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RESEARCH PAPER

Preparation and electrochemical performance of a polyaniline-carbon microsphere hybrid as a supercapacitor electrode

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Abstract: A polyaniline-carbon microsphere (PANI-CMS) hybrid was prepared by an electrochemical deposition method and used as an electrode for supercapacitors. Field emission scanning electron microscopy and Fourier transform infra-red spectroscopy were used to characterize its morphology and structure. The supercapacitive performance of the hybrid was investigated by cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy and cycling tests. Results indicate that polyaniline is uniformly coated on the outer surfaces of the CMSs by the electrochemical deposition. The hybrid has a specific capacitance of 206 $F \cdot g^{-1}$ at a current density of 1 $A \cdot g^{-1}$. It has a higher specific capacitance and more stable cycle performance than PANI, which is ascribed to a synergistic effect between the PANI and the CMSs.

Key Words: Carbon microspheres; Polyaniline; Electrochemical co-deposition; Supercapacitor

1 Introduction

Supercapacitor as a new environment-friendly electrochemical energy storage device, has attracted growing attentions owing to its wide range of application in hybrid electric vehicles, mobile electronic devices, backup power sources for computer memory, etc. [1,2]. As electrode materials for supercapacitor, conducting polymers are recognized as typical representatives because of their unique properties, such as fast charge/discharge kinetics, low cost, mild synthesis condition and suitable morphology. In the series of the conducting polymers, polyaniline (PANI) has been considered as one of the most promising electrode materials for supercapacitors because of its easy synthesis, remarkable environmental stability, simplicity in doping, high electrochemical activity and low cost [3-6]. However, irregular granular or flake PANI films obtained by the conventional polymerization methods show poor cycle stability compared with carbon-based electrodes because the redox sites in its polymer backbone are not sufficiently stable and the backbone can be destroyed within a limited number of charge/discharge cycles. Recently, some researchers used carbons as substrate materials to prepare composites to improve the cycle life of PANI, and there is a number of literature on PANI/carbon composite electrodes such as PANI with activated carbon [7], carbon nanotubes [8], carbon fibers [9] and graphene [10]. For example, Zhu et al. [11] synthesized a PANI-MWCNT hybrid with a capacitance of 515 $F \cdot g^{-1}$ compared to 273 F g^{-1} of pure PANI and a high cycling stability (below 10% capacity loss after 1000 cycles). Feng et al. [12] reported a graphene-PANI hybrid prepared by the electrochemical reduction method with a high specific capacitance of 640 $F \cdot g^{-1}$ with a capacitance retention of 90% after 1000 charge/discharge cycles.

Although above mentioned PANI-carbon material hybrids have improved electrochemical properties [13,14], the difficulties in the preparation of carbon materials (graphene, carbon nanotubes, or carbon nanofibers) in large scale hinder their industrial applications. Among various carbon materials, carbon miscrospheres (CMSs), with fullerenes-like cage structures composed of fairly concentric graphitic shells, have great potential application in many fields such as reinforcing agents, lubrication, and the support of surface molecularly imprinted polymer [15,16]. What is more, CMSs can be prepared continuously by a simple chemical vapor deposition method. However, there are few reports about CMSs as an electrode material for supercapactors. The combination of conducting PANI with CMSs would be an effective way to improve the capacitance and cycling stability of PANI. Wu et al. [5] prepared a PANI-activated mesocarbon microsbead hybrid by

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an in situ chemical oxidation polymerization method. The hybrid possessed both high specific capacitance and excellent cycle stability. The specific capacitance stabilizes nearly at a fixed value (110.21 $F \cdot g^{-1}$) at a current density of 250 $mA \cdot g^{-1}$. Based on the PANI-activated mesocarbon microsbead hybrid, Wu et al. [7] synthesized the nitrogen-enriched carbon materials by carbonization and HNO_3 treatment, and the specific capacitance was 385 $F \cdot g^{-1}$ at a current density of 1 $A \cdot g^{-1}$ in 6 M KOH electrolyte.

Herein, the water-soluble CMSs with a high specific surface area were obtained by a combination of acid-oxidation and heat-treatment [15,17]. PANI-CMS hybrid was synthesized through a one-step electrochemical deposition method in H_2SO_4 solution. The physical and electrochemical properties of the PANI-CMS hybrid were studied.

2. Experimental

2.1 Instruments and Materials

All chemicals were of analytical grade and all solutions were prepared using deionized water. CMSs (~350 nm in diameter) were synthesized by chemical vapor deposition. Aniline was distilled under reduced pressure before use and all other chemical reagents were used as received. Electrochemical experiments were conducted at 25°C on a VMP3 Potentiostat (Princeton, USA) controlled with an EC-Lab software. A standard three-electrode system was used for preparation and characterization of the PANI-CMS hybrid. The hybrid film and platinum plate (10 mm × 10 mm × 0.2 mm) served as the working electrode and the counter electrode, respectively. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials reported herein are referenced to SCE. The morphologies and structures of the products were characterized by field emission scanning electron microscopy (FESEM; JSM-6700F, operated at 10 kV) and Fourier transformation infrared spectroscopy (FTIR; FTS-165).

2.2 Preparation of the PANI-CMS hybrid

CMSs (0.5 g) were dispersed in an acid mixture (120 mL, 96 wt% H_2SO_4 and 65 wt% HNO_3 in volume ratio 3:1) in a flask under ultrasonication for 20 min. To increase the specific surface area, heat-treatment was conducted on the acid-treated CMSs in temperature ranging from 25°C to 800°C at a heating rate of 20°$C \cdot min^{-1}$ in Ar atmosphere. The specific surface area increased to 179 $m^2 \cdot g^{-1}$ from 9 $m^2 \cdot g^{-1}$ [17]. Then, the obtained CMSs (20 mg) was added into a mixed solution (20 mL, 0.1 M aniline and 0.5 M H_2SO_4), and the mixture was sonicated for another 10 min. The PANI-CMS hybrid was electrochemically prepared in the mixed aqueous solution using potentiostat method at 0.9 V for 10 min. The deposition of PANI on CMSs was performed at 25°C under static conditions.

2.3 Electrochemical measurement

Electrochemical performance was determined mainly by the cyclic voltammetry (CV) and galvanostatic charge/discharge in a 0.5 mol/L H_2SO_4 aqueous solution, where the three electrode system was equipped with a platinum plate as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The PANI-CMS hybrid on the platinum plate was used as the working electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 10^5 to 0.01 Hz at open circuit potential with an alternating perturbation of 5 mV. Galvanostatic charge/discharge curves were measured between 0 and 0.6 V at different current densities (1, 5, 10 and 20 $A \cdot g^{-1}$). Galvanostatic cycling was performed between 0 and 0.6 V at a current density of 5 $A \cdot g^{-1}$ for 2 000 times.

3. Results and discussion

3.1 Electrosynthesis of PANI-CMS hybrid

The formation of the PANI-CMS hybrid is summarized in Fig. 1. There were oxygen-enriched (e.g. carboxyl) functionalities on the surfaces of CMSs as a result of the acid-oxidation. These functional groups acted as anchor sites and enabled the subsequent electrochemical polymerization of PANI on the surfaces of CMSs. Meanwhile, the π-π electron interaction between the CMSs and the aniline was beneficial to the polymerization of aniline on the surfaces of CMSs. Then, the PANI would gradually grow along the initial nuclei of PANI and extend along CMSs to form a network structure.

3.2 Structural characterization

Fig. 2 shows the FESEM images of PANI, the PANI-CMS hybrid and CMSs. It can be seen that the PANI film (Fig. 2a and b) was flat and smooth. Besides, there were some holes evenly distributed on the surface of PANI film. Unlike the dense PANI film, it is obviously observed that the PANI-CMS hybrid (Fig. 2c, d and e) had a uniform network structure, and CMSs were with a good spherical shape. Compared with the acid-treated CMSs (Fig. 2f), the surfaces of the PANI-CMS hybrid became rough, indicating that the CMSs had been coated with PANI. The network structure caused by the CMSs is favorable to improve the electrochemical properties of the hybrid.

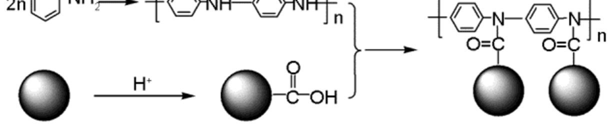

Fig. 1 A schematic representation of the formation of the PANI-CMS hybrid.