Phase transformation mechanism of MnCO₃ as cathode materials for aqueous zinc-ion batteries

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Aqueous rechargeable zinc-ion batteries (ZIBs) have been given more and more attention because of their high specific capacity, high safety, and low cost. The reasonable design of Mn-based cathode materials is an effective way to improve the performance of ZIBs. Herein, a square block MnCO₃ electrode material is synthesized on the surface of carbon cloth by a one-step hydrothermal method. The phase transition of MnCO₃ was accompanied by the continuous increase of specific capacity, and finally maintained good cycle stability in the charge–discharge process. The maximum specific capacity of MnCO₃ electrode material can reach 83.62 mAh g⁻¹ at 1 A g⁻¹. The retention rate of the capacity can reach 85.24% after 1,500 cycles compared with the stable capacity (the capacity is 61.44 mAh g⁻¹ under the 270th cycle).

Ex situ characterization indicates that the initial MnCO₃ gradually transformed into MnO₂ accompanied by the embedding and stripping of H⁺ and Zn²⁺ in charge and discharge. When MnCO₃ is no longer transformed into MnO₂, the cycle tends to be stable. The phase transformation of MnCO₃ could provide a new research idea for improving the performance of electrode materials for energy devices.

KEYWORDS
MnCO₃, doping, zinc-ion battery, phase transformation, cyclic stability

1 Introduction

With the rapid development of information and intelligence in human society and the growth of new energy demand, secondary batteries play an important role in the application of new energy (Deng et al., 2021; Zhu et al., 2021). Lithium-ion batteries were developed for market application because of their excellent energy density, power density, and cycle life (Wang C et al., 2020; Hou et al., 2021; Hua et al., 2021). However, the further development of lithium-ion batteries is seriously restricted and challenged by their lack of resources, high cost, and potential safety hazards of organic electrolytes.
The supplementary scheme of lithium-ion batteries has gradually become an urgent problem. Aqueous zinc-ion batteries stand out among many electrochemical energy-storage devices because of their outstanding advantages such as safety, low cost, high-energy density, and environmental friendliness (Wang T et al., 2020; Du et al., 2020; Zhou and Guo, 2021). At present, the common cathode materials are V-based materials (Li J et al., 2020; Zhang L et al., 2020; Zhou and Guo, 2021). At present, the common cathode materials are V-based materials (Li J et al., 2020; Zhang L et al., 2020; Zhou and Guo, 2021). Mn-based materials (Wang J et al., 2020; Tan et al., 2020; Mao et al., 2021), and Prussian blue (Li Z et al., 2020). Among them, Mn-based oxides are widely used as cathode materials for aqueous zinc-ion batteries due to their low cost and abundant crystal structures (MnO, MnO2, Mn2O3, Mn3O4, etc.) (Zhao et al., 2019a; Gao et al., 2020). In 2012, Xu proposed a safe and environmentally friendly battery, which was made with α-MnO2 as cathode, zinc plate as anode, and ZnSO4 aqueous electrolyte. It is first indicated that the Zn2+ intercalation and desorption mechanism based on Zn2+ was inserted into α-MnO2 (Xu et al., 2012). Ji et al. reported a multi-valence cobalt-doped Mn3O4 with high capacity (Ji et al., 2020). Zhu et al. reported the activation of MnO by inducing Mn defects, wherein the Mn defects are formed through a charging process that converts the MnO with poor electrochemical activities toward Zn2+ into high electrochemically active cathode for aqueous ZIBs (Zhu C et al., 2020). However, the diversity of valence states of Mn-based oxides will lead to more side reactions, resulting in irreversible phase transition in the reaction process. It will damage the cycle stability and capacity. Thus, the new material system needs to be further excavated.

In recent years, the crystal structure of MnCO3 is similar to that of MnO2 composed of [MnO6] and CO32−; generally, MnO2 is synthesized through the decomposition of Mn-based oxyacid salt and hydroxide. However, this process is more complicated and energy consuming than that of MnCO3. Consequently, MnCO3 has been gradually used in electrochemical energy-storage devices due to its rich reserves, environmental friendliness, and simple synthesis (Zhong et al., 2015; Li et al., 2018). It is a potential high-performance anode material for electrochemical energy-storage devices (Yao et al., 2021). Yao et al. reported an electrodeposited MnCO3 as a high-performance electrode material for supercapacitors (Yao et al., 2021). Liu et al. reported in situ N-doped MnCO3 anode material via one-step solvothermal for lithium-ion batteries (LIBs) (Liu et al., 2020). Zhao et al. reported that when MnCO3-RGO composite anode materials are used as anode material, they deliver a large capacity of 873 mAh g−1 even after 400 cycles at 1 °C (Zhao et al., 2019b). However, their chemical properties are more active, and charge transfer occurs in the process of phase transition, which provides a better cycle stability. At present, the application of MnCO3 for ZIBs is still very rare, and its zinc storage mechanism has not been deeply explored.

Herein, we synthesized a square block MnCO3 electrode material on the surface of carbon cloth by the one-step hydrothermal method. The phase transition of MnCO3 was accompanied by the continuous increase of specific capacity and finally maintained good cycle stability in the charge–discharge process. The maximum specific capacity of MnCO3 electrode material can reach 83.62 mAh g−1 at 1 A g−1. The retention rate of the capacity can reach 85.24% after 1,500 cycles compared with the stable capacity (the capacity is 61.44 mAh g−1 under the 270th cycle). Ex situ characterization indicates that the initial MnCO3 gradually transformed into MnO2 accompanied by the embedding and stripping of H+ and Zn2+ in charge and discharge. When MnCO3 is no longer transformed into MnO2, the cycle tends to be stable. The phase transformation of MnCO3 could provide a new research idea for improving the performance of electrode materials for energy devices.

2 Experimental section

2.1 The synthesis of MnCO3/CC

The prepared empty carbon cloth (CC) was immersed in a beaker containing concentrated nitric acid and heated in a water bath at 80°C for 2–3 h, then repeatedly washed with deionized water and absolute ethanol, and finally dried for future use. After pretreatment of empty CC, 10 mmol Mn(CH3COO)2, 50 mmol urea, and 40 ml of deionized water were added to 100 ml of Teflon lining. After stirring for 5 min, putting a 3 cm2 cm carbon cloth, the mixed solution was placed in an autoclave and kept at 100°C for 16 h. The carbon cloth after the reaction was washed three times with deionized water and ethanol, and the sample (MnCO3/CC) was obtained after drying at 80°C for one night.

2.2 Materials characterization

The crystallographic features of the as-prepared samples were characterized by X-ray diffraction (XRD, Philips X′Pert PRO, Cu Kα, λ = 0.1542 nm). The morphology and detailed microstructure were conducted on a scanning electron microscope (SEM, FEI Quanta 200) and transmission electron microscopy (TEM, Philips, Tecnai G220), coupled with energy-dispersive X-ray spectroscopy (EDS). The element composition and surface chemical state were recorded on an X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD-600W).

2.3 ZIBs performance test

In this experiment, the cathode material was MnCO3 grown in situ with carbon cloth, and the anode material was selected from commercial zinc foils with high purity. The electrolyte was 2 M zinc sulfate, and 0.2 M manganese sulfate was added as the electrolyte compensation. The two electrodes were separated by a glass fiber separator. Cyclic voltammetry (CV) and galvanostatic
charge–discharge (GCD) were performed on the ChenHua electrochemical workstation (CHI760E) to test the electrochemical performance and used the eight-channel battery test equipment (NEWARE) to test rate performance and cycle life.

3 Results and discussion

3.1 Structure characterization of MnCO3/CC

The micro-morphology of MnCO3@CC was characterized by a scanning electron microscope (SEM), as shown in Figure 1. Figures 1A–D show that the as-synthesized MnCO3 cubes are grown evenly on the carbon cloth, and the surface of MnCO3 is relatively smooth. Figures 1F–H show the EDS element distribution diagram of C, Mn, and O, respectively. The results are basically consistent with the MnCO3. The crystal structure of the sample was analyzed by XRD, as shown in Figure 2A. The diffraction peaks can be well indexed to the representative peaks of the MnCO3 phase (JCPDS 44-1,472) (Zhu L et al., 2020; Zhu J et al., 2020). In detail, the peaks at 24.25°, 31.36°, 37.52°, 41.42°, 45.18°, 49.67°, 51.68°, 60.13°, 63.88°, and 67.70° correspond to (012), (104), (110), (113), (202), (024), (116), (122), (214), and (300) crystal planes of MnCO3, respectively. In addition, there are no other hetero-planes in the XRD spectrum, which prove that the material we synthesized is pure MnCO3 cathode material. Previously, EDS and XRD confirmed that there were three elements, Mn, C, and O, in the cathode material synthesized by the hydrothermal method in the experimental process, and the phase accorded with the diffraction results of MnCO3.

In order to further confirm the structure of the samples, the valence states of the synthetic materials were analyzed by XPS. Figure 2B demonstrates two typical Mn2p1/2 and Mn2p3/2 orbitals of the MnCO3 phase. The binding energies of the two main peaks are 641.02 and 653.04 eV, with a difference of 12.02 eV, indicating that the valence of Mn in the compound is +2 (Zhang B et al., 2020). In the C1s spectrum in Figure 2C, the binding energies of the two main peaks are 284.3 and 288.9 eV, corresponding to C–C
and C = O. In Figure 2D, the binding energy corresponding to the O1s is 530.3 eV, which further illustrates that O and C are combined and are expressed in the form of CO$_3^{2-}$ (Wang N et al., 2020). Supplementary Figure S1 shows the representative XPS survey spectrum of the sample, which verifies the presence of Mn, O, and C elements, indicating that the sample synthesized in the experiment is MnCO$_3$ without other impurities. This conclusion is consistent with the XRD results in Figure 2A.

The electrochemical performance of MnCO$_3$@CC cathode material is carried out in the coin cell, which utilized zinc foil as the anode and 2 M ZnSO$_4$ + 0.2 M MnSO$_4$ as the electrolyte. Cyclic voltammetry (CV) curves of unactivated MnCO$_3$@CC are obtained at the scan rate of 0.5 mV/s under 0.4–2.0 V, as shown in Figure 3A. In the first cycle, the oxidation potential is 1.63 V, corresponding to two reduction potentials of 1.20 and 1.33 V, respectively. In the second cycle, the original oxidation potential shifted to the left to 1.64 V, while the second oxidation potential appeared at 1.69 V and the reduction potential remained at 1.20 and 1.33 V, respectively. There are also two oxidation potentials in the third circle, which are 1.65 and 1.69 V, respectively. The reduction potential is consistent with the first two cycles, and their response current and peak intensity further increase. The change of oxidation potential should be caused by the phase transition process of Mn ions, corresponding to Mn$^{3+}$ to Mn$^{4+}$, indicating that there is a gradual activation process in the initial stage. The two reduction peaks are mainly attributed to the embedding and stripping behavior of H$^+$ and Zn$^{2+}$. Galvanostatic charge–discharge (GCD) curves under different cycles at 0.1 A g$^{-1}$ are shown in Figure 3B. There is only one discharge platform in 1.33 V under 1, 5, 10, 20, and 50 cycles, which is due to the embedding behavior of Zn$^{2+}$ in the reaction process after the cathode material reaches a stable phase. Figure 3C shows the CV curves of MnCO$_3$@CC at different scanning rates from 0.5 mV/s to 5 mV/s after activation. It is indicated that the response current gradually increases with the increase of the scanning rate. Figure 3D shows GCD curves under different current densities. The specific capacity is the highest at 0.1 A g$^{-1}$, but the Coulomb efficiency is the lowest because the phase change is the most obvious at this stage, which is basically consistent with the previous conclusions.

**FIGURE 2**
(A) XRD pattern of MnCO$_3$@CC. XPS pattern of MnCO$_3$@CC: (B) Mn2p, (C) C1s, and (D) O1s.
After the first cycle, Figure 3E shows the cyclic test of MnCO₃ at 0.2 A g⁻¹. Because the cathode material reaches a stable state after the activation process, its capacity remains stable during the following cycling. The first cycle capacity of the cathode material is 114.82 mAh g⁻¹, the cycle capacity of the 50th cycle is 99.26 mAh g⁻¹, and the retention rate is 87%. Figure 3F shows the rate performances of MnCO₃ at 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, 3.0, and 5.0 A g⁻¹ in 0.4–2.0 V. The specific capacities are 164.17, 108.30, 91.52, 72.64, 56.23, 43.24, 36.59, and 28.89 mAh g⁻¹, respectively. At low current density, the capacity of MnCO₃@CC begins to remain stable after reaching a stable phase. In the subsequent current density, its capacity remains basically stable, indicating that the MnCO₃@CC has good stability and rate performance under different current densities. Figure 3G shows the cycle performance of MnCO₃/CC at 2.0 A g⁻¹. At the higher current density, the cycle curve also rises slowly at first and then remains stable. The initial capacity of the MnCO₃@CC is also low. After 400 cycles, the capacity reaches 48.46 mAh g⁻¹ and then remains stable. After 1,700 cycles, when the capacity is relatively stable, the retention rate can reach 112.5% compared to the 400th cycle, which proves the good stability of the material.

To further explore the phase change and ion intercalation mechanisms of MnCO₃@CC cathode material, the electrodes were tested by EX-XRD, SEM, and XPS in different stages of charge and discharge. Figure 4 shows the EX-XRD patterns of nanocube MnCO₃@CC at 0.1 A g⁻¹. In the initial (position 1), only the original peak of MnCO₃ exists on the electrode (Figure 4A). When charging to 1.68 and 2.0 V, the peak of MnO₂ appears...
near 36.8°, but its peak intensity is weak, indicating that little amount of MnCO₃ changes into MnO₂ during charging. In the discharge, no strong peak of MnCO₃ is observed at positions 6, 7, and 8 in Figure 4A, but the MnO₂ diffraction peak is obvious near 36.8°, which indicated that MnO₂ is generated by the phase transformation of some MnCO₃. When discharging to 0.3 V, the results show that the ZnMn₂O₄ phase appears near 32.9° and 38.9°, indicating that Zn²⁺ embedding behavior occurs in this process. In the charging process (Figure 4B), the diffraction peak deviates to the left between 30° and 34°, 36° and 38°, 44° and 46°, and 51° and 53°, and the crystal plane spacing becomes smaller, which is affected by the stripping behavior of Zn²⁺. Supplementary Figure S2 shows the SEM images of the electrode charging to 2.0 V and discharging to 0.3 V at 0.1 A g⁻¹.

FIGURE 4
(A) EX-XRD patterns of MnCO₃@CC at 0.1 A g⁻¹. (B) Angular shifts of different diffraction peaks. (C–E) The XPS patterns of MnCO₃@CC for Mn, C, and Zn elements under charge to 2.0 V at 0.1 A g⁻¹. (F–H) The XPS patterns of MnCO₃@CC for Mn, C, and Zn elements under discharge to 0.3 V at 0.1 A g⁻¹.

2.0 V. After the original reaction, the smooth surface of MnCO₃ is gradually rough, and the cube is stacked by sheets. Supplementary Figures S2D–S2E are the SEM images after discharging to 0.3 V. The results show that there are lines on the surface of cube edges and corners, which increases its specific surface area. It is conducive to the ion transmission between the host and Zn²⁺ and improves the electrochemistry performance of the cathode material. Figures 4C–E show the Mn, C, and Zn XPS spectrums of MnCO₃@CC cathode material under charging to 2.0 V at 0.1 A g⁻¹. Figure 4C shows the high-resolution Mn2p spectrum. These two groups of spin-orbit resolution peaks can be decomposed into Mn²⁺ (2p3/2, 641.4 eV; 2p1/2, 653.2 eV) and Mn⁴⁺ (2p3/2, 643.2 eV; 2p1/2, 655.6 eV). The content of Mn²⁺ is much greater than that of Mn⁴⁺ because only a small amount of
MnCO$_3$ is transformed into MnO$_2$ in the charging stage, and a large number of cathode materials have not been activated, resulting in two valence states of +2 and +4 at the same time, and the proportion difference is large. The high-resolution spectrum of element C shown in Figure 4D is consistent with the reaction process. Figure 4E shows the high-resolution spectrum of Zn. The existence of Zn$^{2+}$ (2p$_{3/2}$, 1,044.5 eV; 2p$_{1/2}$, 1,021.4 eV) is caused by the residue of ZnSO$_4$ in the electrolyte.

The sample was discharged to 0.3 V for XPS analysis at 1.0 A g$^{-1}$. In the high-resolution spectrum of Mn$_2$p shown in Figure 4F, the two groups of spin orbits can be decomposed into Mn$^{3+}$ (2p$_{3/2}$, 642.4 eV; 2p$_{1/2}$, 654.2 eV) and Mn$^{4+}$ (2p$_{3/2}$, 644.1 eV; 2p$_{1/2}$, 655.6 eV). The existence of Mn$^{3+}$ and Mn$^{4+}$ further proved the formation of MnO$_2$ during charging and the embedding of Zn$^{2+}$ in MnO$_2$ during discharge, and ZnMn$_2$O$_4$ with spinel structure was formed. Due to the low content of MnO$_2$ generated in the charging stage and since only part of MnO$_2$ reacts with Zn$^{2+}$ in the discharge process, the content of Mn$^{3+}$ should be much less than Mn$^{4+}$. Mn$^{2+}$ was not detected because the generated MnO$_2$ covered the original material, so its valence state could not be detected. Figure 4H shows the high-resolution spectrum of Zn2p. Zn is +2 valence in the test sample, which is consistent with the embedding behavior of Zn$^{2+}$.

In order to further explore the activation mechanism and ion intercalation/desorption behavior of the MnCO$_3$/CC, the batteries were analyzed after 10 cycles at a low current density of 0.1 A g$^{-1}$. Figure 5A shows the EX-XRD patterns of charging to 2.0 V and discharging to 0.3 V at 0.1 A g$^{-1}$ after 10 cycles. After charging, the original MnCO$_3$ diffraction peak gradually disappears, while the MnO$_2$ characteristic peak becomes more and the peak intensity becomes stronger. In the discharge stage, a large amount of Zn$^{2+}$ is embedded in MnO$_2$ rather than MnCO$_3$ and transformed into the spinel
ZnMn$_2$O$_4$. The diffraction peak of ZnMn$_2$O$_4$ is positively correlated with MnO$_2$ content, which is also the reason for the continuous increase in the electrochemical capacity of cathode materials. When MnCO$_3$ is not in a phase transition to MnO$_2$, the cycle curve reaches stability. Figure 5B shows the SEM image of the MnCO$_3$@CC charged to 2.0 V after 10 cycles. The initial MnCO$_3$@CC smooth cube block edges and corners basically disappear, and cracks appear on the surface. The change of morphology is conducive to expand the contact area between Zn$^{2+}$ and the host, reduce the ion and charge transmission path and resistance, and then improve performance. Figure 5C shows the SEM image of the MnCO$_3$@CC discharged to 0.3 V after 10 cycles. The result shows that the carbon cloth is covered by nano-spheres, the original nanocube basically disappears, and the specific surface area continues to increase. The gradual change of morphology is also the reason for the continuous increase of specific capacity. The XPS patterns of Mn are shown in Figure 5D under charging to 2.0 V after 10 cycles. The two groups of spin orbits can be decomposed into Mn$^{2+}$ (2p$_{3/2}$, 641.5 eV; 2p$_{1/2}$, 653.8 eV) and Mn$^{4+}$ (2p$_{3/2}$, 641.5 eV; 2p$_{1/2}$, 653.8 eV), and the contents of Mn$^{2+}$ and Mn$^{4+}$ are opposite to the results after the first cycle. At this time, the proportion of Mn$^{4+}$ is much larger than Mn$^{2+}$, which further proves that MnCO$_3$ gradually changes into MnO$_2$. The high-resolution spectrum of Mn2p is shown in Figure 5H, the two groups of spin orbits can be decomposed into Mn$^{3+}$ (2p$_{3/2}$, 642.3 eV; 2p$_{1/2}$, 654.2 eV) and Mn$^{4+}$ (2p$_{3/2}$, 644.2 eV; 2p$_{1/2}$, 655.8 eV). After long-time activation, a large number of MnCO$_3$ change into MnO$_2$, and the increase of MnO$_2$ gradually increases the content of discharge product ZnMn$_2$O$_4$. Therefore, the proportion of Mn$^{3+}$ and Mn$^{4+}$ is basically the same. The changes in valence and content further prove the mechanism that the MnCO$_3$ first changes into MnO$_2$, and then the generated MnO$_2$ reacts with Zn$^{2+}$ in the electrolyte.

4 Conclusion

The MnCO$_3$ nanocubes are synthesized on carbon cloth by the one-step hydrothermal method, which has good electrochemical performance as cathode material for ZIBs. The specific capacity of the MnCO$_3$/CC shows 82.73 mAh g$^{-1}$ at 1.0 A g$^{-1}$ after long-time activation. After 1,500 cycles, the capacity retention rate is 110.6% compared with that at 200 cycles, which indicates that the MnCO$_3$@CC has excellent stability in the charging and discharging process. The Zn$^{2+}$ storage mechanism of the MnCO$_3$@CC was explored by in situ SEM, XRD, and XPS. In the initial stage, MnCO$_3$ transformed into MnO$_2$, and the generated MnO$_2$ reacted with Zn$^{2+}$ in the electrolyte. In the discharge stage, the spinel ZnMn$_2$O$_4$ is gradually formed in the cathode with the embedding of Zn$^{2+}$. In the charging stage, the ZnMn$_2$O$_4$ is gradually transformed into MnO$_2$ with the removal of Zn$^{2+}$. In this study, the MnCO$_3$ cathode material can achieve high specific capacity and cycle stability, which provides a new idea for high-performance aqueous zinc-ion batteries.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

Author contributions

JZ and PL: Data curation, experimental operation, and writing—original draft. JY, YG, JL, and CW: Conceptualization, visualization, and formal analysis. XJ, GM, LI, HW, LT, and JZ: Writing—review and editing. YR and HW: Funding acquisition, project administration, and supervision.

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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. The handling editor YR declared a past co-authorship with the author LL.

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Supplementary material

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Zheng et al. 10.3389/fchem.2022.954592

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