Preparation of Mesoporous Structure Electrode Materials 
ZnMn$_2$O$_4$ by Co-precipitation Method

Jiaxing Song$^1$, Tao Guo$^1$, Qiong Wang$^2$, Miao Yao$^1$ and Yiming Mao$^1$

$^1$College of Field Engineering, Army Engineering University of PLA, Nanjing, Jiangsu, 210007, China  
$^2$International Military Cooperation Office of the CMC, Beijing, Beijing, 100000, China

Abstract. In order to study the fast and efficient method of preparing electrode material ZnMn$_2$O$_4$ in this paper, oxalic acid was selected as the precipitator, oxalic acid dihydrate (C$_3$H$_2$O$_4$•2H$_2$O) as the chemical precipitator, manganese sulfate monohydrate (MnSO$_4$•H$_2$O) as the manganese source and zinc acetate dihydrate (C$_2$H$_4$O$_2$•Zn•2H$_2$O) as the zinc source. The precursor was prepared by co-precipitation method. Then, ZnMn$_2$O$_4$ powders with mesoporous structure were obtained at different calcination temperatures. The phase of ZnMn$_2$O$_4$ 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$_2$O$_4$ prepared by this method has high crystallinity, high preparation efficiency, energy saving, environmental protection and good dispersion.

1 Introduction

Zinc manganate (ZnMn$_2$O$_4$) 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$_2$O$_4$ 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] .

Courtole[2-3] et al. successfully prepared ZnMn$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ powder by mixed solvent thermal method and solid phase method [7-9]. However, it is seldom reported that ZnMn$_2$O$_4$ 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 nanometer 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$_2$O$_4$ nano powder electrode material with mesoporous structure by co-precipitation method. Dihydrate oxalic acid (C$_2$H$_2$O$_4$•2H$_2$O) was selected as the chemical precipitator while manganese sulfate (MnSO$_4$•H$_2$O) was selected as the manganese source, and zinc acetate (C$_2$H$_4$O$_2$•Zn•2H$_2$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$_2$O$_4$ powder with different crystallinity was obtained. The best ZnMn$_2$O$_4$ 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.
2 Experiment

2.1 Experimental materials

Manganese sulfate monohydrate (MnSO₄·H₂O), ≥99.0%, AR, Sinopharm group chemical reagent co. LTD; Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O), ≥99.0%, AR, Sinopharm group chemical reagent co. LTD; Anhydrous ethanol (C₂H₅OH), ≥99.7%, AR, Sinopharm group chemical reagent co. LTD; Oxalic acid dehydrate (C₂H₂O₄·2H₂O), ≥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 ZnMn₂O₄ powder was obtained.

2.3 Characterization analysis

X-ray diffractometer(XRD), Bruker, Germany, D8 Advance, Main parameters of the instrument: Angle reproducibility ±0.02°, Cu target, radius of goniometer ≥200 mm, minimum step length 0.0001°, Angle range (theta /2) 360°, absolute accuracy (theta /2) ±0.005°, single motor drive, maximum scanning speed 200°/ 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 ZnMn₂O₄ 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 ZnMn₂O₄ 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 ZnMn₂O₄ 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, ZnMn₂O₄ powder calcinated at 600°C was selected as the negative electrode material for subsequent further experiments.

![Figure 1 XRD patterns of calcined samples at different temperatures](image-url)

3.2 Material morphology analysis

Figure 2 shows the microstructure of ZnMn₂O₄ 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 ZnMn₂O₄ powder belongs to nanometer level, but there is an obvious high temperature agglomeration phenomenon. Figure 2(b) is the transmission electron microscope photo of ZnMn₂O₄ 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).
To sum up, after the ZnMn$_2$O$_4$ 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 (C$_2$H$_2$O$_4$•2H$_2$O) as the chemical precipitator, manganese sulfate monohydrate (MnSO$_4$•H$_2$O) as the manganese source and zinc acetate dihydrate (C$_2$H$_4$O$_2$Zn•2H$_2$O) as the zinc source. The precursor was prepared by co-precipitation method. Then, ZnMn$_2$O$_4$ powders with mesoporous structure were obtained at different calcination temperatures. The phase of ZnMn$_2$O$_4$ 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$_2$O$_4$ prepared by this method has high crystallinity, high preparation efficiency, energy saving, environmental protection and good dispersion.

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