Ni-doped δ-MnO$_2$ as a cathode for Zn-ion batteries

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Abstract. Among the cathode materials for zinc-ion batteries, manganese oxides have been extensively studied. Thermal decomposition method was adopted to synthesize the Ni-doped δ-MnO$_2$ material, called as Ni$_x$Mn$_{1-x}$O$_2$. The electrochemical performance and energy storage mechanism of Ni$_x$Mn$_{1-x}$O$_2$ were studied in 2M ZnSO$_4$ + 0.2M MnSO$_4$ electrolyte. Nickel doping can significantly improve the electrochemical activity of δ-MnO$_2$. Therefore, Ni-doped δ-MnO$_2$ shows better electrochemical cycling performance than δ-MnO$_2$. At 100 mA g$^{-1}$, Ni$_{0.2}$Mn$_{0.8}$O$_2$ (x=0.2) the specific capacity of 280mAh g$^{-1}$ in the second circle, and the corresponding voltage platform is 1.36V and 1.23 two discharge voltage platforms. After 100 cycles, the specific capacity of Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) still maintain 167 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$. In addition, we also proved that Zn$^{2+}$ and H$^+$ are co-intercalated into Ni$_x$Mn$_{1-x}$O$_2$ during the process of charge and discharge and the electrochemical reaction is highly reversible. This research broadens the thinking of exploring ZIBs cathode materials with good specific capacity and cycle performance.

Keywords: Zn-ion batteries; Cathode materials; Ni-doped δ-MnO$_2$

1. Introduction

As we all know, lithium ion batteries (LIBs) have excellent characteristics in terms of energy density and technological maturity, however, as a commercial energy storage system, LIBs have huge obstacles such as high cost and the existence of dendrites [1]. In the development of multivalent batteries, water-based zinc ion batteries (ZIBs) have been extensively studied due to their low cost and high safety. The main body has the characteristics of high theoretical capacity (820 mAh g$^{-1}$), low redox potential (-0.76 V), rich crust content, and low cost [2].

Manganese oxides are promising cathodes for zinc-ion batteries due to their high specific capacity, rich resources and low cost. Among them, δ-MnO$_2$ has a larger spacing of approximately 0.7 nm, which is theoretically more suitable for Zn$^{2+}$ storage [3]. However, δ-MnO$_2$/Zn with excellent electrochemical performance has not been obtained up to now. Defect engineering is currently one of the means to improve the electrochemical performance of materials [4]. In particular, defect measures are widely used in manganese-based oxides. Currently, various types of defect methods have been used in manganese-based oxides as cathode materials for zinc-ion batteries to enhance electrochemical performance.

In this article, we synthesized layered δ-MnO$_2$ by thermal decomposition and the nickel doping strategy modified δ-MnO$_2$ to obtain Ni$_x$Mn$_{1-x}$O$_2$. The electrochemical performance and energy storage mechanism of Ni$_x$Mn$_{1-x}$O$_2$ were studied in 2M ZnSO$_4$ + 0.2M MnSO$_4$ electrolyte. Nickel doping can significantly improve the electrochemical activity of the material. Therefore, the Ni-doped δ-MnO$_2$ samples show better electrochemical cycling performance than δ-MnO$_2$. At 100 mA g$^{-1}$, Ni$_{0.2}$Mn$_{0.8}$O$_2$
(x=0.2) the specific capacity of 280mAh g$^{-1}$ in the second circle, and the corresponding voltage platform is 1.36V and 1.23 two discharge voltage platforms. After 100 cycles at a current density of 100 mA g$^{-1}$, the specific capacity of Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) is still 167 mAh g$^{-1}$. Besides, we also proved that Zn$^{2+}$ and H$^+$ are co-intercalated into Ni$_x$Mn$_{1-x}$O$_2$ upon cycling and the electrochemical reaction is highly reversible.

2. Material preparation and Characterization

The raw materials used in this experiment are all analytically pure and have not been further purified. δ-MnO$_2$ is synthesized by thermal decomposition method [5]. NiSO$_4$ and KMnO$_4$ were dissolved in 40 mL of distilled water in the proportions of (0:1; 1:10; 1:5; 2:5), followed by stirring at room temperature for 2 hours, and then heating to obtain the precursor. The precursor was put into a muffle furnace and calcined at 350°C for 5 hours with a heating rate of 5°C/min. Then, the resultant was washed by the suction filtration to remove the unreacted potassium permanganate and nickel sulfate in the product, and then dried in a vacuum drying oven at 60 °C overnight. The collected product is Ni$_x$Mn$_{1-x}$O$_2$ doped with different content of nickel (x=0, 0.1, 0.2, 0.4).

3. Results and discussion

3.1. Composition analysis

Figure 1 is the X-ray diffraction (XRD) characterization diagram of Ni$_x$Mn$_{1-x}$O$_2$ (x = 0, 0.1, 0.2, 0.4). Figure 1 shows that the XRD diffraction peaks of Ni$_x$Mn$_{1-x}$O$_2$ are almost similar. All the XRD diffraction patterns of the as-prepared materials correspond to the standard card of birnessite (JCPDS 13-0105). This phenomenon indicates that Ni has successfully entered the crystal lattice of δ-MnO$_2$ to form a single-phase Ni$_x$Mn$_{1-x}$O$_2$ (0≤x≤0.4). Obviously, there is no impurity peak existing in these Ni-doped MnO$_2$ materials. δ-MnO$_2$ possesses a crystal structure shared by the edges of MnO$_6$ on the (001) crystal plane. The diffraction peaks point to different crystal planes of δ-MnO$_2$[6], respectively. In brief, δ-MnO$_2$ and Ni doped derivatives show high crystallinity and high purity.

![Figure 1. XRD diffraction patterns of Ni$_x$Mn$_{1-x}$O$_2$ (x=0, 0.1, 0.2, 0.4).](image)

In order to confirm the element and valence composition of the material before and after nickel doping, the material Ni$_x$Mn$_{1-x}$O$_2$ (x = 0, 0.2) was tested by X-ray Photoelectron Spectroscopy (XPS). Figure 2(a) shows the XPS spectra of δ-MnO$_2$ and Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2). As can be seen in Figure 2(a), the XPS spectra of δ-MnO$_2$ and Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) have the split peaks of Mn 2p and O 1s. In addition, the XPS spectrum of Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) is composed of the Ni2p splitting peak, implying the successful Ni-doping of δ-MnO$_2$. As can be also seen in Figure 2(a), the peak at 373.7 eV corresponds to the K 2s splitting peak, which is attributed to the adsorption of the K$^+$ of the raw material KMnO$_4$. Figure 2(b) shows the Ni 2p spectrum of Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2). The peaks at 855.5 eV and 872.8 eV are assigned to the splitting peaks of Ni 2p$_{3/2}$ and the peak at 861.5 eV corresponds to the satellite peaks of
Ni $2p_{3/2}$, which is consistent with the previous literature reported [7]. This result demonstrates the existence of Ni$^{2+}$ in Ni$_x$Mn$_{1-x}$O$_2$. Figure 2(c) displays the Mn 2p spectra of δ-MnO$_2$ and Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2). As can be seen in Figure 2(c), the spin splitting energies of Mn for δ-MnO$_2$ and Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) are 11.7 eV. According to the relevant literature [8], the corresponding Mn valence of the compound is +4. It is inferred that Ni$^{2+}$ enters the interlayer in the manganese dioxide, existing in the form of ions. Thus, the valence state of Mn in Ni-doped δ-MnO$_2$ has not changed, similar to La$^{3+}$ intercalation into δ-MnO$_2$ [9].

Figure 2. (a) XPS survey spectra (b) Ni2p and (c) Mn2p of Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2).

3.2. Micro-morphology
In order to explore the morphology changes of the material before and after Ni doping δ-MnO$_2$, the material was tested by SEM. Figure 3 shows the morphology of Ni$_x$Mn$_{1-x}$O$_2$ (x=0, 0.2). It can be seen that both materials are in the form of random particles. In brief, the morphology of the material with or without Ni doped material is almost not much different, indicating that Ni doping will not have a significant impact on the morphology of the material.

Figure 3. SEM images of (a-b) Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) and (c-d) Ni$_x$Mn$_{1-x}$O$_2$ (x=0).

3.3. Electrochemical performance
The cyclic voltammogram and galvanostatic charge-discharge measurements are adopted to evaluate the electrochemical performance of Ni$_x$Mn$_{1-x}$O$_2$ as the cathode material of ZIBs in the electrolyte of 2 M ZnSO$_4$ + 0.2 M MnSO$_4$. The cyclic voltammetry curves of Ni$_x$Mn$_{1-x}$O$_2$ (x =0.2) and δ-MnO$_2$ are depicted in Figure 4(a-b), respectively. As can be shown in Figure 4(a), the shape of the CV curves for Ni$_x$Mn$_{1-x}$O$_2$ (x =0.2) is similar to that of the CV curve for δ-MnO$_2$. From Figure 4(a), Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) has a reduction peak at 1.17 V vs. Zn$^{2+}$/Zn and an oxidation peak at 1.61 V vs. Zn$^{2+}$/Zn in the first cycle. In the later loop, there are two obvious redox pairs of redox couple appearing at 1.60/1.36 V and 1.63/1.23 V vs. Zn$^{2+}$/Zn. As for δ-MnO$_2$, the CV curve in Figure 4(b) has stronger oxidation peak and
reduction peak in the first cycle, but the peak intensity is decreased after 3 cycles. Figure 4(c) shows the cycle stability performance of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.0, 0.1, 0.2, 0.4) in different Ni doping amounts at 100 mA g$^{-1}$ for 10 cycles activity, followed by cycling at 200 mA g$^{-1}$. As can be seen in Figure 4(c), the discharge specific capacities of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0–0.4) are decreased with the increasing of cycle number. Obviously, the cycle stability of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) is better than that of δ-MnO$_2$ and other δ-MnO$_2$ in different Ni doped amount. After 110 cycles, the specific capacity of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) still achieves 167 mA g$^{-1}$, which is significantly higher than δ-MnO$_2$ (77 mA h g$^{-1}$) and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.1, 151 mA h g$^{-1}$) and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.4, 145 mA h g$^{-1}$). Therefore, Therefore, Ni doping plays a key role in improving the electrochemical performance of δ-MnO$_2$ and x=0.2 is the optimal doping amount. Figure 4(d) shows the discharge capacity-voltage profiles of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) at 100 mA g$^{-1}$. In Figure 4(d), Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) has obvious discharge plateaus at 1.36 V and 1.23 V vs. Zn$^{2+}$/Zn, in accordance with in the previous CV curve. At 100 cycles, Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) delivers the first discharge specific capacity of ~230mAh g$^{-1}$, then reaches up to ~260mAh g$^{-1}$.

Figure 4. (a) CV curves of δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) at 0.5 mV/s; (b) Cycle stability performance of Ni$_{1-x}$Mn$_x$O$_2$ (x=0, 0.1, 0.2, 0.4) at 200 mA g$^{-1}$ after 10 cycles at 100 mA g$^{-1}$; (d) Specific capacity-voltage curves of Ni$_{1-x}$Mn$_x$O$_2$ (x=0.2) at 100 mA g$^{-1}$.

Figure 5(a) shows the rate cycling performance of δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) at different current densities of 0.1, 0.2, 0.4, 0.8, 1.6, 3.2 A g$^{-1}$. Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) exhibits a higher specific capacity than δ-MnO$_2$. In Figure 5(a), the specific capacity of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) can still reach 100 mA h g$^{-1}$ at 3.2 A g$^{-1}$. When the current density is 0.1 A g$^{-1}$, the specific capacity of Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) is risen to 218 mA h g$^{-1}$, which is much higher than that of δ-MnO$_2$ (167 mA h g$^{-1}$). This result indicates that the Ni doping can improve the rate performance of δ-MnO$_2$. Figure 5(b) and (c) displays the specific capacity-voltage curves of δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) at different current densities. A Figure 5(b-c) shows that at 0.1 A g$^{-1}$, at 0.1 A g$^{-1}$, both δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) have two couples of charge-discharge platforms at 1.55/1.35V and 1.50/1.40V. Compared with δ-MnO$_2$, Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) yields the specific capacity of ~100 mA h g$^{-1}$ at 3.2 A g$^{-1}$, higher than that of δ-MnO$_2$ (~75 mA h g$^{-1}$). Figure 5(d) shows long-term performance and coulombic efficiency of δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) at 1 A g$^{-1}$. In the early stage, their specific capacities undergo rapid capacity decay, and then tend to stability. The coulombic efficiencies of δ-MnO$_2$ and Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) are close to 100%. In contrast to δ-MnO$_2$, Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) has better long-cycle performance. After 600 cycles, Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) still remains the specific capacity of 72 mA h g$^{-1}$, while the specific capacity of δ-MnO$_2$ is only 46 mA h g$^{-1}$. In short, the Ni-doped Ni$_{1-x}$Mn$_x$O$_2$ (x = 0.2) shows
better long-term and rate performance than \( \delta - \text{MnO}_2 \). The Ni doping strategy can effectively increase the performance of layered \( \delta - \text{MnO}_2 \) as the cathode material of ZIBs.

Figure 5. (a) Rate performance of \( \delta - \text{MnO}_2 \) and \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)); Discharge capacity-voltage curves of \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) (b) and \( \delta - \text{MnO}_2 \) (c); (d) The cycle performance of \( \delta - \text{MnO}_2 \) and \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) at 1 A g\(^{-1}\) after 1000 cycles.

3.4. Electrochemical mechanism

Figure 6. (a) Ex-XRD patterns of \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) in the different discharged and charged states; (b) Specific capacity-Voltage curves of 1st and 2nd cycle; (c) XRD peak of Carbon cloth/Super P.

Figure 6(a) shows the ex-XRD patterns of the \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) electrodes at different voltages in the first two cycles, corresponding to the discharge and charge curves of \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) in Figure 6(b). Figure (c) gives the XRD profile of carbon cloth/Super P. In Figure 6(a), the XRD pattern of the \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \) (\( x = 0.2 \)) electrodes in L1 (1.42V) state is similar to that of in L2 (1.0V) state without obvious other phase peaks in the first discharged curve, except for carbon cloth/Super P. This is mainly because the capacity contribution comes from the (de)-intercalation of H\(^+\) in the electrolyte into the \( \text{Ni}_x \text{Mn}_{1-x} \text{O}_2 \)
(x = 0.2) electrodes, leading to no obvious change of the corresponding XRD diffraction profile [12]. In the second cycle, when discharged to 1.34 V (L4) and 1.0 V (L5), the Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) electrode appears the new peaks of ZnSO$_4$(OH)$_2$•xH$_2$O and MnOOH. In the second cycle, it is speculated that H$^+$ and Zn$^{2+}$ are co-intercalated into the Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) electrode. When charged to 1.8 V, the XRD diffraction peaks of the Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) electrode is returned to the initial state, which indicates that the Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) material has good electrochemical reversibility. The discharge and charge reactions of the Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) in 2M ZnSO$_4$ + 0.2M MnSO$_4$ electrolyte are listed as follows [10]:

\[
\begin{align*}
\text{MnO}_2 + \text{H}^+ + \text{e}^- & \rightarrow \text{MnOOH} \\
4\text{MnO}_2 + 2\text{Zn}^{2+} + 4\text{e}^- + \text{H}_2\text{O} & \rightarrow \text{Zn}_2\text{Mn}_4\text{O}_8\cdot\text{H}_2\text{O} \\
2\text{MnOOH} + \text{SO}_4^{2-} + 2\text{Zn}^{2+} + 7\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{Zn}_4\text{SO}_4(\text{OH})_6\cdot5\text{H}_2\text{O} + 2\text{Mn}^{2+}
\end{align*}
\]

3.5. Reaction kinetic analysis

In order to explore the ion diffusion kinetics of Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) in zinc-ion batteries, the cyclic voltammetry tests are conducted at the sweep rates of 0.2-1.0 mV/s. Figure 7(a) and (b) show the CV curves and its corresponding Log(i)-log(v) linear fitting diagrams, respectively. As shown in Figure 7(a) as the sweep rate is increased, the intensity of the oxidation peaks and the reduction peaks also are increased. Generally speaking, from the formula $i = av^b$ in the CV curves. According to the value of b, the electrochemical mechanism of surface capacitance and diffusion capacitance can be determined. As can be seen in Figure 7(b), the b values of Peak 1 and Peak 4 are ranged from 0.5 to 1, which demonstrates that electrochemical process is dominated by the diffusion capacitance and the surface capacitance. In addition, the b values of the Peak 2 and Peak 3 are close to 0.5, which are mainly controlled by the diffusion capacitance. Figure 7(c) shows the proportions of diffusion capacitance and surface capacitance for the Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) electrode at different scanning rates. As the scanning rate is increased, the proportion of surface capacitance contribution also is improved, from 43.3% at 0.2 mV/s to 63.3% at 1.0 mV/s. These results, indicate that the Ni-doped Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) electrode has the characteristics of fast ion diffusion kinetics in ZIBs.

Figure 7. (a) Ni$_x$Mn$_{1-x}$O$_2$ (x = 0.2) CV curve at different scan rates; (b) Linear fitting graph of peak 1-peak 4; (c)the of diffusion capacitance and surface capacitance of the Ni$_x$Mn$_{1-x}$O$_2$(x = 0.2) electrodes at different scan rates.

4. Conclusion

All in all, we have developed a Ni-doped layered birnessite δ-MnO$_2$ as an excellent cathode material for water-based ZIBs. promotes nickel Zn$^{2+}$ intercalation/deintercalation kinetics, advanced Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) has larger zinc storage capacity and better rate performance. The specific capacity of Ni-doped materials is obviously better than that of undoped materials. Among them, Ni$_x$Mn$_{1-x}$O$_2$ (x=0.2) has the most superior electrochemical performance. After 100 cycles of 200 mA g$^{-1}$, the specific capacity is still
167 mAh g⁻¹, the discharge voltage is maintained at 1.36 V and 1.23 V, the capacity retention rate is 70%, and the coulombic efficiency is 97.69%. Whether it is rate performance or long cycle performance, doped materials are better than undoped materials. Through a series of characterizations, we proved that Zn²⁺ and H⁺ participate in the process of embedding and extraction together during the charging and discharging process.

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