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Performance of MnO_2 Nano-Particles for Electrochemical Hybrid Capacitor Electrode Material

Jon Min Ung, Ri Hyok Chol

Abstract MnO_2 nano-particles, as electrode material for electrochemical hybrid supercapacitor(EHC), were sucessfully prepared by solid–state reaction of potassium permanganate($KMnO_4$) with manganese sulfate($MnSO_4$). The structure of MnO_2 nano–particles was analyzed using X-ray diffraction(XRD) and scanning electron microscopy(SEM). The capacitive characteristics of the MnO_2 electrode were investigated with three–electrolytic cell system in 7mol/L KOH aqueous electrolyte. The results showed that the nano-MnO_2 was amorphous with the particle size of 60～80nm. The specific capacitance of the MnO_2 electrode was decreased with increasing the discharge current, it was 276F/g for constant current density of 5mA/cm^2.

Key words capacitor, electrode material, manganese dioxide

Introduction

EHC has been recognized as unique charge storage devices, exhibiting specific power higher than batteries and specific energy higher than conventional capacitors. The promising application fields of EHC include hybrid electric vehicles, uninterruptible power supplies and other electronic devices[8]. Electrode materials for EHC can be divided into three main categories; activated carbon, metal oxides and conducting polymers[2].

In recent years, manganese dioxide has been considered as an active electrode material of EHC, due to its low cost, excellent electrochemical performance and environmental friendly nature. In addition, several methods have been developed for preparing manganese dioxide, such as sol-gel method[9, 10], chemical precipitation[11], electrochemical deposition[3, 4], chemical redox deposition[12], solid–state reaction[1, 13] and physical vapor deposition[5]. Recently, a simple, novel and promising process for preparing the nano-sized oxide by solid-state reaction at low temperature has been demonstrated[6, 7].

In this paper, we have prepared the nano-MnO_2 by solid–state reaction, manufactured the MnO_2 electrode for EHC, and measured the capacitive characteristics of the MnO_2 electrode using three electrolytic cell system.

1. Experimental Method

1.1. Preparation of MnO_2 nanoparticles

The nano-manganese dioxide was synthesized from $KMnO_4$(chemical), $MnSO_4 \cdot H_2O$(analytical) and NaOH(chemical) by solid–state reaction, and polyethylenglycol(PEG) was used as the dispersion agent.

Every reagent was powdered smaller than 40μm on the agate mortar, and then they were mixed.

Then, the mixture was heated in a water bath at 60℃ for 2.5h to make the reaction proceed completely: then, it was washed several times with deionized water, and washed twice with ethanol, and then filtered. The final product was dried at 100℃ to obtain the dark–brown powder.

1.2. Characterization of structure and morphology

The X-ray diffraction (XRD) pattern of the product was recorded using a "XL–30" with CuKα radiation (λ=0.154 056nm) operated at 10～30kV and 40mA. The morphology and particle size of the product were analyzed by scanning electron microscopy (SEM, "RINT2000").

1.3. Electrode preparation and electrochemical characterization

The nano-MnO_2, acetylene black(AB) and polytetrafluoroethylene(PTFE) binder were mixed completely in the weight ratio of 75∶15∶10, and pressed with a hand oil press under 30MPa onto a nickel-foam current collector, followed by drying at 80℃ for 12h.

The specific capacitance of the MnO_2 electrode was measured with three-electrolytic cell system, the active carbon electrode as a counter electrode, and Hg/HgO electrode as a reference electrode in 7mol/L KOH aqueous electrolyte.

2. Results and Discussion

2.1. Structure and morphology of MnO_2

It is generally accepted that the necessary condition for the occurrence of solid state reaction at room temperature is that one of the reactances should have crystalline water or low melting point, on the one hand, sufficient grinding is also required to provide the reactant molecules with more contact opportunities[14].

The solid-state reaction between $KMnO_4$ and $MnSO_4 \cdot H_2O$ with NaOH proceeds as follows.

$$2KMnO_4+3MnSO_4 \cdot H_2O+4NaOH = 5MnO_2+2K_2SO_4+2Na_2SO_4+6H_2O$$

When solid $KMnO_4$ was mixed with $MnSO_4 \cdot H_2O$ and NaOH at room temperature, during the grinding process, the color of the mixture gradually darkened, and this indicated that the chemical reaction occurred successfully.

The XRD pattern of the product is shown in Fig. 1, the main diffraction peak appeared at 2θ 37.46 ° corresponding to α–MnO_2, while other peaks were broadened and lowered. Structural investigation indicated that the product has amorphous structure.

The morphology of the product was examined by SEM. Typical image of the product is shown in Fig. 2, the particles were dispersed well, although some agglomeration is found. We could observe

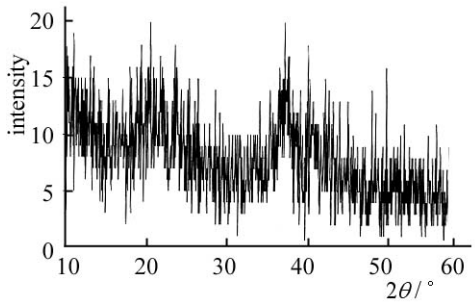

Fig. 1. XRD pattern of the nano-MnO_2

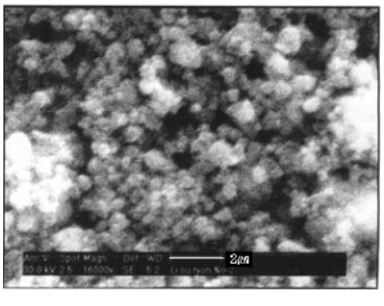
Fig. 2. SEM image of the nano-MnO_2

that the product particles are in the size of 60～80nm and the typical shape of the particles is spherical.

2.2. Electrochemical performances

Fig. 3 shows constant current discharge curves of the MnO_2 electrode under different current densities.

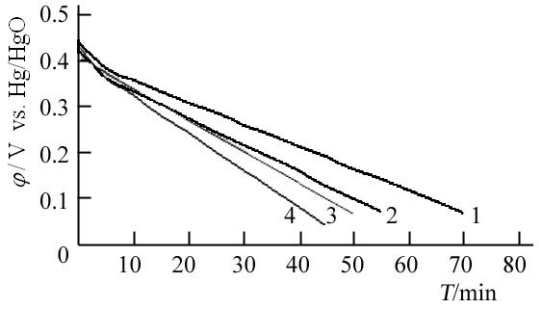

Fig. 3. Constant current discharge curves of the MnO_2 electrode
1–5mA/cm^2, 2–10mA/cm^2, 3–15mA/cm^2, 4–20mA/cm^2

We found that the discharge curves were approximately linear. Furthermore, the results show that the nano–MnO_2 electrode has excellent capacitive characteristics.

Table shows specific capacitances of the MnO_2 electrode at different discharge current densities. The specific capacitance was calculated by the following equation.

$$Cs = I \cdot \Delta t / (\Delta V \cdot m)$$

where I is the discharge current, ΔV is the voltage change, Δt is the discharge time, and m is the mass of MnO_2 deposited on the working electrode.

The results showed that a specific capacitance of 276F/g can be obtained by constant current density of 5mA/cm^2. This was much higher than that of 184F/g which was introduced in the reference[11].

Table 1. Specific capacitances of the MnO_2 electrode at different discharge current densities

Discharge current density/(mA·cm^{-2})	5	10	15	20
Specific capacitance/(F·g^{-1})	276	254	243	229

In addition, the specific capacitance of the MnO_2 electrode was decreased with increasing the discharge current density.

Therefore, we can conclude that the nano-MnO_2 is a promising electrode material for EHC.

Conclusion

MnO_2 nano-particles as the electrode material for EHC was sucessfully prepared by solid-state reaction of $KMnO_4$ with $MnSO_4 \cdot H_2O$. Characterization by XRD and SEM showed that the nano-MnO_2 particles was amorphous with the size of 60～80nm.

The capacitive characteristics of the MnO_2 electrode was investigated with three–electrolytic cell system in 7mol/L KOH aqueous electrolyte. By constant current density of 5mA/cm^2, the MnO_2 electrode could provide a specific capacitance of 276F/g.

Therefore, the nano-MnO_2 is a promising electrode material for EHC.

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