2.0	1,600	0.8–1.8	~100	100	Fu et al., 2018
Mn_3O4	0.5	300	0.8–1.9	~45	~100	Hao et al., 2018
SSWM@Mn_3O_4	0.5	500	1.0–1.8	~120	~130	Zhu et al., 2018
Mn_5O_8/NCm	0.2	110	1.0–1.8	~300	~150	Li D.-S. et al., 2019
Mn_2O_4/Mn_2O_3	0.5	300	0.8–1.9	82.6	~105	Yang et al., 2019
C-MnO	1.0	1,500	0.8–1.8	117.2	116.4	Zhu et al., 2020
ZMO/C	0.5	50	0.8–2.0	~90	~80	Zhang et al., 2016
H-$ZnMn_2O_4$	0.1	300	0.8–1.9	~85	~100	Wu et al., 2017
KMn_8O_{16}	0.1	100	0.8–1.9	~130	77	Cui et al., 2018
$ZnMn_2O_4$/NG	1.0	2,500	0.8–1.8	76	74	Chen et al., 2019c

(Continued)

TABLE 1 | Continued

Material	Current density ($A\ g^{-1}$)	Cycle number (n)	Voltage window (V)	Initial capacity ($mAh\ g^{-1}$)	Post-cycle capacity ($mAh\ g^{-1}$)	References
$Zn_{1.67}Mn_{1.33}O_4$	0.1	40	0.8–1.9	∼310	175	Lee et al., 2019
ZNCMO@N-rGO	1.0	900	0.7–1.7	∼30	∼100	Tao et al., 2020
LMO-GN-CNT CNT	0.296	600	1.4–2.1	112	93	Yuan et al., 2020

AZIBs, aqueous rechargeable zinc-ion batteries; MnO_2/a-CNT, the rod-like manganese dioxide/acid-treated carbon nanotube (a-CNT) nanocomposites; MnO_2@C, carbon-coated α-MnO_2 nanoparticles; MGS, α-MnO_2/graphene scrolls; Ti-MnO_2 NWs, Ti-MnO_2 nanowires; α-MnO_2/OLC, onion-like carbon integrated α-MnO_2 nanorods; MnO_2@CC, β-MnO_2 nanolayer coated on carbon cloth; D-β-MnO_2, β-MnO_2 with rich oxygen defects; Ce-MnO_2, Ce-doped MnO_2 nanorod; MnO_2-graphene, γ-MnO_2-graphene composite; δ-MnO_2-HN, hollow-structured δ-MnO_2; δ-MnO_2-NS, δ-MnO_2 nanosheets; δ-MnO_2-NFG, δ-MnO_2 nanoflower/graphite composite; V-MnO_2, V-doped MnO_2; P-MnO_2, polyaniline-intercalated MnO_2; MBC, manganese-based complex; MnO_2/CNT, MnO_2/carbon nanotube composites; MnO_x@N-C, porous MnOx nanorods coated by N-doped carbon; SSWM@Mn_3O_4, stainless steel welded mesh@flower-like Mn_3O_4; Mn_5O_8/NCm, Mn_5O_8/N-doped carbon composites; ZMO/C, $ZnMn_2O_4$ with carbon composite; H-$ZnMn_2O_4$, hollow porous $ZnMn_2O_4$; ZNCMO@N-rGO, nickel and cobalt co-substituted $ZnMn_2O_4$ with N-doped reduced graphene oxide composites; LMO-GN-CNT, $LiMn_2O_4$-graphene carbon nanotubes composite with the cross-linked conductive graphene; D-β-MnO_2, β-MnO_2 with oxygen defects; C-MO, carbon-coated MnO.

morphology (Alfaruqi et al., 2015a; Guo et al., 2018), and add structural stabilizer (Kao-ian et al., 2019) are common ways to improve the performance of δ-MnO_2. For instance, Guo et al. (2019a) synthesized δ-MnO_2 nanosheets with a thickness of 2–4 nm by reduction of $KMnO_4$. During the initial discharge process, H^+ inserted into the δ-MnO_2, followed by co-insertion of Zn^{2+} and H^+. Ultrathin nanosheets shortened the diffusion path of Zn^{2+} and H^+ and improved the ion diffusion coefficient. The Zn/δ-MnO_2 cells still showed 86 $mAh\ g^{-1}$ at 0.5 $A\ g^{-1}$, which show excellent cycle stability.

ε-MnO_2 with face-shared MnO_6 and YO_6 octahedra (Y denotes vacancy) structure was also reported in AZIBs (Sun et al., 2017; Song et al., 2018). For instance, Sun et al. (2017) deposited MnO_2 on the carbon fiber paper with no binder is required (**Supplementary Figure S1E**). They first reported that during the discharge process, H^+ and Zn^{2+} inserting corresponded to the generating of MnOOH and $ZnMn_2O_4$, respectively, in AZIBs.

Other manganese dioxides, such as λ-MnO_2 and todorokite-type MnO_2, have also been reported in AZIBs (Lee et al., 2013; Yuan et al., 2014). In 2014, Yuan et al. (2014) removed Li from $LiMn_2O_4$ with H_2SO_4 and synthesized λ-MnO_2. The Zn/λ-MnO_2 cell displayed 442.6 $mAh\ g^{-1}$ at 13.8 $mA\ g^{-1}$. Lee et al. (2013) turned Na-birnessite into Mg-containing solution and synthesized $Mg_{1.8}Mn_6O_{12}.4.8H_2O$ with todorokite-type structure. The cell could deliver specific capacity of 108 $mAh\ g^{-1}$ at 0.5 C (1 C = 255 $mA\ g^{-1}$).

Other Manganese Oxides

In addition to manganese dioxide, other manganese oxides such as Mn_3O_4 (Hao et al., 2018; Zhu et al., 2018), Mn_2O_3 (Jiang et al., 2017), and others (Fu et al., 2018) are also widely studied in AZIBs.

Mn_2O_3 is an alternative cathode material for AZIBs. In 2017, Jiang et al. (2017) first reported α-Mn_2O_3 as the cathode material of AZIBs. The α-Mn_2O_3 has a bixbyite structure. In this structure, the Mn^{3+} ions are in octahedral coordination and each oxygen ion is surrounded by four Mn ions. During the discharge process, the Mn^{3+} of Mn_2O_3 was reduced to Mn^{2+}, accompanied the generation of $Zn_xMn_2O_3$ without other phases generated. Based on this property, after 2,000 cycles, the α-Mn_2O_3 displays a reversible discharge capacity of 38 $mAh\ g^{-1}$ at 2 $A\ g^{-1}$.

Mn_3O_4 has a mixed valence state of +2 and +3, in which Mn^{2+} occupies the tetrahedral gap and Mn^{3+} occupies the octahedral gap. Inspired by multiple Mn valences may contribute to the diffusivity and migration of Zn^{2+} (Zhang et al., 2016; Ma J. L. et al., 2020). Zhu et al. (2018) synthesized a flower-like Mn_3O_4 on stainless steel welded mesh (SSWM@Mn_3O_4) *via* a one-step hydrothermal method (**Supplementary Figures S1A,B**). They used *ex situ* XRD and *ex situ* scanning electron microscope to reveal the structure and morphology evolution of SSWM@Mn_3O_4 electrode. During the discharge process, Mn^{3+} is reduced to Mn^{2+} and exists in the form of MnO after discharge. The $ZnSO_4$ and H_2O in the aqueous electrolyte react with the sequent OH^- ions to form large flake-like $ZnSO_4[Zn(OH)_2]_3.5H_2O$. Due to the intimate contact between the material and current collector, the SSWM@Mn_3O_4 electrode shows great stability with higher than 100 $mAh\ g^{-1}$ capacity at 0.1 $A\ g^{-1}$ after 500 cycles.

In addition to the manganese oxides described above, some non-stoichiometric manganese oxides were also reported in AZIBs. For instance, Fu et al. (2018) synthesized N-doped carbon porous MnO_x nanorods (MnO_x@N-C) by using metal organic framework (MOF) materials. Amorphous carbon and onion-like nitrogen-doped carbon on the surface formed an electronic conductive network, which not only improves the electron conductivity but also alleviates the volume change caused by the insertion or extraction of Zn^{2+}. Benefiting from the special structure, the electrode still could deliver 305 $mAh\ g^{-1}$ after 600 cycles at 0.5 $A\ g^{-1}$.

Manganate

Manganate is an important component of manganese-based materials. Some manganates are investigated as cathode materials for AZIBs, such as $LiMn_2O_4$ (Wu et al., 2015), $ZnMn_2O_4$ (Zhang et al., 2016; Wu et al., 2017; Chen et al., 2019c), KMn_8O_{16} (Cui et al., 2018), and their derivatives (Tao et al., 2020).

Benefiting from the low cost, non-toxicity, easy fabrication, and high safety, $LiMn_2O_4$ has been well studied as a positive electrode material for lithium-ion batteries. Recently, this material has been also reported in AZIBs. For instance, Wu et al. (2015) investigated the effect of thiourea as the electrolyte additive on the electrochemical performance of AZIBs, using

$LiMnO_4$ as a cathode material. Similarly, $LiMnO_4$ was also applied as a cathode material for AZIBs by Hoang et al. (2017) to study the suppression of zinc dendrite growth, in which pyrazole was used as an additive for the electrolyte.

Zhang et al. (2016) fabricated non-stoichiometric $ZnMn_2O_4$/carbon composite and applied it as a cathode material for AZIBs. They found the unoccupied octahedral sites (8c) of the $ZnMn_2O_4$ have cation vacancies, which can provide additional pathways for Zn^{2+} migration (**Supplementary Figure S1F**). During the discharge process, Zn^{2+} inserted to the Zn-O tetrahedron sites, while the charge process is opposite (**Supplementary Figure S1D**). Benefiting from the oxygen vacancy caused by cationic vacancies, the $ZnMn_2O_4$/carbon electrode shows remarkable performance of 150 mAh g^{-1} at 50 mA g^{-1} and an unprecedented capacity retention of 94% after 500 cycles at 0.5 A g^{-1} (**Supplementary Figure S1G**). Later, Cui et al. (2018) synthesized KMn_8O_{16} microspheres by the hydrothermal method. During the initial charge process, partial K^+ extracted from KMn_8O_{16}. And in the following charge/discharge cycles, Zn^{2+} inserted or extracted from the electrode reversibly. The Zn/KMn_8O_{16} cell delivered 77.0 mAh g^{-1} after 100 cycles and exhibited low self-discharge, indicating stable electrochemical performance.

CONCLUSION AND OUTLOOK

In summary, AZIBs have attracted considerable attention in recent years mainly due to their high safety, low cost, and high volumetric energy density. This mini review basically summarized the application of manganese-based materials, including manganese oxide, manganate, and their composite materials in AZIBs. Although tunnel or layered structures of manganese-based materials provide a path for Zn^{2+} insertion/extraction, the poor ionic and electrical conductivity restricts their further application. In this regard, it is particularly important to shorten the transport path of zinc ions and composite with materials with a high electronic conductivity. Hence, some aspects could be focused on to further improve the electrochemical performances of manganese-based AZIBs. And also some problems still exist and need to be resolved for their further development.

(1) MnO_2 with different structures such as α, β, γ, δ, etc., has been well investigated as a cathode material for AZIBs. The mechanism of insertion or extraction properties of Zn^{2+} and their phase transformation during cycling are not clear enough and still need to be explored. *In operando* techniques, such as *in situ* X-ray technique, *in situ* electron microscopy, and *in situ* scanning probe technology, as well as synchron X-ray-based techniques, are very helpful to obtain time-dependent information. So, more research using *in operando* techniques needs to be conducted to get insight and understanding of the zinc-ion storage mechanism of manganese-based materials for AZIBs.

(2) Poor conductivity of MnO_2 and volume change caused by phase transformation often lead to poor rate and cycling performances of the Zn/MnO_2 batteries. Special MnO_2 morphologies such as nanospheres, core-shell structures, or nanowires growing on a conductive substrate such as carbon cloth/paper or stainless steel mesh will effectively solve these issues. Therefore, this research direction may deserve further study.

(3) Other manganese oxides (mainly includes Mn_3O_4, Mn_2O_3, and MnO_x) and manganate (such as $LiMn_2O_4$, $ZnMn_2O_4$, and KMn_8O_{16}) have also been reported for AZIBs, but compared to MnO_2, more work on related materials as well as their zinc-ion storage mechanism should be further explored.

We hope this review is helpful and can inspire more innovative ideas for manganese-based or even transition metal-oxide materials as cathode materials for AZIBs.

AUTHOR CONTRIBUTIONS

WZ, YL, and SW conceived the idea. YL and XZ wrote the draft. All authors contributed to the writing, discussion, and revision of the final version of the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2020.00195/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.