Facile synthesis and Electrochemical Properties of ActiveCarbon/MnO_2 composites

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Keywords: AC/MnO_2 composite materials, Specific capacitance, Supercapacitor

Abstract. MnO_2 is directly deposited on active carbon (AC) to synthesize AC/MnO_2 composite to improve the capacitance of electrode material. AC/MnO_2 composites are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2 adsorption–desorption, and the electrochemical properties are evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) test in 1M Na_2SO_4 aqueous solution. The results suggest that the AC/MnO_2 composites show a double layer capacitive behavior in the potential window of -1~0 V. The specific capacitance of AC/MnO_2 (250 F g^{-1} at current densities of 2A/g^{-1}) is notably higher than that of AC (200 F g^{-1} at current densities of 2A/g^{-1}).

Introduction

The development of energy storage devices has attracted a great attention due to the depletion of fossil fuels and environmental pollution[1-3].Supercapacitor has the advantages of high power density, rapid charging/discharging, longer service time and good temperature characteristics [4-6]. It is a new kind of efficient and practical energy storage device.

The energy density of a supercapacitor mainly depends on the nature of electrode materials. Several materials which have been made in previous investigations are capable of delivering high energy density. Carbon[7], transition metal oxides [8-10] and conducting polymer [11, 12] based materials have been traditionally used. Carbon materials due to their good conductivity, high surface area and favorable mechanical integrity, have been proved to be good candidates for electrode materials of supercapacitor, but low capacitance and energy densities limit further development.

In order to obtain excellent capacitance and high energy densities, transition metal oxides are employed to modify the carbon materials, such asMnO_2[13, 14],and Co_3O_4[15, 16]. Manganese dioxide is a material with the advantage of high specific capacitance, and widely used as an electroactive material with low cost of raw materials. However, the poor electronic conductivity of MnO_2 limits the facilitated ion/electron transport, leading a poor capacitive performance.

In the present work, the AC/MnO_2 composite is prepared through a reduction reaction between potassium permanganate and AC. The prepared AC/MnO_2 composite displays a high specific capacitance in 1.0 M Na_2SO_4 electrolyte and an excellent cycling stability with 88.5% capacitance retention after 1000 cycles.

Experimental

Sample Preparation

All chemicals were of analytical grade and were used without further purification. 80 mg of $KMnO_4$ was dissolved in 60 mL deionized water and 200 mg of AC was added to the above solution under magnetic stirring at 80°C for 6h. After cooling to room temperature, the product was centrifuged and washed with ethanol for three times, and then dried at 80 °C in vacuum oven for 12 h.

Characterization

The surface characterization of the materials was evaluated by the N_2 adsorption/desorption isotherms based on Brunauer–Emmett–Teller (BET) theory, and was determined using a high-speed surface area and pore size analyzers (NOVA 2000e, Quantachrome Instrument, US). The surface morphologies and nanostructures of the AC/MnO_2 were observed using an X-ray diffractometer (D-Max-c type A, RigakuCo. Japan) with a Ni-filtered Cu Ka radiation and a 0.15406 nm wavelength operated at 40 kV and 40 mA. Data were obtained from 2θ = 20° to 90° at a scan rate of 4 per step.

Electrochemical Measurements

To prepare the AC/MnO_2 hybrid coating electrode sheets, the as-prepared powders were mixed with carbon black and styrene-butadiene rubber (SBR, 20 mg mL-1) at a mass fraction of 8:1:1. The viscous slurry was laminated on a 1 mm-thick nickel foam and dried in a vacuum oven at 80℃ for 12 h.

Three electrode data were collected using a MetrohmAutolab B.V. electrochemical workstation (PGSTAT302N, Netherlands) with a three-electrode system. All tests were performed in a 1 M Na_2SO_4 aqueous solution at room temperature and normal pressure. A platinum wire, the active materials and a saturated calomel electrode (SCE) were used as counter, working and reference electrodes. GCD tests were performed in the three-electrode system by using a CT2001A rapid sampling battery testing system (LAND, China) at room temperature.

Results and Discussion

Fig. 1 Shows the XRD patterns of the AC and AC/MnO_2 composite. The AC possesses two broad peaks at 26° and 43° indicating the microcrystalline graphitic character. The XRD pattern of AC/MnO_2 composite with weak diffraction peaks located at 12.40°, 18.10°, 37.20°, 43.97°, 65.11° and 78.95° suggesting a poor crystallinity of MnO_2 in the composite, which is favorable for the supercapacitor.

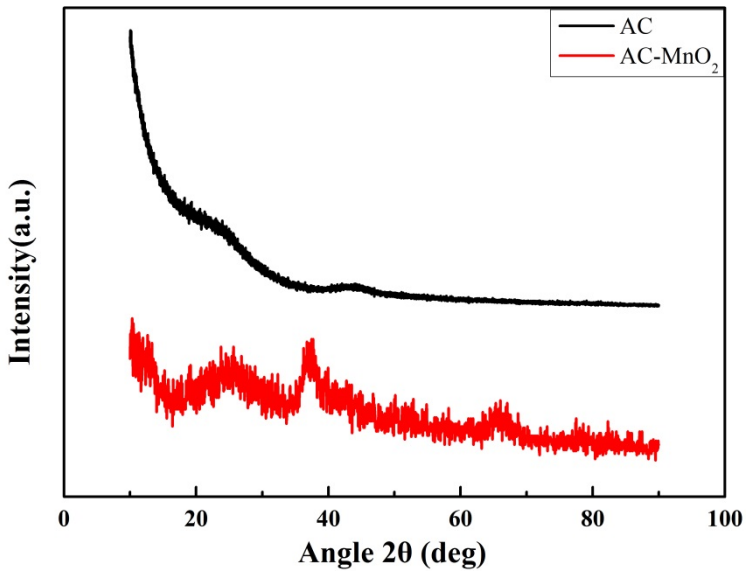

Fig. 1 (A) XRD pattern of AC; (B) XRD pattern of AC/MnO_2

Fig. 2 shows the morphologies of the AC and AC/MnO_2 composite. As shown in Fig. 2(A), the AC is composed of smooth particle with prominent edges and corners. It can be found in Fig. 2(B) that clubbed nanoparticles are deposited on the surface of AC which results in the improvement of capacitance [17].

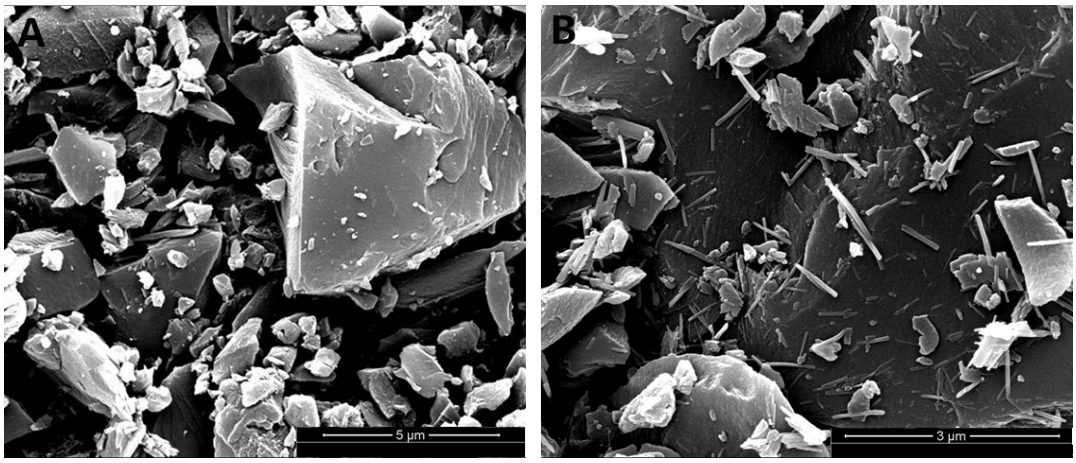

Fig. 2 SEM images of (A) AC and (B) AC/MnO_2

The pore structure property and specific surface area of the AC are measured from the N_2 adsorption–desorption measurements at 77 K. As shown in Fig.3 (A), the AC sample exhibits a type-I isotherm well-defined plateaus, suggesting a microporous nature of the AC. The AC shows a high BET specific surface area of 1657.2m^2g^{-1} and the pore volume is 0.86cm^3g^{-1}. In Fig. 3(B), after MnO_2 nanoparticles deposited on the surface of AC, the AC/MnO_2 composite shows a smaller surface area (1087.7m^2g^{-1}) and pore volume (0.60 cm^3 g^{-1}).

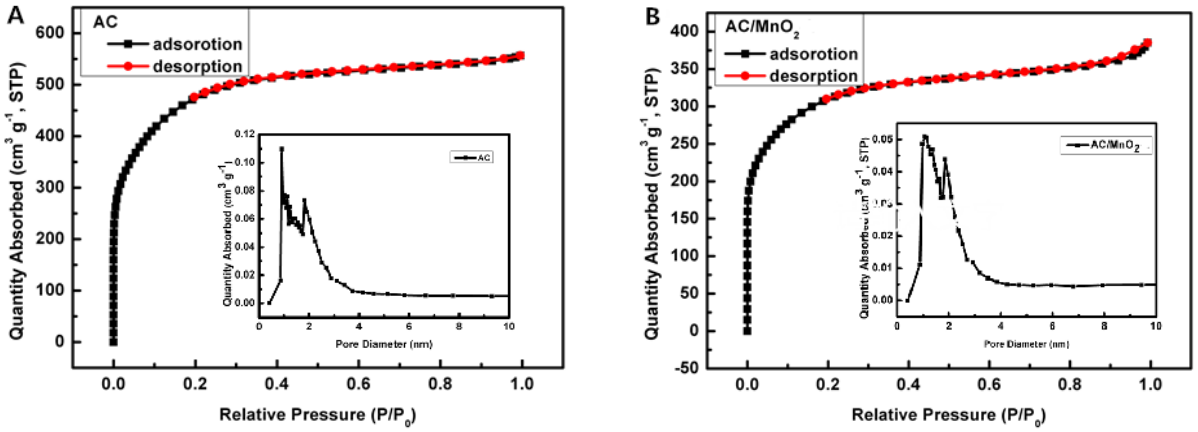

Fig.3. N_2 adsorption–desorption isotherms of (A) AC and (B)AC/MnO_2

CV measurements are performed to evaluate the electrochemical properties of the AC and AC/MnO_2 composite in a 1M Na_2SO_4 electrolyte using a three electrode system. Fig. 4(A) shows the CV curves of AC from -1V to 0V atscan rates of 1–100 mV/s, which exhibit a quasi-rectangular shape, indicating that the main contribution to the capacitance is the charge and discharge of the electrical double layer. In Fig. 4(B), the CV curves of the AC/MnO_2 are close to a rectangle without a redox peak in the potential range of -1-0 V. According to the previous reports [18], the charge storage mechanism of AC/MnO_2 in Na_2SO_4 electrolytes could be described as the eq (1)

$$MnO_2 + Na^+ + e^- \; f \quad MnOONa \tag{1}$$

The capacitance values of AC and AC/MnO_2 composite obtained from GCD experiments. As shown in Fig. 4 (C), the charge and discharge curves have a triangular shape which corresponds to a capacitive behavior, which indicates that the electrode materials retain good electrochemical properties and quickly undergo ion exchange in the charge–discharge process. In order to evaluate the durability of AC/MnO_2, the charge–discharge cycling test is performed at a current density of 2 A/g^{-1}, which is shown in Fig. 4(D). Apparently, the AC/MnO_2 composite presents a good electrochemical stability with 88.5% capacitance retention after 1000 cycles.

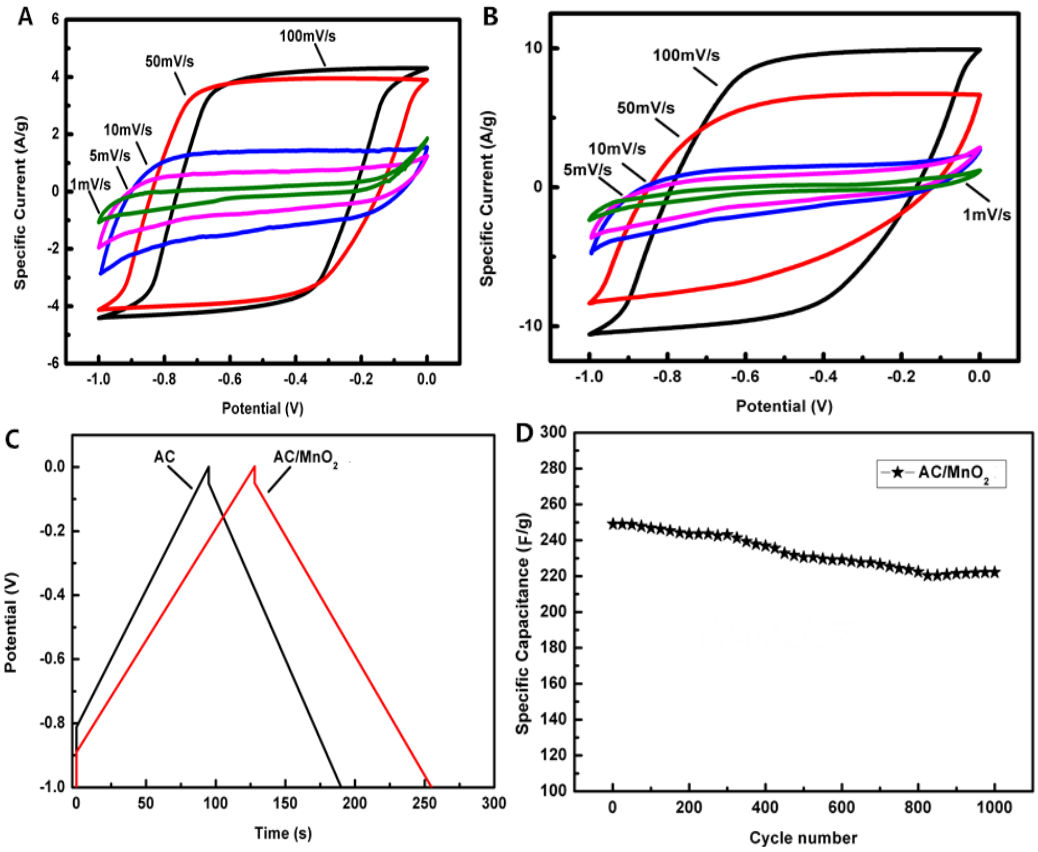

Fig.4. Electrochemical performances of composites in a three-electrode system: (A) CV curves of AC at different scan rates; (B) CV curves of AC/MnO_2 at different scan rates; (C) GCD profiles of AC and AC/MnO_2 at a charge discharge current density of 2 A g^{-1};(D) The cycling performance of AC/MnO_2exhibits capacitance retention after 1000 cycles at a charge discharge current density of 2 A g^{-1}

Conclusions

We suggest a facile and inexpensive process to prepare AC/MnO_2 composite for electrode material of supercapacitor. The AC/MnO_2 composite shows an excellent electrochemical performance due to the high specific surface area and composite structure. The capacitance of the AC based materials is highly improved after the AC coated with MnO_2. The CV curves show a quasi-rectangular shape in the potential range of -1–0 V. The charge–discharge cycle test delivers a triangular shape and a high capacitance of 250 F g^{-1} at a current density of 2A/g^{-1}, which is increase about 25% comparing with the pure AC. It also possesses a good electrochemical stability with 88.5% capacitance retention after 1000 cycles..

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