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

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., 2019b; 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., 2019; 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 low cost, high safety, and long cycle life. 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). Significantly, it differs 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$_3$O$_4$ 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$_3$O$_4$ (Zhu et al., 2018), etc. Due to their special structure, they could be used as cathode materials for AZIBs (Khamnsanga 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$_2$ (Khamnsanga 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 MnSO$_4$[Zn(OH)$_2$]$_3$.xH$_2$O 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$_4$·3Zn(OH)$_2$·5H$_2$O.
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$_3$SO$_3$)$_2$ with 0.1 M Mn(CF$_3$SO$_3$)$_2$ 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$_2$O-containing Zn-buserite framework. Mn$^{3+}$ dissolution can be effectively inhibited by the addition of Mn(CF$_3$SO$_3$)$_2$ 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$_2$O$_4$, γ-Zn$_x$MnO$_2$, and L-Zn$_y$MnO$_2$), 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          |
|---------------------------|-------------------------|------------------|--------------------|-----------------------------|------------------------------|----------------------|
| MnO₂ powder               | 1.0                     | 50               | –                  | ~171                        | ~171                         | Xu et al., 2009      |
| α-MnO₂                    | 1.26                    | 100              | 1.0–1.9            | ~135                        | ~100                         | Xu et al., 2012      |
| α-MnO₂                    | 0.1                     | 50               | 0.8–1.8            | ~96.8                       | ~100                         | Guo et al., 2020     |
| α-MnO₂ nanorods           | 0.083                   | 50               | 1.0–1.8            | 233                         | ~160                         | Alfaruqi et al., 2015b |
| MnO₂/α-CNT                | 5.0                     | 500              | 1.0–1.9            | ~110                        | ~100                         | Xu et al., 2014      |
| α-MnO₂ nanorods           | 0.083                   | 75               | 1.0–1.8            | 190                         | 104                          | Alfaruqi et al., 2016 |
| α-MnO₂                    | 1.3                     | 5,000            | –                  | ~100                        | ~92                          | Pan et al., 2016     |
| MnO₂@δC                   | 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      |
| MnO₂                      | 1.0                     | 1,000            | 0.8–1.8            | 157.6                       | 134                          | Zhao K. et al., 2018 |
| MnO₂                      | 0.1                     | 50               | 1.0–1.8            | ~225                        | 97                           | Alfaruqi et al., 2018 |
| MnO₂                      | 1.0                     | 100              | 1.0–1.8            | ~280                        | ~220                         | Liu et al., 2019a    |
| α-MnO₂@δIr₂O₃             | 3.0                     | 1,300            | –                  | ~60                         | 75                           | Gou et al., 2019     |
| Ti-MnO₂ NWs               | 1.0                     | 4,000            | –                  | ~175                        | ~145                         | Liu et al., 2019     |
| α-K₂O₂/MnO₂              | 1.54                    | 400              | 0.8–1.9            | ~170                        | 180                          | Liu et al., 2019b    |
| α-MnO₂/OLC                | 0.246                   | 100              | 1.0–1.8            | 181                         | 168                          | Palaniyandy et al., 2019 |
| α-MnO₂                    | 0.3                     | 100              | 0.9–1.9            | 62                          | 103                          | Poyraz et al., 2019  |
| α-MnO₂                    | 0.1                     | 300              | 0.9–1.8            | 240                         | 140                          | Gao X. et al., 2020  |
| α-MnO₂ nanorods           | 0.1                     | 50               | 1.0–1.8            | ~270                        | ~150                         | Islam et al., 2017a  |
| α-MnO₂                    | –                       | 2,000            | 0.8–1.9            | 144                         | 135                          | Zhang et al., 2017   |
| D-β-MnO₂                  | 0.5                     | 300              | 0.8–1.8            | 225                         | 200                          | Han et al., 2020     |
| MnO₂@δCC                  | 2.0                     | 700              | 1.0–1.8            | ~100                        | ~90                          | Deng et al., 2019    |
| M-MnO₂                    | 0.1                     | 100              | 1.0–1.8            | ~100                        | ~105                         | Guo et al., 2019b    |
| D-β-MnO₂                  | 0.5                     | 300              | 0.8–1.8            | ~210                        | ~200                         | Han et al., 2020     |
| Ce-MnO₂                   | 1.54                    | 100              | 1.0–1.8            | 134                         | ~78                          | Wang et al., 2019a   |
| MnO₂ - graphene           | 10                      | 300              | 0.8–1.8            | ~100                        | ~64                          | Wang C. et al., 2020 |
| γ-MnO₂                    | –                       | 40               | 0.8–1.8            | ~160                        | ~158                         | Alfaruqi et al., 2015c |
| δ-MnO₂                    | 0.1                     | 100              | 1.0–1.8            | 126                         | 96                           | Guo et al., 2019b    |
| δ-MnO₂                    | 0.1                     | 150              | 0.4–1.9            | ~              | ~45                          | Guo et al., 2018     |
| δ-MnO₂-NFG                | 0.4                     | 100              | 1.0–1.8            | 230                         | 113.4                        | Guo et al., 2019a    |
| MnO₂@δCFP                 | 1.885                   | 10,000           | 1.0–1.8            | 50                          | 70                           | Sun et al., 2017     |
| Mg₂(MnO₂)₄·4·H₂O          | 0.05                    | 50               | 0.7–2.0            | 98                          | ~85                          | Lee et al., 2013     |
| V-MnO₂                    | 0.066                   | 100              | 1.0–1.8            | 260                         | ~130                         | Alfaruqi et al., 2017 |
| P-MnO₂                    | 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    |
| MnO₂-bixinite             | 2.0                     | 2,000            | 1.0–1.8            | 164                         | 134                          | Qiu et al., 2018a    |
| MnO₂@CNT                  | 0.155                   | 100              | 1.0–1.8            | ~200                        | 145                          | Zhao L. et al., 2018  |
| MnO₂ nanospheres          | 3.0                     | 2,000            | 1.0–1.85           | 124                         | ~80                          | Wang et al., 2019b   |
| α-MnO₂                    | 2.0                     | 1,000            | 1.0–1.9            | 73.6                         | 82.2                         | Jiang et al., 2017   |
| MnO₂@N-C                  | 2.0                     | 1,600            | 0.8–1.8            | ~100                        | 100                          | Fu et al., 2018      |
| Mn₄O₄                    | 0.5                     | 300              | 0.8–1.9            | ~45                         | ~100                         | Hao et al., 2018     |
| SSWM@Mn₂O₄                | 0.5                     | 500              | 1.0–1.8            | ~120                        | ~130                         | Zhu et al., 2018     |
| MnO₂@NCm                  | 0.2                     | 110              | 1.0–1.8            | ~300                        | ~150                         | Li D.-S. et al., 2019 |
| MnO₂@Mn₂O₃               | 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     |
| ZnO/C                     | 0.5                     | 50               | 0.8–2.0            | ~90                         | ~80                          | Zhang et al., 2016   |
| H-ZnMn₂O₄                 | 0.1                     | 300              | 0.8–1.9            | ~85                         | ~100                         | Wu et al., 2017      |
| KMn₄O₄·H₂O               | 0.1                     | 100              | 0.8–1.9            | ~130                        | 77                           | Cui et al., 2018     |
| ZnMn₂O₄@NG                | 1.0                     | 2,500            | 0.8–1.8            | 76                          | 74                           | Chen et al., 2019c   |

(Continued)
morphology (Alfarqui et al., 2015a; Guo et al., 2018), and add structural stabilizer (Kao-ian et al., 2019) are common ways to improve the performance of $\delta$-MnO$_2$. For instance, Guo et al. (2019a) synthesized $\delta$-MnO$_2$ nanosheets with a thickness of 2–4 nm by reduction of KMnO$_4$. During the initial discharge process, $H^+$ inserted into the $\delta$-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-$\delta$-MnO$_2$ cells still showed 86 mAh g$^{-1}$ at 0.5 A g$^{-1}$, which show excellent cycle stability.

$\varepsilon$-MnO$_2$ with face-sharing 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$_2$O$_4$, respectively, in AZIBs.

Other manganese dioxides, such as $\lambda$-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$_2$O$_4$ with H$_2$SO$_4$ and synthesized $\lambda$-MnO$_2$. The Zn/$\lambda$-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$_{1.2}$O$_{4.8}$H$_4$O 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$_3$O$_4$ (Hao et al., 2018; Zhu et al., 2018), Mn$_3$O$_5$ (Jiang et al., 2017), and others (Fu et al., 2018) are also widely studied in AZIBs.

Mn$_3$O$_4$ is an alternative cathode material for AZIBs. In 2017, Jiang et al. (2017) first reported $\alpha$-Mn$_2$O$_3$ as the cathode material of AZIBs. The $\alpha$-Mn$_2$O$_3$ has a bixbyte 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$_3$O$_4$ was reduced to Mn$^{2+}$, accompanied the generation of Zn$_2$Mn$_2$O$_4$ without other phases generated. Based on this property, after 2,000 cycles, the $\alpha$-Mn$_2$O$_3$ displays a reversible discharge capacity of 38 mAh g$^{-1}$ at 2 A g$^{-1}$.

Mn$_3$O$_4$ 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$_3$O$_4$ on stainless steel welded mesh (SSWM@mMn$_3$O$_4$) 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@mMn$_3$O$_4$ 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$_2$O in the aqueous electrolyte react with the sequent OH$^-$ ions to form large flake-like ZnSO$_4$[Zn(OH)$_2$]$_2$·5H$_2$O. Due to the intimate contact between the material and current collector, the SSWM@mMn$_3$O$_4$ 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 electrode 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$^{-1}$.

### Manganese Oxide

Manganate is an important component of manganese-based materials. Some manganates are investigated as cathode materials for AZIBs, such as LiMn$_2$O$_4$ (Wu et al., 2015), Mn$_3$N$_2$O$_4$ (Zhang et al., 2016; Wu et al., 2017; Chen et al., 2019c), KMn$_3$O$_6$ (Cui et al., 2018), and their derivatives (Tao et al., 2020).

Benefiting from the low cost, non-toxicity, easy fabrication, and high safety, LiMn$_2$O$_4$ 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...
LiMnO₄ as a cathode material. Similarly, LiMnO₄ 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 ZnMn₂O₄/carbon composite and applied it as a cathode material for AZIBs. They found the unoccupied octahedral sites (8c) of the ZnMn₂O₄ have cation vacancies, which can provide additional pathways for Zn²⁺ migration (Supplementary Figure S1F). During the discharge process, Zn²⁺ 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 ZnMn₂O₄/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 KMn₄O₁₆ microspheres by the hydrothermal method. During the initial charge process, partial K⁺ extracted from KMn₈O₁₆. And in the following charge/discharge cycles, Zn²⁺ inserted or extracted from the electrode reversibly. The Zn/KMn₈O₁₆ 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 Zn²⁺ 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) MnO₂ 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 Zn²⁺ 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 MnO₂ and volume change caused by phase transformation often lead to poor rate and cycling performances of the Zn/MnO₂ batteries. Special MnO₂ 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 Mn₃O₄, Mn₂O₃, and MnO₂) and manganate (such as LiMn₂O₄, ZnMn₂O₄, and KMn₄O₁₆) have also been reported for AZIBs, but compared to MnO₂, 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

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