Tuning Structure of Manganese Oxides to Achieve High-performance Aqueous Zn Batteries①

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ABSTRACT As a key material for the development of mild aqueous rechargeable Zn/MnO_2 cells, MnO_2 has attracted much attention. This article presents some issues of MnO_2, provides some strategies improving battery performance of MnO_2 electrode, as well as makes a perspective on future research and development of MnO_2 materials. This article offers a profound insight on structure/property relationship of MnO_2, and benefits a lot to those involved in energy storage and conversion applications.

Keywords: manganese oxides, aqueous Zn battery, phase structure, charge storage mechanism, electrochemistry; DOI: 10.14102/j.cnki.0254–5861.2011–2765

1 INTRODUCTION

The aqueous rechargeable batteries are a promising class of batteries due to their high operational safety, low-cost, and environmental benignity. To date, large amount of researches on aqueous batteries based on alkali metal cations (e.g., Na^+ and K^+) and multivalent charge carriers (e.g., Mg^{2+}, Al^{3+}, and Zn^{2+}) have been reported[1, 2]. Among all aqueous batteries, rechargeable Zn/MnO_2 batteries with mild $ZnSO_4$ or $Zn(CF_3SO_3)_2$ aqueous electrolytes presented outstanding advantages, including low cost, high energy density (~820 mAh g^{-1} for Zn anode, and ~308 mAh g^{-1} for 1 e^- transfer of MnO_2 cathode), high operating potential (~1.35 V), as well as high safety and environmental friendliness[3]. Although the alkaline Zn-MnO_2 batteries have become dominant in primary battery market, the rechargeable mild Zn-MnO_2 batteries are still in the experimental stage, and are plagued by their capacity fading problem due to issues in both sides of MnO_2 cathode (Mn^{2+} dissolution, phase conversion, collapse of layered structure, and formation of inactive $ZnMn_2O_4$) and zinc anode (hydrogen evolution, zinc dendrite, and corrosion).

In the past 10 years, researches focusing on improving battery performance of MnO_2 cathode in aqueous Zn batteries (ZIBs) have been extensively conducted. Various manganese oxide phases have been reported as host materials for H^+/Zn^{2+} insertion in a mild aqueous electrolyte, including α-, β-, γ-, δ-, and λ-MnO_2, etc[4]. This diverse phase structure of MnO_2 influences greatly on their electrochemical reactions during cycling. Despite the variation of electrochemical reactions,

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reasons for the capacity fading problems of manganese oxides during cycling are nearly the same, i. e., the formation of electrochemically inactive $ZnMn_2O_4$. Thus, in this perspective, we provided a brief review on the phase structures, charge storage mechanisms, as well as the capacity fading issues of MnO_2 in mild aqueous ZIBs. Besides, the strategies applied for improving battery performance of MnO_2 cathode are also demonstrated. Finally, some potential future research directions based on our personal perspectives and related research topics from other researchers are also demonstrated. This article provides a comprehensive overview focusing on recent progress and future perspectives of MnO_2 cathode for developing superior aqueous ZIBs.

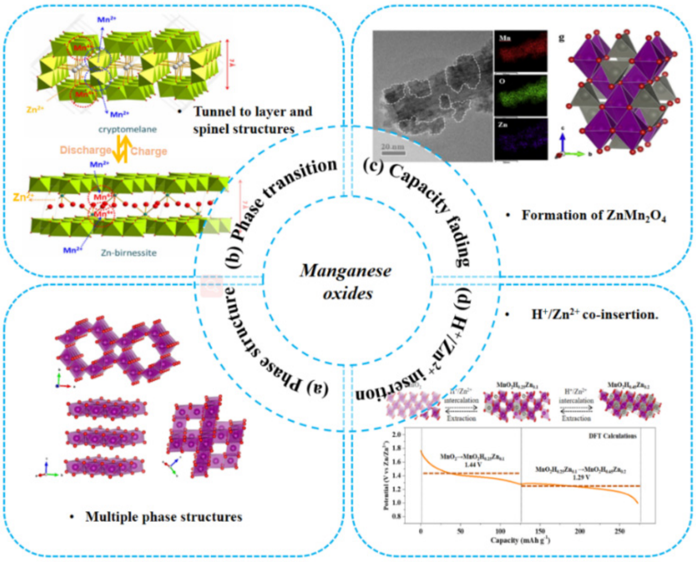

Fig. 1. Examples illustrating characteristics of MnO_2 cathode. (a) Multiple phase structures of MnO_2; (b) Schematic illustrating the phase transition mechanism of α-MnO_2 during Zn^{2+} intercalation process. From ref.[8], copyright of nature; (c) TEM morphology and EDS mapping of Mn, O and Zn for β-MnO_2 nanofiber after long-term cycle, and the schematic of $ZnMn_2O_4$ structure. From ref.[14], copyright of elsevier; (d) H^+/Zn^{2+} synthetic intercalation mechanism for a manganese oxide nanosheet. From ref.[22], copyright of Wiley

2 SOME ISSUES FOR MnO_2ELECTRODES

For a MnO_2 cathode in ZIBs, some very striking features are listed as follows: diverse phase structure, phase transition during cycling, multiple charge storage mechanisms, as well as capacity fading issues. It is well known that MnO_2 exhibits a lot of crystal structures, typically including α-MnO_2 with [2×2] tunnels, β-MnO_2 with [1×1] tunnels, γ-MnO_2 with [1×2] tunnels, δ-MnO_2 with layer structure, λ-MnO_2 with 3D structure, and so on (Fig. 1a). The diverse crystallographic forms of MnO_2 are attributed to the different arrangement of $[MnO_6]$ octahedra which are linked by sharing their edges or corners to form the tunnel, layer, or 3D structures. Some cations reside in the [2×2] tunnels of α-MnO_2 or interlayer space of δ-MnO_2, including Na^+, K^+, NH^{4+}, Mg^{2+}, Cs^+, H_2O, etc., which play an important role in stabilizing the tunnel or layer structures, and greatly affect the battery performance of MnO_2 cathode[4]. Besides, even though the manganese oxides present similar crystal structures, slight differences exist due to the different synthesis methods, hydrothermal temperature, annealing time, electrolyte addictive, as well as the choices of oxidant ($KMnO_4$, $(NH_4)_2S_2O_8$, etc.) and reductant ($MnSO_4$, carbon, ethanol, etc.)[5, 6]. These slight differences are inflected in the following aspects: chemical valence of Mn, crystal orientation, amount of pre-inserted H_2O or other cations, micro-morphology, the BET surface area, and so forth, and present vital effect on tuning the electrochemical reactions of MnO_2 during cycling. Looking through the reported literatures, *α*- and *δ*-MnO_2 have been mostly investigated as cathode in ZIBs because of their large open tunnels and large interlayer spacing facilitating the H^+/Zn^{2+} intercalation/extraction processes[7-11]. However, for the industrialization development of mild aqueous Zn/MnO_2 batteries, *γ*-MnO_2 also displays high research value due to its possibility of mass production through electrolytic or chemical methods.

For MnO_2 with tunnel structures, such as *α*-MnO_2, *β*-MnO_2 and *γ*-MnO_2, some researchers have reported the existence of phase transitions between tunnel structures and layer or/and spinel structures during cycling (Fig. 1b)[9, 12,13]. This phase conversion upon cycling is very harmful to the cycling stability of MnO_2 cathode, and the reasons may be as follows: a) the structure collapse of MnO_2 due to the internal microscopic stresses generated from repeated phase transitions[13], b) the inevitable Mn^{2+} dissolution from tunnel walls of MnO_2 during discharging[9], and c) the formation of spinel-type $ZnMn_2O_4$ with weak electrochemical activity (Fig. 1c)[14]. Based on this standpoint, researchers wish to find a cathode material with well maintained crystal structure during cycling, for example, the layer-type *δ*-MnO_2[15], spinel-type Mn_3O_4 and $ZnMn_2O_4$[16], *etc*. However, when applied as cathode in ZIBs, the *δ*-MnO_2 suffers from poor rate properties, and Mn_3O_4 or $ZnMn_2O_4$ presents low capacity delivery. To resolve the above issues, strategies promoting battery performance of *δ*-MnO_2 and $ZnMn_2O_4$ have been proposed in recent years, which will be described in the next section.

Except phase transition issues during cycling, the charge storage mechanism is also important for achieving high-performance of MnO_2 cathode in ZIBs. Single Zn^{2+} insertion[17] and single H^+ insertion[18] for *α*-MnO_2 cathodes have been proposed in 2015 and 2017, respectively. Nowadays, it has been widely accepted that H^+ and Zn^{2+} are co-inserted into MnO_2 cathode during discharge in a mild aqueous media (Fig. 1d)[19]. However, controversies remain on the insertion sequence of H^+ and Zn^{2+}. For example, Wang's group reported a subsequent H^+ and Zn^{2+} insertion mechanism for an electrodeposited MnO_2[20]; Liu's group presented a non-diffusion controlled Zn^{2+} intercalation and subsequent H^+ conversion reaction for *δ*-MnO_2[21]; and our group proposed a H^+/Zn^{2+} synthetic intercalation mechanism for a novel phase of manganese oxide[22]. Despite these differences, we find that all manganese oxides with H^+/Zn^{2+} co-insertion mechanisms exhibit superior rate and capacity properties. Especially, the high rate performance of MnO_2 is mainly attributed to the capacity contribution of H^+ insertion. However, when applying H^+ insertion, the electrode integrity of MnO_2 cathode can be destroyed by the repeated generation and diminish of the by-products ($Zn_4(OH)_6(SO_4)\cdot 5H_2O$) during cycling[23], which is bad for cycling stability of MnO_2 cathode. By tuning the H^+/Zn^{2+} insertion ratio, a balance among rate performance, capacity property, and cycling stability can be obtained to achieve a high-performance MnO_2 cathode, which is a very valuable research direction for ZIBs in the future.

3 STRATEGIES TO PROMOTE ELECTROCHEMISTY OF MnO_2 ELECTRODES

Recently, some strategies for improving the cycling stability and capacity of MnO_2 cathode have been reported, and a new concept based on deposition-dissolution mechanism was also proposed for the future energy storage. To enhance cycling stability of MnO_2 cathodes, two effective methods are reported, including 1) tuning discharge/charge potential ranges, and 2) stabilizing the layer-structure of MnO_2 through pre-insertion of large cations or molecules. A pioneering discovery was conducted by Liu's group[24], in which they present that the rate-limiting and irreversible conversion reactions occur at cell voltage lower than 1.26 V. Thus, by limiting the charge/discharge reactions in a potential range (1.8~1.3 V) higher than 1.26 V, ultra-long life of

Zn/MnO_2 cells can be achieved (Fig. 2a and b). Here, we consider that the "rate-limiting and irreversible conversion reactions" refer to the sluggish Zn^{2+} intercalation process and the formation of inactive $ZnMn_2O_4$.

Although the cycling stability of MnO_2 is greatly improved by tuning potential ranges, the capacity delivery is seriously reduced. Thus, it is not an ideal optimization solution for MnO_2 cathodes. However, this work gives an inspiration to us, that is, the key to improve the cycling stability of MnO_2 cathode is inhibiting the formation of inactive $ZnMn_2O_4$. Based on this principle, the stabilizing effects of cations (K^+, Na^+, other molecules, etc.) on the layer-structure of MnO_2 have been adapted to prevent the generation of inactive $ZnMn_2O_4$. For example, Zhi's group reported a Na^+ stabilized δ-MnO_2 (Fig. 2c)[25], Xia's group presented a polyaniline-intercalated δ-MnO_2 (Fig. 2d)[19], and Zhang's group proposed a K^+ pre-intercalated α-MnO_2 (Fig. 2e)[26] as high-performance cathode materials in ZIBs. Here, for K^+ pre-intercalated α-MnO_2, K^+ presents impressing stabilizing effect on the layer structure of manganese oxide which transformed from the original tunnel structure during discharge. It should be noticed that the stabilizing K^+ not only comes from the pre-inserted K^+ in α-MnO_2, but also from the K^+ containing salts pre-added in electrolyte.

Some researches exploring higher capacity of MnO_2 have also been reported in 2019. MnO_2 cathode present a theoretical capacity of ~308 mAh g^{-1} for 1 e^- transfer (Mn^{4+}/Mn^{3+}) in ZIBs. Generally, the charge/discharge cycle is controlled in a potential range from 1.8 to 1.0 V *vs*. Zn/Zn^{2+}, and most of capacity deliveries of MnO_2 cathode are lower than ~308 mAh g^{-1}. Defect engineering in the MnO_2 lattice has been proved as an effective way enhancing the attainable capacity. Xue's group[27] propose that the Zn^{2+} adsorption/desorption process on oxygen-deficient MnO_2 is more reversible as compared to pristine MnO_2 due to a thermos-neutral value of Gibbs free energy of Zn^{2+} adsorption in the vicinity of oxygen vacancies (Fig. 2f). Thus, the oxygen-deficient MnO_2 presented one of the highest capacities of 345 mAh g^{-1} for a birnessite MnO_2 system. Similar results are also reported by Mai's group[28]. They produce defects in α-MnO_2 lattice through Ti substitution, which facilitates both the H^+ and Zn^{2+} intercalation processes, and achieves a high capacity delivery.

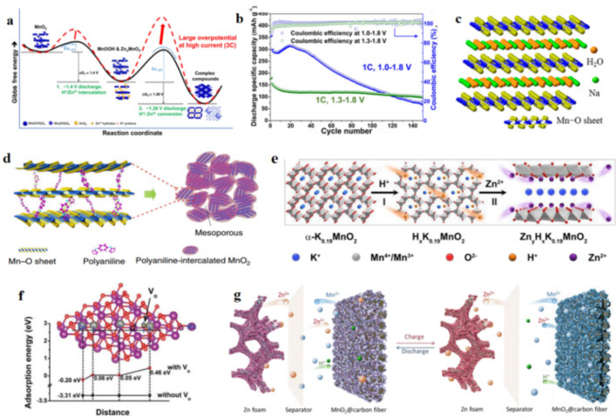

Fig. 2. Strategies improving the battery performance of MnO_2 cathode. (a) Gibbs free energy *vs*. reaction coordinate showing the thermodynamic and kinetic properties of the redox reactions in Zn/MnO_2 cells with different rates; (b) Cycling performance of the cells at different voltage ranges (1.0～1.8 and 1.3～1.8 V); From ref.[24], of ACS; (c) Structural illustration of the Na^+ and H_2O intercalated layered δ-MnO_2; From ref.[25], copyright of ACS; (d) Expanded intercalated structure of polyaniline-intercalated δ-MnO_2 nanolayers; ref.[19], copyright of Nature; (e) Schematic illustration of the subsequent H^+ and Zn^{2+} intercalation in α-$K_{0.19}MnO_2$ nanotubes; From ref.[26], copyright of RSC; (f) Calculated adsorption energies for Zn^{2+} on the surfaces of perfect σ-MnO_2 and σ-MnO_2 with oxygen vacancies; From ref.[27], copyright of Wiley; (g) Reversible charge/discharge processes based on deposition-dissolution mechanism. From ref.[29], copyright of Wiley

Based on the above discussions, the existing strategies enhancing battery performance of MnO_2 cathode are all based on a conventional charge storage mechanism: promoting the H^+/Zn^{2+} insertion process in a stable structure of MnO_2. However, it has got a bottleneck on further improving energy densities of Zn/MnO_2 battery systems. Thus, a new novel deposition-dissolution mechanism was proposed to provide the maximized electrolysis process (Fig. 2g). Qiao's group[29] proposed a high-voltage electrolytic Zn-MnO_2 battery, with a theoretical voltage of ~2 V and energy density of ~700 Wh kg^{-1}. In their study, Mn^{2+} ions in electrolyte can be oxidized to form solid MnO_2 on the carbon fiber during charging, and then reduced to Mn^{2+} ions dissolving back to electrolyte during discharging. This unique two-electron redox electrolysis reaction of Mn^{4+}/Mn^{2+} was produced via a reversible proton and electron dynamics, and exhibited high capacity delivery of MnO_2. Zhi's group[30] also reported a similar deposition-dissolution mechanism in Zn/MnO_2, Cu/MnO_2 and Bi/MnO_2 systems, respectively. This new kind of simple battery electrochemistry presents excellent capacity and rate performances, and is a prospective direction for further researches of ZIBs. Although this new mechanism is impressing, the practical use of Zn/MnO_2 battery encounters unprecedented challenges in the Zn anode side due to the very serious hydrogen evolution issue during charging in a strong acidic electrolyte.

4 SUMMARY & PERSPECTIVE

In summary, we have provided a brief introduction on charge storage mechanisms and some strategies to improve electrochemistry of MnO_2 cathode in ZIBs. Some solid conclusions and perspectives based on existing reports, including experiments and theoretical calculations, are as follows: a) A clear acknowledgement on the relationship between the diverse phase structures and electrochemical reactions of MnO_2 is vital for designing high-performance MnO_2 cathode materials; b) Tuning H^+/Zn^{2+} intercalation processes in a stable structure of MnO_2 phase is a promising research direction for the development of superior ZIBs; c) The key to improve the cycling stability of MnO_2 cathode is to prevent the formation of $ZnMn_2O_4$ during cycling; d) The method of pre-insertion of large-size cations or other molecules inside the layer-structure of MnO_2 is an effective way to prevent the generation of inactive $ZnMn_2O_4$, and hence improving the cycling property of MnO_2 electrode; e) Defect engineering will be an effective method for improving both capacity and rate properties of MnO_2 cathodes; f) The dissolution/deposition mechanism of MnO_2 cathode is impressive, but the very serious hydrogen evolution issue in Zn anode side restricts its practical application in future. We believe the rechargeable aqueous Zn/MnO_2 batteries will play an important role in the next-generation energy storage devices, and to achieve this goal, further researches need to be done on electrochemical reactions and correlated strategies improving battery performance of MnO_2 cathode. This article combining reviews and perspectives of manganese oxides may aid in the future development of advanced cathodes for aqueous Zn ion batteries.

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