

Preparation of Mesoporous Structure Electrode Materials ZnMn_2O_4 by Co-precipitation Method

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Abstract. In order to study the fast and efficient method of preparing electrode material ZnMn_2O_4 , in this paper, oxalic acid was selected as the precipitator, oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) as the chemical precipitator, manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) as the manganese source and zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$) as the zinc source. The precursor was prepared by co-precipitation method. Then, ZnMn_2O_4 powders with mesoporous structure were obtained at different calcination temperatures. The phase of ZnMn_2O_4 powders at different calcination temperatures was characterized by XRD analysis. After considering the crystallinity and high temperature agglomeration, samples calcinated at 600°C were selected as the cathode material of the battery, and were characterized by SEM and TEM. The experimental results show that the electrode material ZnMn_2O_4 prepared by this method has high crystallinity, high preparation efficiency, energy saving, environmental protection and good dispersion.

1 Introduction

Zinc manganate (ZnMn_2O_4) has a high theoretical specific capacity (784mAh/g) and large reserves of raw materials and environmental protection, which is one of the best substitutes for traditional graphite negative materials. Therefore, this material has become a hot spot in the field of battery materials in recent years [1-2]. As a manganese based composite metal oxide, ZnMn_2O_4 has the inherent advantages of manganese metal oxide, but at the same time, due to the addition of Zn, the electrode potential between each other is different. In the process of charge and discharge cycle, the two components can coordinate and buffer each other, thus effectively improving the original cycle performance [3-4].

Courtel [2-3] et al. successfully prepared ZnMn_2O_4 nanoparticles by hydrothermal method and studied their electrochemical characteristics as a lithium ion electrode material. Zhao [5] et al. selected zinc acetate and manganese acetate as zinc and manganese sources respectively, and prepared the pure phase ZnMn_2O_4 by hydrothermal method under the condition of 100°C for 4 hours, but the electrochemical performance was not good, and the specific capacity after repeated cycles was low. Yang [6] et al. used the electro spinning method to spray the precursor of zinc manganate onto the surface of Al foil with the electric injection technology at a high voltage of 12kV. ZnMn_2O_4 was obtained by roasting the fibrous precursor at high temperature. Electrochemical behavior test shows that it has good electrochemical stability. But the preparation process is more complex and requires more equipment. In addition, some scholars successfully prepared nano ZnMn_2O_4 powder by mixed

solvent thermal method and solid phase method [7-9]. However, it is seldom reported that ZnMn_2O_4 powder was prepared by co-precipitation method as electrode material.

Co-precipitation method is a solution containing a variety of cation, add a certain precipitator, reaction formation of uniform components of precipitation. The nanometre powder material is obtained directly through various chemical reactions in the solution. The main advantages of the powder are uniform chemical composition, small particle size, uniform particle size and large yield. At the same time, the preparation conditions and technology are simple and convenient [10-11]. Besides, this method has low requirements on equipment, short production cycle and is suitable for commercial production.

Therefore, this paper studied and prepared ZnMn_2O_4 nano powder electrode material with mesoporous structure by co-precipitation method. Dihydrate oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was selected as the chemical precipitator while manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) was selected as the manganese source, and zinc acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$) was selected as the zinc source. The white precursor material was prepared by co-precipitation method. After calcinating the precursor at different high temperatures, the brown ZnMn_2O_4 powder with different crystallinity was obtained. The best ZnMn_2O_4 powder was selected as the cathode material by X-ray diffraction (XRD) based on the crystallinity and particle size. It provides a new idea for the preparation of cathode materials for lithium ion batteries and has certain reference value for the research and development of chemical battery technology.

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2 Experiment

2.1 Experimental materials

Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), $\geq 99.0\%$, AR, Sinopharm group chemical reagent co. LTD; Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), $\geq 99.0\%$, AR, Sinopharm group chemical reagent co. LTD; Anhydrous ethanol ($\text{C}_2\text{H}_6\text{O}$), $\geq 99.7\%$, AR, Sinopharm group chemical reagent co. LTD; Oxalic acid dehydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), $\geq 99.5\%$, AR, Nanjing chemical reagent co. LTD; All the above chemical reagents were used directly without further treatment during the experiment. The experimental water was self-made deionized water.

2.2 Sample preparation

An aqueous solution of zinc acetate and manganese sulfate was prepared according to the molar ratio of zinc salt and manganese salt 1:2; an appropriate amount of oxalic acid was weighted and then was prepared into ethanol solution. The molar concentration of zinc acetate was 0.1M and that of oxalic acid was 1.5M; under vigorous magnetic stirring, the aqueous solutions of zinc acetate and manganese sulfate were slowly added to the ethanol solution of oxalic acid. The drop acceleration is 5ml/min. After dripping, the mixture was centrifuged with washing by water and alcohol for several times. The white precursor was obtained by vacuum drying the product. Then, it was calcinated in muffle furnace at high temperature. The calcination temperature was between 300 °C and 900 °C, and the calcination time was 3h. In the end the brown ZnMn_2O_4 powder was obtained.

2.3 Characterization analysis

X-ray diffractometer(XRD), Bruker, Germany, D8 Advance, Main parameters of the instrument: Angle reproducibility $\pm 0.02^\circ$, Cu target, radius of goniometer ≥ 200 mm, minimum step length 0.0001° , Angle range (theta /2) 360° , absolute accuracy (theta /2) $\pm 0.005^\circ$, single motor drive, maximum scanning speed $200^\circ/\text{min}$.

Transmission electron microscope (TEM), Japan JEOL company, Jem-2100, acceleration voltage 200kV, Cu network;

Field emission scanning electron microscope (SEM), Hitachi, Japan, S-4800 II, magnification 20-800000, maximum resolution 1nm, acceleration voltage 0.5~30kV.

3 Results and Discussion

3.1 Phase analysis of materials

XRD was used to analyze the phase and crystallinity of the brown ZnMn_2O_4 powders calcined at different temperatures, as shown in Figure 1. As can be seen from

Figure 1, with the continuous increase of sintering temperature, the diffraction characteristic peak of ZnMn_2O_4 powder becomes sharper, which indicates that the crystallinity is increasing. But at the same time, with the increase of calcination temperature, the diffraction characteristic peak width is weakened, indicating that high temperature sintering resulted in increased agglomeration of ZnMn_2O_4 powders and increased average particle size. For the selection of materials, the influence of crystallinity and agglomeration factors should be considered comprehensively. In Figure 1, when the calcination temperatures are 600 °C and 700 °C, the diffraction characteristic peaks of the two have little difference. Namely, there is little difference in crystallinity. However, the higher temperature will definitely lead to more serious powder agglomeration [12-13]. Therefore, ZnMn_2O_4 powder calcinated at 600 °C was selected as the negative electrode material for subsequent further experiments.

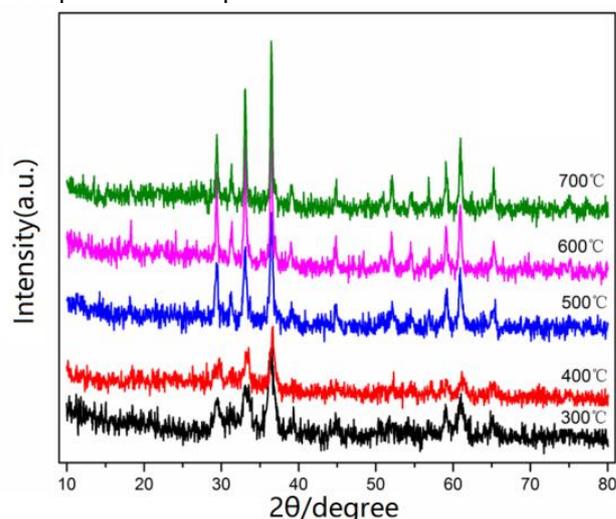


Figure.1 XRD patterns of calcinated samples at different temperatures

3.2 Material morphology analysis

Figure.2 shows the microstructure of ZnMn_2O_4 powders calcinated at 600 °C by means of field emission scanning electron microscope and transmission electron microscope. Figure 2(a) is a scan electron microscope image at 50,000x magnification. The particle size of ZnMn_2O_4 powder belongs to nanometer level, but there is an obvious high temperature agglomeration phenomenon. Figure 2(b) is the transmission electron microscope photo of ZnMn_2O_4 powder after adding oxalic acid calcination. There is an obvious mesoporous structure inside, and the particle aggregation is directional, which is neatly arranged along the direction of the red line in Figure 2(b).

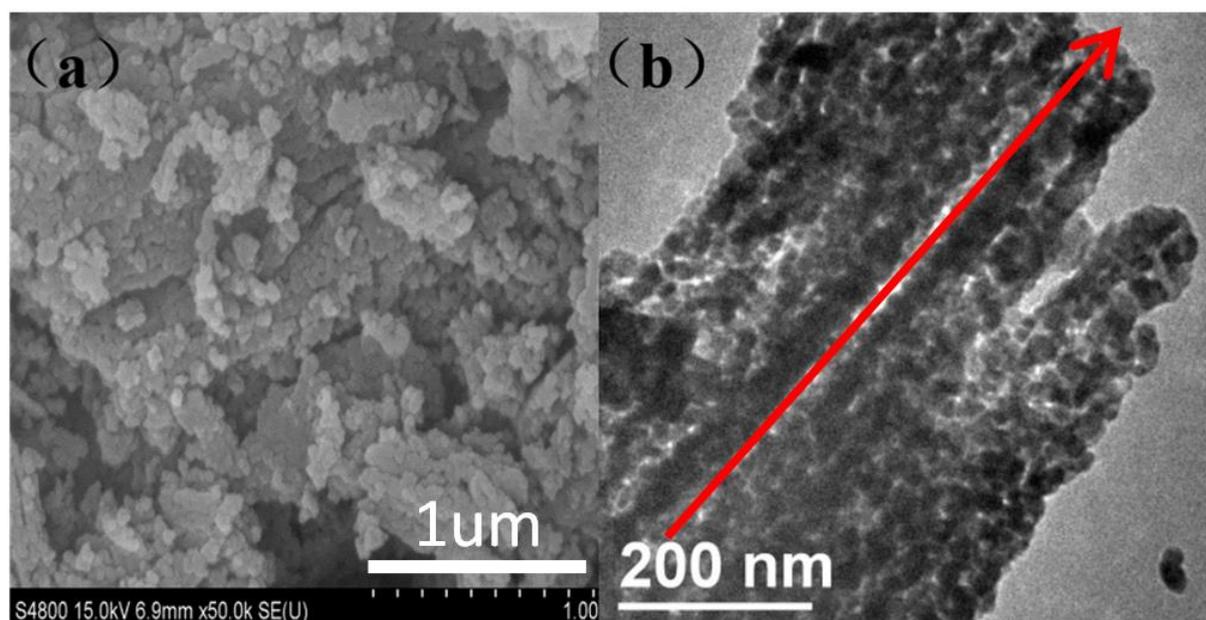


Figure.2 Images of samples (a) ZnMn₂O₄ powder SEM (b) ZnMn₂O₄ powder TEM at 600°C

To sum up, after the ZnMn₂O₄ powder is calcinated at 600°C, on the one hand, the high crystallinity can be guaranteed; on the other hand, the microscopic morphology of the sample is regular. Although there is a certain agglomeration phenomenon, the mesoporous structure is obvious and has good directivity according to transmission electron microscope photos.

4 Conclusions

In this paper, oxalic acid was selected as the precipitator, oxalic acid dihydrate (C₂H₂O₄•2H₂O) as the chemical precipitator, manganese sulfate monohydrate (MnSO₄•H₂O) as the manganese source and zinc acetate dihydrate (C₄H₆O₄Zn•2H₂O) as the zinc source. The precursor was prepared by co-precipitation method. Then, ZnMn₂O₄ powders with mesoporous structure were obtained at different calcination temperatures. The phase of ZnMn₂O₄ powders at different calcination temperatures was characterized by XRD analysis. After considering the crystallinity and high temperature agglomeration, samples calcinated at 600°C were selected as the cathode material of the battery, and were characterized by SEM and TEM. The experimental results show that the electrode material ZnMn₂O₄ prepared by this method has high crystallinity, high preparation efficiency, energy saving, environmental protection and good dispersion.

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