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A Binder-Free Amorphous Manganese Dioxide for Aqueous Zinc-Ion Battery

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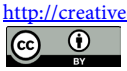

Abstract

Aqueous zinc-ion battery has attracted much attention due to its low price, high safety, and high theoretical specific capacity. However, most of their performances are limited by the unsatisfied architecture of cathodes. Herein, we fabricated amorphous manganese dioxide by an in situ deposition method. The amorphous manganese dioxide can directly serve as the cathode of an aqueous zinc-ion battery without a binder. The resultant cathode exhibits a high specific capacity of 133.9 mAh/g at 200 mA/g and a capacity retention of 82% over 50 cycles at 1 A/g.

Keywords

Binder-Free, Amorphous Manganese Dioxide, Aqueous Zinc-Ion Battery

1. Introduction

Lithium-ion batteries occupy the commercial energy storage battery market because of their high energy density and long life [1]. However, the high cost and low safety of lithium seriously limit its application in the field of large-scale energy storage. Aqueous zinc-ion batteries (ZIBs) are considered as promising candidates because of the high theoretical specific capacity (820 mAh/g) low cost and intrinsic safety of aqueous electrolytes [2] [3].

In recent years, various materials have been proved to be cathodes of ZIBs, such as vanadium-based materials [4] [5], Prussian Blue [6] [7], manganese-based materials [8] [9] [10] [11] and so on. Among them, manganese dioxide has attracted the strongest attention because of its natural abundance, low cost, and high theoretical capacity (308 mAh/g). The preparation of manganese dioxide is generally carried out by hydrothermal and coprecipitation methods. While achieving encouraging properties, these preparation methods are gener-

ally time-consuming, rigid, or complex, which would substantially limits their practical applications in the massive production of ZIBs' cathode materials. In addition, these active materials are usually mixed with conductive additives and polymer adhesives and then coated on the collector to manufacture the cathode of aqueous ZIBs [12] [13]. However, the addition of polymer adhesives hinders the effective utilization of the surface area of active materials [14]. Therefore, the new cathode structure of ZIBs must be considered.

In view of this problem, one simple and efficient method was adopted to prepare a binder-free amorphous manganese dioxide (A-MnO_2) as cathode materials of ZIBs. A uniformly distributed MnO_2 layer was deposited on the surface of carbon cloth by constant voltage deposition. The zinc storage properties of amorphous manganese oxide were systematically studied. It can provide a high capacity of 133.9 mAh/g at 200 mA/g and 82% of capacity retention after 50 cycles.

2. Experimental Method

2.1. Preparation of A-MnO_2

Carbon cloth (CC) and carbon paper were purchased from shengernuo shopping mall (China). All other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. The battery was assembled in CR2032-type coin cell with carbon paper as anode, $MnSO_4$ solution as electrolyte and carbon cloth as cathode collector. First charge the battery to 1.8 V, and then charge it at constant voltage for 8 h to electrodeposit MnO_2 on the carbon cloth. The as-obtained A-MnO_2 electrode was washed with DI water and dried in vacuum oven at 80˚C for 10 h.

2.2. Characterization

The morphology and phase structure of A-MnO_2 electrode were characterized by scanning electron microscopy (SEM, Carl Zeiss Co., Germany, (GeminiSEM 500)), and X-ray diffraction (XRD, Rigaku Co., Japan (Cu Kα radiation, λ = 1.540593)), respectively.

2.3. Electrochemical Measurements

The Zn//MnO_2 coin cells were 2032-type, where zinc foils were anodes, A-MnO_2 @CC were cathodes, 2 M $ZnSO_4$/0.1 M $MnSO_4$ hybrid solutions were electrolytes, and glass fibers were separators, respectively. Cyclic voltammetry (CV) curves were measured separately at 0.1 mV/s. Galvanostatic cha-discharge (GCD) curves were studied at various current densities. The all electrochemical performance was measured through the electrochemical station (CHI660e).

3. Results and Discussion

The structure of the A-MnO_2 was first characterized by XRD. As shown in **Figure 1**, Removing the peak of carbon cloth, no distinct peaks can be detected in the XRD pattern except for a broad and weak peak around 37˚, due to the formation of hydrous manganese oxide [15] [16]. This indicates that the manganese

oxide has a very low crystallinity. The morphology of the A-MnO_2 sample is further confirmed by SEM. As shown in Figure 2, it can be observed that A-MnO_2 is composed of uniform nanosheets, which can realize a short Zn^{2+} transport pathway and fast Zn^{2+} diffusion.

The electrochemical properties of the A-MnO_2 samples were tested using zinc foil as anode and 2 M $ZnSO_4$/0.1 M $MnSO_4$ mixture solution as the electrolyte. First, as shown in Figure 3, CV measurements have been performed at a scanning rate of 0.1 mV/s in a potential window of 1.0 - 1.8 V. There is an intense cathodic peak at 1.22 V within the first cycle, caused by the reduction of Mn^{3+} and Zn^{2+}/H^+ adsorption [17]. In the next cycle, there are two cathodic peaks at 1.37 V and 1.26V, caused by the reaction of H^+ and Zn^{2+} insertion [18].

The capacity of the Zn//MnO_2 cells at different current densities is shown in Figure 4. The A-MnO_2 electrodes deliver a discharge capacity of 133.9 mAh/g at 0.2 A/g. More importantly, even under a high current density of 1.5 A/g, the ZIBs could also discharge a considerable capacity of 38.4 mAh/g. In order to assess the ZIBs stability with A-MnO_2 cathode, the cycling stability and Coulombic efficiency of the Zn//MnO_2 cells are presented in Figure 5. At the current density of 1 A/g, the battery delivers 82% capacity retention after 50 cycles, with retaining a high Coulombic efficiency of nearly 100%.

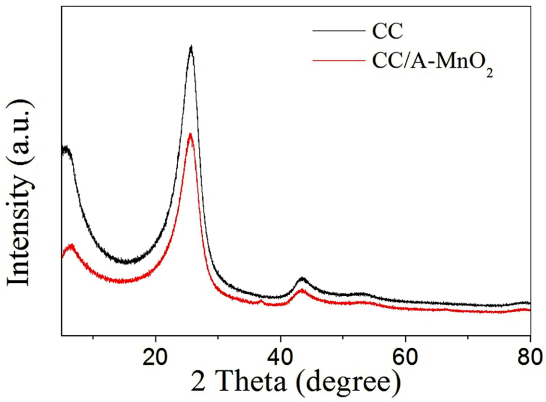

Figure 1. XRD patterns for CC and A-MnO_2 samples.

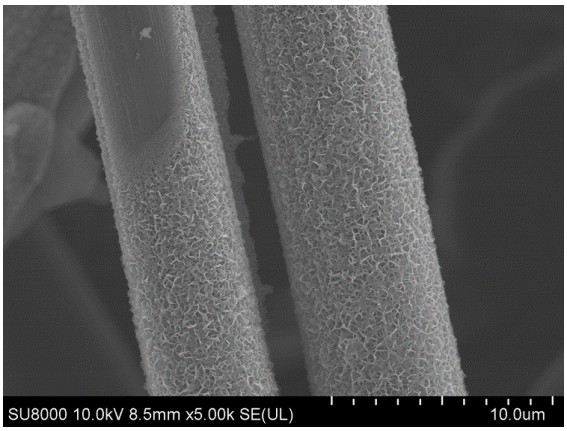

Figure 2. SEM images of A-MnO_2 samples.

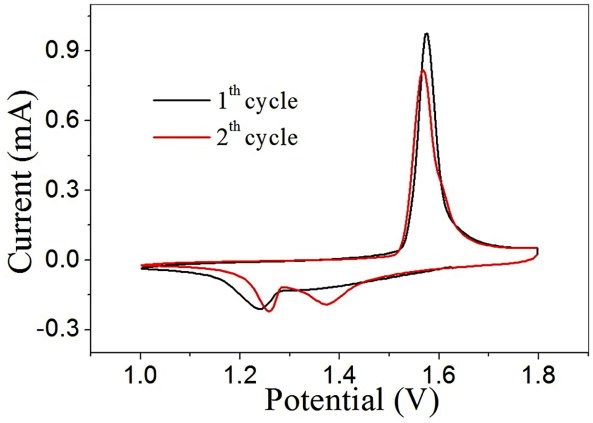

Figure 3. The CV curves of the Zn//MnO_2 cells at initial two cycles under 0.1 mV/s.

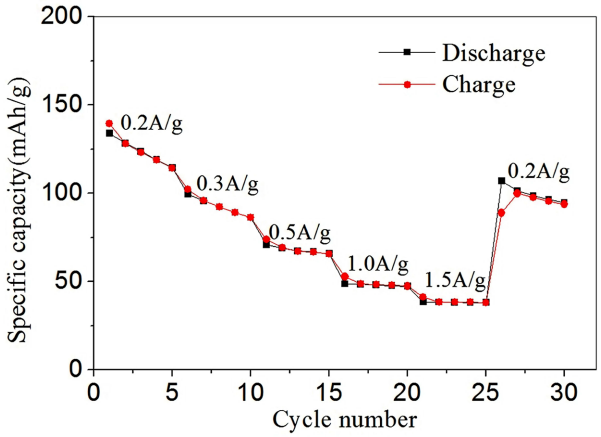

Figure 4. The rate performance of the Zn//MnO_2 cells under different current densities.

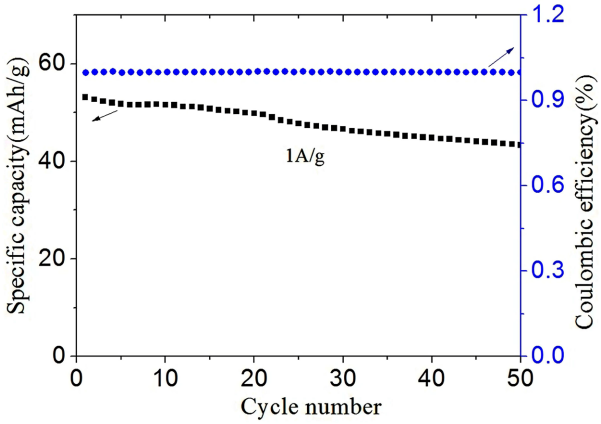

Figure 5. The cycling performance of the Zn//MnO_2 cells at 1 A/g.

4. Conclusion

In summary, a binder-free amorphous manganese dioxide was prepared by an in situ deposition method. A uniformly distributed MnO_2 layer was deposited on the surface of carbon cloth by constant voltage deposition. Moreover, the amorphous state of MnO_2 and interconnected nanosheets structure endow the

cathode with rapid ion diffusion and high conductivity, resulting in excellent electrochemical performance. It can provide a high capacity of 133.9 mAh/g at 200 mA/g and 82% of capacity retention after 50 cycles.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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