Facile electrodeposited MnO$_2$ as cathode materials for Zn-ion batteries

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Abstract. MnO$_2$ prepared through facile electrochemical-deposition method at different deposition time on Ni foam substrates are used as cathode materials for Zn-ion batteries. The results show that the electrode using the condition of deposition current of 80 mA for 10 min has the best overall electrochemical performances. The specific capacity measured by the electrode position of the MnO$_2$ electrode for 5 min is the highest, but the cycle performance of the sample is poor. The specific capacity measured by electrode position of the MnO$_2$ electrode sample for 20 min is the lowest, but the cycle performance of the sample is the best.

Keyword: Manganese dioxide; Electrochemical deposition; Cathode material; zinc ion battery.

1. Introduction

The energy and environmental issues facing human society are imminent, which directly affect the survival and development of human civilization in the future. With the depletion of non-renewable resources (such as natural gas, oil and coal, etc.) and the deteriorating global ecological environment, the development of renewable energy (such as wave energy, geothermal energy, and tidal energy) has become a global trend [1]. The use of renewable energy is inseparable from the use of energy storage devices, and batteries are a relatively mature and reliable energy storage device [2]. Batteries such as lithium-ion batteries, as a modern convenient and efficient electrochemical energy storage device, have been widely used in many fields such as commercial entertainment, power transportation, and Internet communications. However, its organic electrolyte is flammable, explosive and toxic, and has certain safety hazards. At the same time, this kind of battery needs to be produced under completely anhydrous conditions, and strict production requirements result in higher production costs. The above several shortcomings greatly limit the application of this type of battery in large-scale energy storage.

In recent years, zinc-ion batteries have once again become a research hotspot, mainly because zinc-ion batteries have many advantages such as high safety in use, no pollution to the environment, low manufacturing cost, and fast charge and discharge [3]. At the same time, the zinc anode has a higher hydrogen evolution overpotential and a lower oxidation-reduction potential, and has the advantages of non-toxicity, abundant reserves and easy preparation [4]. Therefore, a secondary zinc ion water-based battery with low manufacturing cost, low risk during use, low environmental hazard and strong energy storage capacity is one of the important choices for future batteries.
At present, the development of cathode materials for secondary zinc ion batteries is still in the preliminary stage. Commonly used cathode materials for zinc-ion batteries mainly include manganese dioxide [5], vanadium-based oxides and Prussian blue analogs [6-7]. Among them, manganese dioxide has the highest charge and discharge voltage advantage. Methods of preparing manganese dioxide include chemical methods, hydrothermal methods, sol-gel methods, electrochemical methods, and the like. Electrochemical preparation of the electrode substrate has strong surface binding force, small crystal particle diameter, uniform crystal distribution, and has the advantages of easy preparation of raw materials, convenient reaction conditions, and controllable electrode shaping. This study is based on a simple electrochemical deposition method, which directly grows manganese dioxide on Ni foam. Through the adjustment of different deposition times and deposition currents, the optimal method suitable for zinc-ion battery cathode materials is explored.

2. Experimental

2.1. Preparation of manganese dioxide cathode material
Firstly, the nickel foam was ultrasonically cleaned for 10 minutes immersed in acetone and alcohol respectively, and then cleaned with deionized water three times. The nickel foam was then placed in a 0.5 mol/L sulfuric acid solution for 15 minutes to etch away the oxide film on the surface and cleaned with deionized water three times. The processed nickel foam was used as the working electrode, the platinum electrode was the counter electrode, and the reference electrode was calomel electrode. 0.5mol/L MnSO4 solution was used as electrodeposition solution, and constant current method was used for deposition. The deposition current was set to 80 mA, the electrode area was 1.5 cm2, and the electrodeposition time was 5 minutes, 10 minutes, 20 minutes, and 30 minutes. After deposition, the working electrodes were rinsed with deionized water, and dried in oven. Electrodeposition equipment is CHI660E.

2.2. Zinc ion battery assembly
A pure zinc flake was polished to remove the surface oxide film and used as the negative electrode of the battery. It was placed in absolute ethanol and ultrasonic washed for 15 minutes before using. The above-mentioned electrodeposited manganese dioxide was used as the positive electrode, Whatman glass fiber membrane filter paper was used as the battery separator, and the zinc sulfate was used as the electrolyte to assemble the battery. Then the Neware battery tester was used to test the cyclic charge and discharge performance.

2.3. Battery characterization and testing
UltimaIV X-ray diffraction (XRD) and DXR-2 Raman spectroscopy (Raman) were used to study the crystal structure and composition of the cathode material. CHI660E electrochemical workstation was used for impedance and cyclic voltammetry analysis. The impedance is 1000000Hz at high frequency and 0.1Hz at low frequency. Cyclic voltammetry uses a three-electrode method for cyclic voltammetry. The voltage range is 0.8V to 1.8V, and the scanning speed is 0.2mV/s

3. Results and discussion
Figure 1 shows the XRD patterns of manganese dioxide electrodes prepared by electrodepositing nickel foam as a substrate for 1 min, 5 min, 10 min, and 20 min, respectively. Using Jade 5 software to analyze the obtained XRD pattern, it can be seen from the figure that there are three sharp diffraction peaks corresponding to nickel metal at the positions of 44.4°, 51.7°, and 76.3° [8]. The XRD pattern failed to show the characteristic peak of MnO2, which may be due to the small amount of MnO2 deposited on the electrode surface.

Figure 2 is a Raman diagram of manganese dioxide electrodes prepared by electrodepositing nickel foam as a substrate for 1 min, 5 min, 10 min, and 20 min, respectively. It can be analyzed from the figure that there is an obvious characteristic peak of MnO2 near 650 cm^{-1}, and a characteristic peak of metallic
nickel near 2300 cm\(^{-1}\), so it can be inferred that manganese dioxide was successfully deposited on the surface of the nickel foam [9].

**Figure 1.** XRD patterns of sample electrodes under different deposition times.

**Figure 2.** Raman patterns of sample electrodes under different deposition times.

Figure 3 is an electrochemical impedance analysis diagram of manganese dioxide electrodes prepared by electrodepositing nickel foam as a substrate for 1 min, 5 min, 10 min, and 20 min, respectively. It can be seen from the figure that the image is composed of two parts: a circular arc in the high frequency area and a straight curve in the low frequency area. The arc in the high frequency area represents the impedance of the electrochemical reaction, and the straight line in the low frequency area represents the diffusion-related impedance. The ohmic internal resistances of the four samples are
similar, and the arc radius of the electrode material is the smallest for electrodeposited for 10 minutes, so the electrode has the smallest charge transfer resistance. In the most perfect case, the low frequency part of the AC impedance curve is at 90 degrees to the horizontal axis. Therefore, it can be seen from Fig. 3 that the electrode samples deposited for 5 min and 10 min show better specific volume characteristics [10].

**Figure 3.** AC impedance diagram of sample electrodes under different deposition times.

**Figure 4.** Cyclic voltammetry curves of sample electrodes under different deposition times.

Figure 4 is the cyclic voltammetry test diagram of manganese dioxide electrodes prepared by electrodepositing nickel foam as the substrate for 1 min, 10 min, and 20 min, respectively. It can be seen
from Figure 4 that the electrode undergoes a significant oxidation-reduction reaction during the test. Among them, the oxidation peak and reduction peak of the electrode sample electrodeposited for 10 minutes are the most obvious, and the cyclic voltammetry curve is almost symmetrical, indicating that the reversible cycle performance of the battery based on electrodeposited MnO2 at 10 minutes is the best.

Figure 5 shows the discharge capacity-cycle curves of MnO2 electrodes prepared by electrodepositing nickel foam as the substrate for 1 min, 5 min, 10 min, and 20 min in a zinc ion battery. The current densities are 50 mA g\(^{-1}\), 100 mA g\(^{-1}\), 150 mA g\(^{-1}\), 200 mA g\(^{-1}\), 250 mA g\(^{-1}\) and 100 mA g\(^{-1}\), respectively. It can be clearly seen from the figure that the maximum capacitance of the electrode sample deposited for 5 minutes is higher than that of other electrode samples, but its cycle performance is poor. The electrode capacitance value of electrodeposition for 10 min is high, and the cycle performance is good.

![Figure 5. Discharge capacity-cycle curves of sample electrodes under different deposition times.](image)

### 4. Conclusion

In this study, a facile constant current electrochemical deposition method is used to prepare MnO2 electrodes whose basic electrochemical properties in zinc-ion batteries are investigated. The MnO2 electrodes prepared with different deposition times are characterized by X-ray diffractometer and Raman spectrometer. Among them, the MnO2 electrode sample electrodeposited for 5 minutes has the highest specific capacity, but the cycle performance of this sample is poor. The measured specific capacity of the MnO2 electrode sample deposited for 20 minutes is the lowest, but the sample has the best cycle performance. Based on comprehensive considerations, the MnO2 electrode material electrodeposited for 10 minutes in this test not only has a higher specific capacity, but also has good cycle performance, which is the most excellent performance in zinc ion batteries.

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