Short communication

Preparation and electrochemical characterization of porous SWNT–PPy nanocomposite sheets for supercapacitor applications

Jiyoung Oh\textsuperscript{a,c}, Mikhail E. Kozlov\textsuperscript{c}, Bog Gi Kim\textsuperscript{a}, Hyung-Kook Kim\textsuperscript{b}, Ray H. Baughman\textsuperscript{c}, Yoon Hwae Hwang\textsuperscript{b,*}

\textsuperscript{a} Department of Physics, Pusan National University, Geumjeong gu, Busan 609-735, Republic of Korea
\textsuperscript{b} Department of Nanomaterials, Pusan National University, Miryang 609-735, Republic of Korea
\textsuperscript{c} NanoTech Institute, the University of Texas at Dallas, Richardson, TX 75080, USA

\textbf{Article info}

\textbf{Article history:}
Received 6 November 2007
Accepted 10 April 2008
Available online 2 June 2008

\textbf{Keywords:}
SWNT–PPy
Cyclic voltammetry
Polymer

\textbf{Abstract}

Highly porous sheets comprised of single walled carbon nanotubes and doped polypyrrole (SWNT–PPy) were prepared by vacuum filtration of SWNT–PPy methanol dispersions. The employed preparation procedure is an extension of conventional bucky-paper fabrication technique for the multi-component system. A number of nanocomposites with nominal SWNT:PPy compositions ranging from 1:0 to 1:1 were obtained and tested. Electrochemical properties of the nanocomposites were investigated by cyclic voltammetry and galvanostatic spectroscopy technique in aqueous 1 M NaCl electrolyte. The highest specific capacitance of 131 F/g was obtained for nanocomposite with 1:1 SWNT:PPy ratio. Prospective applications of prepared materials range from supercapacitors to electrodes for batteries and electromechanical actuators.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Supercapacitors, also called electrochemical capacitors or ultracapacitors, have attracted much attention for their higher capacitance compared to normal capacitors and higher specific power compared to batteries [1–3]. Electrochemical supercapacitors can be divided into two main classes based on the charge-storage mechanism. One is the electrical double-layer capacitor, which utilizes mainly the separation of electronic and ionic charges at the interface between electrode materials with high-surface area and the electrolyte solution. Another is the redox capacitor, which can utilize Faradaic reactions involving dopant intercalation into the electrodes. While the latter can also be designed as a battery, the sometimes obtained linear dependence of cell voltage on cell potential justifies listing it as a supercapacitor, though Faradaic processes typically lead to lower discharge rates and higher charge-storage capabilities than those for true electrochemical supercapacitor, which use double-layer-based charge injection.

Between these two extremes there are supercapacitors that use both electrochemical double layer and Faradaic processes. The electrode materials investigated for electrochemical capacitor applications include carbon and carbon nanotubes [4], metal oxides [5] and conducting polymers [6].

Carbon nanotubes are attractive materials for electrodes of electrochemical energy storage devices due to their high accessible surface area, chemical stability, high conductivity and low mass density [7]. They can be easily processed into thin conductive sheets or “bucky-paper” by vacuum filtration of nanotube dispersions [8]. A number of studies of bucky-paper showed that the electrochemical double layer charge injection in the nanotube sheets is a highly efficient non-Faradaic process [9] that provides high specific capacitance, as well as dimensional changes as a function of charge injection that can be used to provide the stroke of an artificial muscle [5,6]. The excess charge on the nanotubes is compensated at the nanotube–electrolyte interface by ions (cations or anions). In the case of carbon nanotube sheet electrodes, performance is limited by the effective surface area. The observed capacitance values does not exceed 15–40 F/g [9,10]. There is therefore a need to improve the electrode materials for achieving highest capacity.

The modification of the carbon nanotube sheet electrode by the addition of electrically conducting polymers is the way for increasing the capacitance value. Markedly higher capacitance values have been reported for devices based on conducting polymers that utilize Faradaic processes in their operation. However because of repeated redox reactions involving solid-state ion diffusion and the dependence of polymer conductivity on intercalation level, Faradaic electrodes show low cycle-life and low charge and discharge rates [11,12]. The latter issues can be addressed by introduction of carbon nanotubes into the polymer matrix in order to
improve its stability, electrical conductivity and mechanical properties \[13,14\].

In particular, recent study by Frackowiak et al. \[15\] reported encouraging data on polypyrrole (PPy)–carbon nanotube composites prepared by the chemical polymerization of pyrrole \[16\]. Capacitance values as high as 170 F/g have been observed \[15\]. Using in situ chemical polymerization of pyrrole, Conway \[17\] prepared nanocomposites consisting of single-walled carbon nanotubes (SWNT) uniformly coated with PPy. The composites exhibited quite high specific capacitance due to both Faradaic and non-Faradaic processes.

Using a similar approach, we developed an efficient, easily scalable method for preparation of highly porous SWNT–PPy nanocomposite electrodes suitable for industrial supercapacitor applications. This method is an extension of conventional bucky-paper fabrication method for the multi-component system. The electrochemical properties of prepared nanocomposites were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy methods. Systematic dependence of electrode capacitance on PPy to SWNT ratio in the nanocomposites was observed.

2. Experimental

Single-walled carbon nanotubes were obtained by high-pressure CO decomposition process or HiPco (Carbon Nanotechnologies Inc.) and used without further purification. Fine powder of doped PPy (synthesized chemically with the aid of organic sulfuric acid as dopant \[18\]) was purchased from Aldrich Inc.; methanol (99.8% grade) was used as received. Different quantities of SWNT (20, 16, 15, 13.3 and 10 mg) were first dispersed in 15 ml of methanol using a probe sonicator at 150 W power for 30 min. After this different amounts (0, 4, 5, 6.7 and 10 mg) of doped PPy powder were
added to the SWNT dispersion and sonicated using the probe sonicator for another 30 min.

Prepared SWNT–PPy dispersions were then redispersed in 80 ml of methanol using an ultrasonic bath for 30 min. Obtained suspensions were then vacuum filtered through a PTFE filter membrane (Millipore, 0.45 μm pores), rinsed with 200 ml of pure methanol and dried. After drying, surfactant-free sheets of SWNT–PPy nanocomposites were peeled off the filter membrane.

Electrochemical properties of prepared sheets were characterized using a three-electrode electrochemical cell with platinum mesh as counter electrode and a saturated calomel electrode (SCE) as reference electrode. SWNT–PPy nanocomposite sheets were attached to a thin platinum wire and used as a working electrode. The measurements were performed in aqueous 1 M NaCl electrolyte. In order to improve wetting of the material, the nanocomposite electrode was first conditioned (cycled) in the electrolyte at voltages −0.5 to +0.5 mV for 10 cycles at 100 mV/s.

Cyclic voltammetry measurements were performed in the voltage range −0.5 to 0.5 V at different scan rates. Galvanostatic charge–discharge measurements were performed at a constant current density of 100 mA/g, with cutoff voltage of 0–0.5 V. Electrical conductivity of the nanocomposites was measured using four-probe technique with Keithley 2425-C source meter. Contacts were attached to samples with a silver paste.

3. Results and discussion

A typical scanning electron microscopy (SEM) image of the SWNT sheet is shown in Fig. 1. One can see that the sheet consist of randomly entangled bundles of carbon nanotubes mixed with small amount of carbon particles. Due to quite flexible fabrication technique employed, the density of the sheets could be tuned over a wide range, typically 0.1–0.9 g/cm³ [8,19]. The sheets prepared by us from HiPco nanotubes had density of about 0.4 g/cm³ and an electrical conductivity of 160 S cm⁻¹.

The distribution of the PPy in the SWNT–PPy nanocomposite sheets was observed by SEM imaging, as shown in Fig. 2. In the nanocomposite material SWNT bundles are mixed with fine PPy particles that fill the interstitial space of the nanotube matrix. In the case of 20 wt.% PPy (Fig. 2a), the SWNT–PPy nanocomposite sheet looks like the pristine SWNT sheet. In contrast, Fig. 2d reveals both SWNT bundles and a large amount of PPy particles. Unlike electro deposited PPy films [16], the particles do not create continuous coating on the SWNT surface but instead form a highly porous, electrolyte-accessible aggregates adjacent to carbon nanotube bundles. The gravimetric density of the nanocomposites decreases with increasing PPy content reaching 0.23 g/cm³ for the nanotube bundles. The gravimetric density of the nanocomposites with 0, 20, 25 and 34 wt.% of PPy is almost independent of the scan rate in the range of 10–100 mV/s and is similar to that of the SWNT sheet. Such behavior is characteristic of an ideal capacitor. The specific capacitance of SWNT–PPy with 50 wt.% of PPy decreases with increasing scan rate. The latter can be ascribed to enhancement of contributions from PPy redox processes.

Using the CV data in the vicinity of 0 V, the capacitance for nanocomposite electrodes can be calculated as \( C = \frac{S}{t} \), where \( S = \frac{(\Delta V \Delta t)}{m} \) is scan rate, \( t \) the discharge current, \( \Delta V \) the discharge time corresponding to the voltage difference \( \Delta V \), and \( m \) the electrode mass. The dependence of calculated specific capacitance on scan rate is shown in Fig. 4. One can see that specific capacitance of nanocomposites with 0, 20, 25 and 34 wt.% of PPy is almost independent of the scan rate in the range of 10–100 mV/s and is similar to that of the SWNT sheet. Such behavior is characteristic of an ideal capacitor. The specific capacitance of SWNT–PPy with 50 wt.% of PPy decreases with increasing scan rate. The latter can be ascribed to enhancement of contributions from PPy redox processes.

Fig. 5 shows charge–discharge curves for SWNT–PPy nanocomposite electrodes recorded in galvanostatic regime at the constant current density of 100 mA/g. In order to obtain stable reading at these measurements, the samples were first conditioned for a few cycles. The recorded charge–discharge curves are similar to those for the SWNT and electropolymorized SWNT–PPy films reported in the literature [20]. It is known that for an ideal capacitor the slope of discharge curves should be independent of electrode voltage. The charge–discharge curves show that these slopes are almost constant at small PPy content in the nanocomposite and decrease...
with increasing discharge time in nanocomposites having large PPy fraction. The charge–discharge time also gradually increases with decreasing SWNT to PPy ratio. The largest charge–discharge time is observed for SWNT–PPy nanocomposite with 50 wt.% of PPy.

The dependence of specific capacitance on wt.% of PPy in SWNT–PPy nanocomposite electrodes is shown in Fig. 6. One can see quite good agreement between results obtained by cyclic voltammetry (open circles) and galvanostatic charge–discharge measurements (closed circles). Both sets of data reveal the same trend—continuous increase in capacitance of nanocomposites with increasing PPy content. The largest values of 131 and 92 F/g were obtained for SWNT–PPy nanocomposite with 50 wt.% PPy by CV and galvanostatic charge–discharge measurements, respectively.

The increase in capacitance of nanocomposites with increasing PPy content can be associated with pseudo capacitance contribution coming from PPy, which undergo rather rapid pseudo-Faradaic reactions. The SWNT network probably plays the role of a pathway for electron transfer at the charge–discharge processes in the material. It also provides structural integrity to the highly porous nanocomposite electrode, as well as an increases electrode electrical conductivity.

Taking into account capacitance values for pure SWNT sheet (17 F/g) and pure PPy (90 F/g [15]), there is a considerable enhancement of performance due to the association of these two materials in the nanocomposite. The high degree of entanglement of the SWNT creates an open network of mesopores that can be filled with PPy particles in the process of the electrode formation. As a result, the density of prepared composites (and electrical conductivity) significantly decreases with increasing PPy content, while porosity (and surface area) increases. High accessible surface area and low resistivity of the SWNT create a conductive matrix for the porous PPy filler. The nanoporous three-dimensional network probably enables effective electrolyte access making available more active sites for Faradaic reactions and larger specific capacitance than that in pure SWNT and the pure PPy electrodes.

4. Conclusions

We report preparation and characterization of highly porous SWNT–PPy nanocomposite electrodes for supercapacitor applications. The electrodes were obtained by easily scalable vacuum filtration of surfactant-free methanol SWNT and PPy dispersions. This process enables convenient fabrication of highly porous nanocomposite sheets with tunable SWNT–PPy ratio, whose size is limited only by the filtration setup. The specific capacitance of the electrodes increases with increasing PPy content reaching 131 F/g value for SWNT–PPy nanocomposite with 50 wt.% PPy. The nanotube network provides mechanical strength and improved electrochemical performance of the nanocomposites. Prospective applications of the materials range from supercapacitors to electrodes for batteries and electromechanical actuators. The proposed technology is easily scalable for device fabrication on an industrial scale.

Acknowledgments

This work was supported by the International Research Internship Program of the Korea Research Foundation (KRF). The Pusan National University team was supported by Korea Research Foundation Grant (KRF-2006-005-J02802 and KRF-2006-005-J02803). The NanoTech Institute team was supported by the Robert A. Welch Foundation grant AT-0029 and LINTEC Corporation.

References