Electrochimica Acta 78 (2012) 122–132

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Asymmetric deposition of manganese oxide in single walled carbon nanotube films as electrodes for flexible high frequency response electrochemical capacitors

Jianmin Shen[a,b], Andong Liu[a], Yu Tu[a], Hong Wang[a], Rongrong Jiang[a], Jie Ouyang[c], Yuan Chen[a,*]

[a] *School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore*
[b] *Institute of Chemical and Engineering Sciences, Singapore 627833, Singapore*
[c] *Department of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, PR China*

ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form 16 April 2012
Accepted 10 May 2012
Available online 18 June 2012

Keywords:
Manganese oxide nanoparticles
Single walled carbon nanotube
Electrochemical capacitor
High frequency response
Flexible energy storage devices

ABSTRACT

Manganese oxide (MnO_2) is a promising pseudocapacitive electrode material because of its high capacitance, abundant resource, low-cost, and environmental friendliness. However, its poor electrical and ionic conductivities and low stability hinder applications. Forming MnO_2 nanocomposites with high surface area porous metal, carbon materials, or conducting polymers is a possible solution. In this work, we have developed a facile and scalable asymmetric *in situ* deposition method to incorporate MnO_2 nanoparticles in conductive single walled carbon nanotube (SWCNT) films. The high porosity of vacuum filtrated SWCNT films accommodates pseudocapacitive MnO_2 nanoparticles without sacrificing the mechanical flexibility and electrochemical stability of SWCNT films. We exposed one side of SWCNT films to acidic potassium permanganate ($KMnO_4$) solution. The infiltrated $KMnO_4$ solution partially etches SWCNTs to create abundant mesopores, which ensure electrolyte ions efficiently access deposited MnO_2. Meanwhile, the remaining SWCNT network serves as excellent current collectors. The electrochemical performance of the SWCNT–MnO_2 composite electrodes depends on the porosity of SWCNT films, pH, and concentration of $KMnO_4$ solution, deposition temperature and time. Our optimized two-electrode electrochemical capacitor, with 1 M Na_2SO_4 in water as electrolyte, showed a superior performance with specific capacitance of 529.8 F g^{-1}, energy density of 73.6 Wh kg^{-1}, power density of 14.6 kW kg^{-1}, excellent capacitance retention (99.9%) after 2000 charge and discharge cycles, and one of the highest reported frequency responses (knee frequency at 1318 Hz). The high performance flexible electrochemical capacitors have broad applications in portable electronics and electrical vehicles, especially when high frequency response is desired.

1. Introduction

Electrochemical capacitors (ECs) are receiving increasing consideration in recent years because of their fast charge and discharge rate, high electrical power density and long cyclic stability [1–4]. The capacitance of ECs results from two charge storage mechanisms. The first is a non-Faradic process, in which electrolyte ions are physically adsorbed at or near the electrode and electrolyte interface, causing double-layer capacitance. The second is a Faradic process, in which surface redox reactions of electrode materials produce pseudocapacitance [1]. Various high surface area carbonaceous materials [5–16] and conductive polymers [17–22] have been employed as electrodes in ECs for achieving high double-layer capacitance. However, the energy storage density of ECs based on double-layer capacitance alone is not high enough for many important applications [23]. Pseudocapacitive metal oxides, such as ruthenium oxide [24–26], manganese oxide (mainly MnO_2) [27–39], cobalt oxide [40,41], nickel oxide [42–44], and copper oxide [45], have much higher specific capacitances. Among them, MnO_2 is a promising pseudocapacitive electrode material because of its high specific capacitance (theoretical specific capacitance of ~1370 F g^{-1}) [28], abundant resources, low-cost, and environmental friendliness [46,47].

The advancements of ECs using MnO_2 electrodes are currently hindered by their poor electrical conductivity (10^{-5} to 10^{-6} S cm^{-1}), low structural stability and possible electrochemical dissolution of MnO_2 [36,48,49]. To address these problems, several strategies are studied by researchers: chemical or structural modification of MnO_2 to introduce more electrochemically active sites, and forming nanocomposites with high surface

---

* Corresponding author. Tel.: +65 63168939; fax: +65 65156046.
E-mail address: chenyuan@ntu.edu.sg (Y. Chen).

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2012.05.138

area porous metal, carbon materials, or conducting polymers [34,36,50]. A key challenge in developing high performance MnO_2 nanocomposite electrodes is to achieve controllable, efficient, and reproducible deposition of MnO_2 nanoparticles in large surface area conducting networks. This has been attempted by physical mixing, layer-by-layer assembly, thermal decomposition, chemical co-precipitation, chemical, electrophoretic, and electrochemical deposition [29–34,36,38,39,51]. The electrochemical performances of ECs resulting from these methods strongly depend on the loading and distribution of MnO_2 in nanocomposite electrodes. Large aggregated MnO_2 particles would certainly increase charge transport resistance. The microstructure of MnO_2 nanocomposite electrodes also strongly influences electrolyte ion diffusion. In several previous studies [30,32,52,53], although MnO_2 nanoparticles have been successfully incorporated into conductive carbonaceous networks with uniform distribution, the specific capacitance of ECs (150–450 F g^{-1}) is still much lower than their expected theoretical value. This may be attributed to the lack of mesopores in densely packed electrodes, which significantly increase ion diffusion resistance. Moreover, the direct contact between MnO_2 nanoparticles and metal current collectors increases the contract resistance in ECs. In this regard, novel design of MnO_2 nanocomposite electrodes with large surface area and high porosity is highly desired.

We previously fabricated single-walled carbon nanotube (SWCNT) thin film electrodes by vacuum filtration for flexible ECs [54]. In these thin films, high purity SWCNTs form interconnected three dimensional porous conductive networks with high specific surface areas (322.8–366.1 $m^2\,g^{-1}$). The assembled ECs exhibit the specific capacitance of 32.1–146.1 F g^{-1} in sulfuric acid aqueous electrolyte. We envision that the high porosity of these SWCNT films is beneficial to accommodate pseudocapacitive MnO_2 nanoparticles, which can further increase the specific capacitance and energy density of assembled ECs without sacrificing their mechanical flexibility and performance stability.

In the present work, we deposited MnO_2 nanoparticles in SWCNT films by a facile and scalable asymmetric *in situ* deposition method. As illustrated in Fig. 1, one side of the vacuum filtrated SWCNT film is exposed to acidic potassium permanganate ($KMnO_4$) solution. With the infiltration of the $KMnO_4$ solution, a thin layer of MnO_2 nanoparticles is deposited on SWCNT surface. The mass loading of MnO_2 in the composite can be controlled by deposition conditions. Concurrently, SWCNTs were partially etched away by the $KMnO_4$ solution, resulting in abundant mesopores in the composite. Nanotubes at the other side of the SWCNT film can be spared from the $KMnO_4$ solution by regulating reaction conditions. The intact SWCNT layer serves as a current collector. We demonstrate that flexible ECs assembled using these MnO_2–SWCNT composite thin film electrodes exhibit a high gravimetric specific capacitance in neutral Na_2SO_4 aqueous electrolyte, excellent cyclic stability, and one of the highest frequency responses to date.

2. Experimental

2.1. Preparation of SWCNT dispersion

SWCNT dispersion was obtained following the previously reported centrifugation method [55]. Briefly, 20 mg of SWCNT powder (Carbon Solutions Inc., batch: AP-407) was first dispersed in 100 mL 1 wt% sodium dodecyl benzene sulfonate (SDBS) (Sigma) solution by ultrasonication. The SWCNT dispersion was then centrifuged at 50,000 × g to remove large nanotube bundles and impurities such as metal catalyst residues, amorphous carbon, graphitic particles and multi-walled carbon nanotubes. The upper 50% of the supernatant, containing individually dispersed SWCNTs, was extracted for further uses. The standard concentration–absorbance calibration curve was obtained by weighting dried SWCNTs filtered on membrane. The concentration of SWCNT dispersion was adjusted to 0.1 mg mL^{-1} based on its absorbance at 800 nm.

2.2. Asymmetric deposition of MnO_2 in SWCNT film

First, 20 mL of 0.1 mg mL^{-1} SWCNT dispersion was filtered on a mixed cellulose estate (MCE) membrane (Millipore) with the pore size of 50 nm under 220 ± 2 mbar, producing a uniform SWCNT film about 10 μm in thickness. Next, 10 mL of preheated acidic potassium permanganate (KMnO4) solution (0.1 g mL^{-1}, pH 1, 60 °C) was transferred into the filtration funnel, and came into direct contact with the SWCNT thin film under atmospheric pressure. The temperature of the solution and SWCNT film was kept at 60 °C. A spontaneous redox reaction occurs ($4MnO_4^- + 3C + 4H^+ \rightarrow 4MnO_2\downarrow + 3CO_2\uparrow + 4H_2O$), producing MnO_2 on SWCNT surface and partially consuming carbon materials [51]. The $KMnO_4$ solution was decanted after 5, 10, or 15 min to deposit different amount of MnO_2. It should be noted that the mass loading of MnO_2 can be controlled by several parameters, such as SWCNT film density, pH and concentration of $KMnO_4$ solution, deposition temperature and time. In this study, we limited our discussion to three deposit time, while keeping all other parameters constant. The resulting composites are denoted as SWCNT–L-MnO_2, SWCNT–N-MnO_2, and SWCNT–H-MnO_2, respectively. SWCNT films containing MnO_2 was washed with plenty of deionized water to remove the remaining $KMnO_4$ solution. Last, SWCNT or SWCNT–MnO_2 films were cut into several pieces with the size of 1 cm × 1 cm each, and further dried at 90 °C for 12 h.

2.3. Characterization of SWCNT–MnO_2 composite films

The phase and composition of SWCNT–MnO_2 composite films were studied by X-ray diffraction (XRD) on a Bruker AXS D8 X-ray diffractometer with Cu-Kα radiation. Fourier transform infrared (FT-IR) spectra were collected on a Perkin Elmer FT-IR spectrometer in the range of 450–4000 cm^{-1}. Raman spectra were obtained on a Renishaw Raman spectrometer under the laser excitation at 633 nm. The elemental composition was characterized by X-ray photoelectron spectroscopy (XPS) on a VG Escalab 250 Spectrometer equipped with an Al anode (Al Kα = 1846.6 eV) under high vacuum (<1 × 10^{-7} Pa). The morphology, elemental mapping and microstructure were imaged by field emission scanning electron microscopy (FESEM), energy dispersive spectrum (EDS) on a JEOL-6300F FESEM at 5 kV, and high-resolution transmission electron microscopy (HRTEM) on a JEOL-2010 instrument at 200 kV, respectively. Absorption spectra of SWCNT dispersions were measured on a Varian 5000 UV–vis–NIR spectrometer from 400 to 1350 cm^{-1}. Specific surface areas (SSA) and pore size distributions of SWCNTs and composites were measured on a static volumetric instrument Autosorb-6B (Quanta Chrome) at liquid nitrogen temperature (−196 °C). Prior to each measurement, samples were degassed at 200 °C for 10 h under vacuum (<0.01 mbar). The pore size distribution was determined based on the Barrett–Joyner–Halenda (BJH) model using desorption branches of isotherms. Thermogravimetric analysis (TGA) was applied to determining the mass loading of MnO_2. Sheet resistances of composite films were measured by a CMT-SR 2000N 4-point probe station from Advanced Instrument Technology.

2.4. Assembling ECs using SWCNT–MnO_2 electrodes

Each tested EC is composed of two pieces of SWCNT or SWCNT–MnO_2 films as electrodes, a separator membrane and 1.0 M Na_2SO_4 aqueous solution as electrolyte. SWCNT films were first transferred to the surface of separator membrane (Nippon