Synthesis and Capacitive Properties of Manganese Oxide Nanoparticles Dispersed on Hierarchical Porous Carbons

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ARTICLE INFO

ABSTRACT

A growing manganese dioxide (MnO_2) nanoparticles on hierarchical porous carbons (HPCs) is conducted via a simple route starting with $KMnO_4$ and ethanol aimed to enhance the electrochemically active surface area of MnO_2. It is found that these MnO_2 nanoparticles are uniformly grown on the external surface of the HPCs and still maintain hierarchical porous structure, yielding a composite electrode showing good electron transport, rapid ion penetration, fast and reversible Faradic reaction when used as supercapacitor electrode materials. HPCs–MnO_2 composite displays the specific capacitance as high as $167\,F\,g^{-1}$ and $192\,F\,cm^{-3}$ in 3 M KOH aqueous electrolyte and $94\,F\,g^{-1}$ and $113\,F\,cm^{-3}$ in 1 M tetraethylammonium tetrafluoroborate/propylene carbonate (Et_4NBF_4/PC) organic electrolyte. Furthermore, it also exhibits a superior cycling stability with 96% retention of the initial specific capacitance after 1000 cycles and stable Coulombic efficiency of 99% in 3 M KOH measured using the galvanostatic charge–discharge technique.

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1. Introduction

The increasing demand for energy and growing concerns about the development of renewable energy production have stimulated intense research on energy storage and conversion from alternative energy sources. Among the various energy-storage devices, supercapacitors exhibit significant higher power density than batteries and would be excellent candidates for numerous electronic device applications if their energy density could be further enhanced without sacrificing the power density and the cycle life [1–5]. In order to increase the energy density of supercapacitors while retaining their intrinsic high power density, many researchers have devoted themselves to the development of electrode materials including carbonaceous materials (such as carbon nanotubes, graphene, activated carbons, etc.) and transition metal oxides (such as NiO, ZnO, Co_3O_4, RuO_2, MnO_2, etc.) [5–16]. In the former case, the electrical charge is stored at the interface between the electrode and the electrolyte, and in the latter case, energy is stored through fast Faraday redox reaction taking place at the electrode/electrolyte interface [4,17]. In general, carbon materials usually display excellent reversibility and stability, but the capacitance is limited by the microstructures in the materials

[3]. On the contrary, the transition metal oxides show high specific capacitances. Unfortunately, most of them are of high cost and exhibit poor rate capability and reversibility during the charge/discharge process [18–20]. Therefore, high capacitive performance and fascinating stability may be achieved if integrating two kinds of materials into the electrodes of supercapacitors.

Currently, hierarchical porous carbons (HPCs) are always synthesized by template methods. With this approach, carbon precursor/template composites are first formed, followed by carbonization, and finally etching of the template material. However, such method is tedious, which requires multiple synthetic steps, including the precursor infiltration into the template, caustic chemical treatments, and long curing times. So, scale-up is difficult and not cost-effective due to the destruction of expensive templates [21–23]. Developing an easy synthesis route for HPCs is urgent and would be highly useful to overcome the weaknesses of the template methods. Natural materials are generally abundant, renewable, inexpensive and environmental friendly. Using natural biomass to prepare carbon materials has received great attention [24]. Fortunately, we find a kind of biomass, namely humic acid (as shown in Fig. 1), which can be converted into HPCs.

Here, we demonstrate the fabrication of MnO_2 nanoparticles and HPCs as high performance electrodes of supercapacitors. The method used to develop MnO_2 nanoparticles on HPCs is a simple way starting with $KMnO_4$, ethanol and HPCs. HPCs obtained by
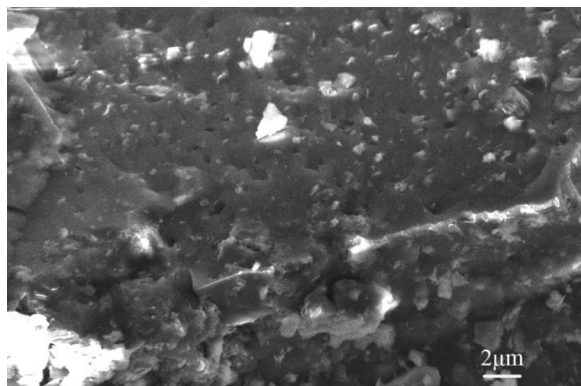
Fig. 1. SEM of humic acid.

Table 1
Ultimate analyses of HPCs.

Sample ID	Ultimate analysis (wt%, daf)[a]			
	C	H	N	O[b]
HPCs	85.07	0.57	0.88	13.48

[a] "daf" names dry ash-free basis.
[b] By difference.

activation of humic acid are rich in oxygen-containing functional groups (as shown in Table 1), which allows the formation and uniform anchoring of fine MnO_2 via strong chemical interactions between the functional groups of HPCs and the nanomaterials. This method has a lot of advantages such as uniform growth, high material utilization efficiency, easy to control the deposition content and large area deposition. Due to their outstanding hierarchical porous structure as well as excellent electrical properties, high chemical stability, high active surface area, HPCs are attractive electrode materials in energy storage devices. Successful integrating of hybrid electrode materials having both high storage capacity MnO_2 and highly conductive HPCs will lead to enhanced charge storage properties. The HPCs-MnO_2 electrode displayed improved electronic conductivity due to the presence of HPCs and a dual charge storage mechanism (double layer in the case of HPCs and intercalation/deintercalation charges in the case of MnO_2 nanoparticles).

2. Experimental

2.1. Synthesis of HPCs

The humic acid purchased from market (Shanxi, china) were ground, and mixed with KOH with alkaline-Humic acid mass ratio of 0.7, follow by adding some deionized water and stirring over night. The compound were activated under N_2 atmosphere using the following heating program: (1) ramp at $5\,°C\,min^{-1}$ to $100\,°C$, and hold for 30 min; (2) ramp at $5\,°C\,min^{-1}$ to $800\,°C$, and hold for 60 min; (2) cool naturally to room temperature. The obtained products soak in 3 M HCl for a few hours, rinsed with deionized water until PH = 7, and dried at $110\,°C$ for 5 h. The final product was named as HPCs.

2.2. Synthesis of MnO₂/HPCs composites

The MnO_2-HPCs composites with different weight ratios were prepared by a simple method. Briefly, the starting materials to prepare MnO_2 are $KMnO_4$ and ethanol. Firstly, a given amount of $KMnO_4$ (0.5, 1 or 2 g) was used to make a homogeneous solution in deionized water. Then, 1 g HPCs were dispersed in the solution of $KMnO_4$ and stirred for 1 h in a magnetic stirrer. After complete homogenization of the mixture, 10 mL of ethanol was added drop-wise under constant stirring. Immediate precipitation of black MnO_2 was observed. The well mixed precipitate of MnO_2 and HPCs were filtered and dried at $110\,°C$ for 5 h. The stoichiometric redox reaction between ethanol and MnO_4^- yields three HPCs–MnO_2 composite samples. The mass ratio of MnO_2 to HPCs–MnO_2 composites are about 0.22, 0.36 and 0.52, respectively. Therefore, we denoted three HPCs–MnO_2 composite samples as HPCs–MnO_2-22, HPCs–MnO_2-36, and HPCs–MnO_2-52, respectively.

2.3. Characterization

The morphology of the samples was observed on a JEOL JSM-6390LV scanning electron microscope (SEM) operated at 15 kV and SEM micrographs are in secondary electrons mode. Transmission electron micrographs (TEM) were obtained using a JEOL JEM-2100 operated at 200 kV. Ultimate analyses were conducted on an elemental analyzer (Vario Macro Cube, Elementar, Germany). Powder X-ray diffraction (XRD) experiments were taken on a Bruker D8 Advance diffractometer with Cu Kα radiation at a scan rate of $2°\,min^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an AXIS ULTRA spectrometer using a monochromatic Al Kα X-ray source at 150 W. Fourier transformation infrared (FTIR) spectra were measured in KBr pellets on a Bruker VERTEX 70 spectrometer. Nitrogen adsorption/desorption
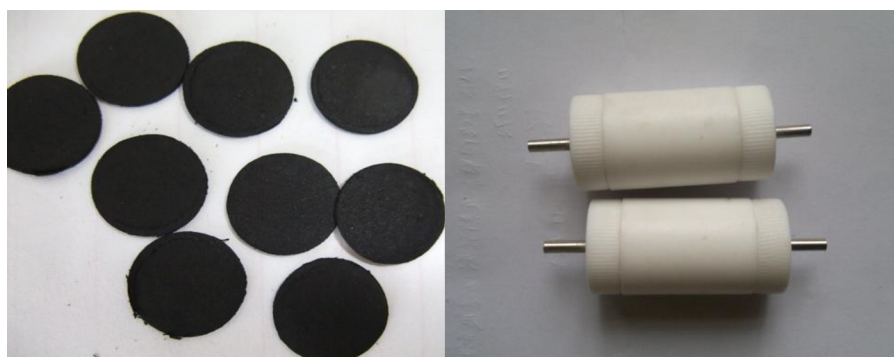

Fig. 2. Working electrodes and supercapacitors.