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The facile one-step hydrothermal method to prepare MnO_2 nanoparticles: Structural and electrochemical properties

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Abstract. MnO_2 nanoparticles were synthesized by one-step hydrothermal method. The structural and morphological properties of the sample were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The elemental composition of the sample was characterized by energy dispersive X-ray spectrometer (EDS). Brunauer-Emmett-Teller (BET) was used to study the surface area properties of the MnO_2 nanoparticles. The XRD analyses confirm the formation of γ-MnO_2, having orthorhombic crystal phase (JCPDS file no.14-0644). FE-SEM analysis reveals the combination of massively small spherical particles with average particle size 54.8 nm. The electrochemical performance of MnO_2 nanoparticles was evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). The electrochemical results showed that the MnO_2 nanoparticles delivered the specific capacitance of 200.83 F/g at a current density of 1A the rate capability of 30% after 500 cycles charge and discharge at a current density of 5 A/g. The energy density was 3.62 Wh/kg under a power density of 43.11 W/kg.

1. Introduction

Current demand for energy is increasing, due to the energy crisis and global warming. This has led to the development of many energy storage devices such as capacitors, supercapacitors, batteries and fuel cells etc. Supercapacitors are one of the promising renewable energy storage devices compared with other conventional capacitors and batteries as they, exhibit high power and energy densities, fast charging-discharging rate and long cycle capability [1, 2]. One main objective for studying in this field is to explore some electrode material that gives high electrochemical performance [3]. Generally, the conventional electrode materials are conducting polymers and transition metal oxides. The transition metal oxides (viz. NiO, CO_2O_3, TiO_2, RuO_2, MnO_2, Fe_2O_3, etc) [4-9] have been demonstrated as electrode materials for pseudocapacitors. Among transition metal oxides, MnO_2 is prominent as it shows superior electrochemical behaviour and has applications in catalysts, artificial oxides, dry cell components, inorganic dye for ceramics, electrochemical battery electrodes, and supercapacitors [10-12]. It is well-known that the morphology, porosity and surface area strongly affect the

electrochemical properties of MnO_2. One can tune them by using different synthesis techniques to improve pseudocapacitive properties. Hydrothermal method is one of the important techniques to synthesis materials with different morphology by varying various parameters like temperature, pressure, dwell time, concentration of reagents, active fill level and solvent used in the reaction. Xiao *et al.* [13] have grown a single crystal of α-MnO_2 nanotube which exhibit specific capacitance 220 F/g at scan rate 5 mV/s in 0.1M Na_2SO_4 electrolyte solution prepared by the hydrothermal method. Moreover, different shape of MnO_2 such as nanospheres, hollow urchins and smooth balls could show quite high capacitance of 337, 204 and 276 F/g at a scan rate of 5 mV/s, respectively [14].

In this paper, we report structural and electrochemical properties of MnO_2 nanoparticles synthesized by the one-step hydrothermal method. The structural analysis of the MnO_2 nanoparticles was performed with X-ray diffraction (XRD). The morphological and elemental properties were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometer (EDS). The specific surface area and pore size analysis of the MnO_2 nanoparticles was studied using Brunauer-Emmett-Teller (BET) method. The electrochemical properties were examined by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD).

Experimental procedure

In this study, manganese oxide nanoparticles were prepared by the one-step hydrothermal method. Manganese nitrate [$Mn(NO_3)_2.6H_2O$] and potassium permanganate [$KMnO_4$] were used as starting chemicals and dissolved in 100 mL of deionized water with magnetic stirring at room temperature. The homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave, sealed and maintained at 180 ˚C for 3 h. After the autoclave was cooled naturally to room temperature, the nanoparticles were washed several times with deionized water and ethanol separately. Then the product was dried vacuum oven at 70 ˚C for 24 h. The structural analysis of the MnO_2 nanoparticles was investigated using XRD (Bruker-D8 advanced X-ray diffractometer). The morphology and elements of the sample were characterized by FE-SEM and EDS, respectively. The N_2 adsorption-desorption isotherm and pore size analysis of the MnO_2 nanoparticles were performed using BET method. The electrochemical properties were examined by CV and GCD.

3. Results and discussion

The XRD pattern of the sample is shown in figure 1. The XRD pattern shows the diffraction corresponded to the γ-MnO_2 phase of the standard data JCPDS No.14-0644 with the orthorhombic structure. Moreover, the α-MnO_2 phase was also observed corresponding to the standard data JCPDS No.44-0141 and consistent with the research of Zhang *et al.* [15]. The peaks of impurity phases of Mn, Mn_2O_3 or Mn_3O_4 are not observed in the sample.

The elemental composition of MnO_2 nanoparticles was investigated by EDS as shown in figure 2. The sample reveals peaks of Mn and O, no evidence of impurity phases, the presence of Au came from Au coated on the sample. The morphology of the MnO_2 nanoparticles sample was studied by FE-SEM as shown in the inset of figure 2. FE-SEM image shows the small spherical particles of a uniform particle size. Moreover, these platelets are densely overlapped and aggregated. The average particle size is approximately 54.8 nm. The aggregation of particles was caused by the short reaction time of the hydrothermal process, consistent with the research of Wang *et al.* [16] synthesized a spherical α-MnO_2 using the hydrothermal method.

We investigated the specific surface area, pore volume and pore diameter of the sample by N_2 adsorption-desorption. Figure 3 shows the hysteresis loop signifies that the sample was of Type III isotherm, according to IUPAC classification. The representative the N_2 adsorption-desorption isotherm and corresponding Barrett–Joyner-Halenda (BJH) pore size distribution curves for a representative of the sample are shown in the inset of figure 3. The surface area, pore volume and average pore diameter of the sample was found to be 7.01 m^2/g, 0.30 cm^3/g and 3.30 nm. According to the obtained structure of MnO_2 and those of low specific surface area, pore volume and pore diameter, this could result in a low specific capacity value.

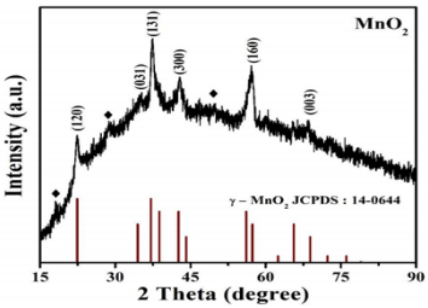

Figure 1. XRD pattern of MnO_2 nanoparticles, ♦ represents the phase of α-MnO_2.

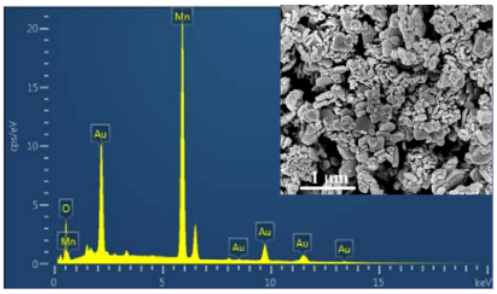

Figure 2. EDS spectrum and the inset shows the FE-SEM image of MnO_2 nanoparticles.

The capacitive properties of the sample were examined by CV analysis. CV curves of the sample within the scan range 2 to 200 mV/s in a potential range -1 to 0.55 V are shown in figure 4. The CV curves show the pseudocapacitive behaviour of the sample, anodic peak appearing at 0.0 to 0.2 V and the cathodic peak shows two peaks at 0.2 and -0.3 to -0.4 V. The occurrence of more than one reaction in an intercalation / deintercalation process of the MnO_2 ion group follows the equation [17, 18].

$$MnO_2 + OH^- \rightarrow MnOOH + e^- \quad (1)$$
$$MnOOH + e^- \rightarrow HMnO_2 + e^- \quad (2)$$
$$MnOOH + HMnO_2^- \rightarrow Mn_3O_4 + H_2O + OH \quad (3)$$

From these reactions, it can be seen that the oxidation number of Mn has been changed from Mn^{4+} to Mn^{3+} and Mn^{2+}, during the reaction between the electrolyte and the electrode material. As a result, the electrode resistance and reaction resistance are increased. This result is consistent with the research of Kaiyu *et al*. [18]. The increase in resistance could result in a lower specific capacitance value.

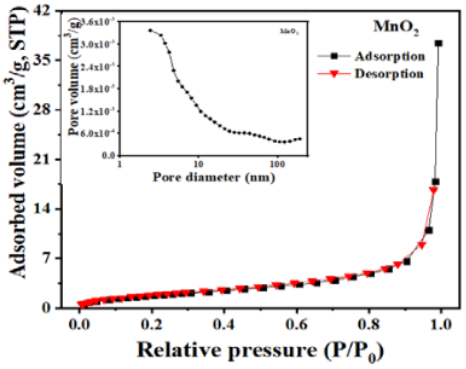

Figure 3. Nitrogen adsorption-desorption isotherms of MnO_2 nanoparticles.

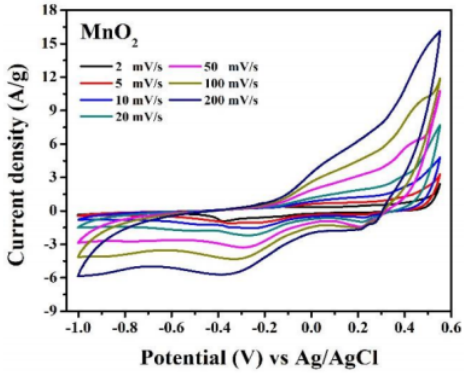

Figure 4. CV curves of the MnO_2 nanoparticles at different scan rates in 6 M of KOH.

The electrochemical performance of the sample was further evaluated by GCD analysis as shown in figure 5. The GCD curves of the sample at different current densities of the sample electrode have three levels of discharge. The first level is in a potential range -0.1 to 0.55V, the second level is in a potential range -0.5 to -0.1V and the third level is in a potential range 0.6 to -1V. The discharge is due to the change in the oxidation number of MnO_2, according to the reversible redox-reaction [19]. The specific

capacitance is 200.83 F/g at a current density of 1 A/g. The cycle stability of sample reveals a usability of 30% after 500 cycles of charge and discharge at a current density of 5 A/g as shown in figure 6. The sample exhibited an energy density of 3.62 Wh/kg under a power density of 43.11 W/kg. This low specific capacitance is due to the spherical shape of MnO_2, resulting in less contact area. In addition, it has a low pore diameter and pore volume.

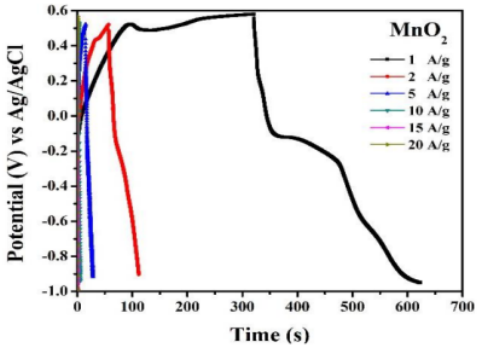

Figure 5. GCD curves of the MnO_2 nanoparticles at different current densities.

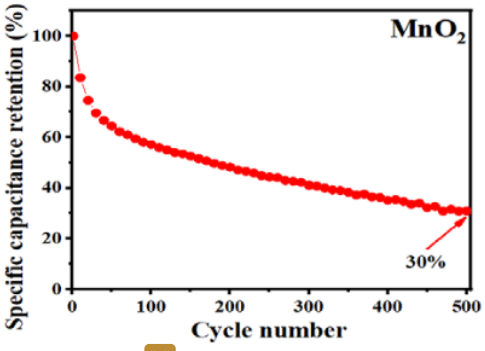

Figure 6. The cycle stability of MnO_2 nanoparticles at a current density of 5 A/g.

4. Conclusion

MnO_2 nanoparticles were synthesized by the one-step hydrothermal method. Phase of γ-MnO_2 and α-MnO_2 are detected in the structures. The average particle size is approximately 54.8 nm. More than one reaction occurred at the MnO_2 electrode resulting from change in the oxidation numbers of Mn^{4+} to Mn^{3+} and Mn^{2+} ions. The MnO_2 nanoparticles showed a specific capacitance of 200.83 F/g, good cycle stability of 30% after 500 cycles of charge and discharge at a current density of 5 A/g. This research may be useful for further development of oxide synthesis techniques for fabrication of electrode materials.

Acknowledgments

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