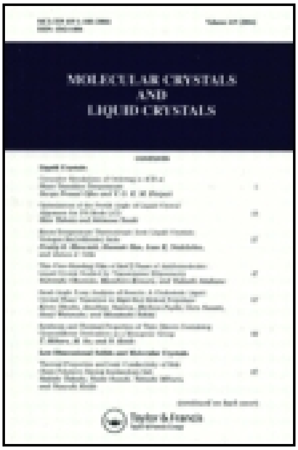

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Synergy of components in supercapacitors based on nanotube/polypyrrole composites

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SYNERGY OF COMPONENTS IN SUPERCAPACITORS BASED ON NANOTUBE/POLYPYRROLE COMPOSITES

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Multiwalled nanotubes (MWNTs) composites with electrodeposited polypyrrole (PPy) have been proposed as electrode materials for supercapacitors. The total capacitance of the nanocomposite combines a pure electrostatic attraction of ions and the electrochemical redox reactions of the π-conjugated system of PPy. A synergy effect has been found between the two components of the nanocomposite. The mesoporous network of the nanotubular material supplies very good transport conditions for ions, and PPy enhances its conducting properties. A high ability of charge accumulation in such volumetric capacitor was obtained with capacitance values of 165 F/g of material.

Keywords: supercapacitor; multiwalled nanotubes; polypyrrole

INTRODUCTION

Peculiar properties of nanotubes (microtexture, entanglement, presence of central canal) allow to use them as attractive electrode material for supercapacitors [1–4]. Especially due to the open network of nanotubes with an accessible electrode/electrolyte interface, a good frequency response is expected, that is very useful for many practical applications.

Different types of nanotubes supplied various capacitance values, for example single walled SWNTs (Rice University) in the form of bucky paper

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used as capacitor electrodes in 6 M KOH gave a specific capacitance of 40 F/g [4]. The entangled MWNTs obtained by decomposition of acetylene at 700°C using Co/SiO_2 catalyst (A/CoSi700) reached 80 F/g. Due to the presence of pyrolytic carbon coating at the surface of MWNTs capacitance even increases up to 130 F/g after functionalization by hot nitric acid [2,3], however, the contribution of pseudocapacitance connected with the presence of surface groups diminishes with cycling due to the irreversible character of some redox reactions. Our first investigations with coating of nanotubes by conducting polymer PPy [5] have shown an enhancement of capacitance values because PPy can be doped rapidly to high charge density.

In the present work, nanotubes have been modified by PPy to reach a stable pseudo-faradaic effect and to correlate the thickness of polypyrrole deposit with capacitance values.

EXPERIMENTAL

The MWNTs/PPy nanocomposite has been obtained by electrodeposition of PPy on nanotubes using a solution of dissolved monomer in sulfuric acid. A galvanostatic method with a strict control of potential has been selected using a potentiostat/galvanostat VMP (Biologic–France). For the preparation of the nanocomposite, different types of carbon nanotubes have been used, e.g. A/CoSi700, A/CoNaY600 obtained by decomposition of acetylene at 700°C and 600°C on cobalt supported by silica or zeolite NaY, respectively. Bamboo-like nanotubes PAl800 obtained on alumina template by propylene decomposition at 800°C were also used for deposition of PPy.

Scanning Electron Microscopy (Hitachi S 4200) and Transmission Electron Microscopy (TEM, Philips CM20) have been used for the observation of the obtained nanocomposites.

The electrodes for capacitor were either bucky paper or pellets formed by pressing a mixture of nanotubular material (85 wt%) + acetylene black (5 wt%) + polyvinylidene fluoride PVDF (10 wt%). Two electrode capacitors were built with a glassy fibrous separator and 1 M H_2SO_4 electrolyte. The values of capacitance were estimated by voltammetry (scan rate of potential from 1 to 10 mV/s) and galvanostatic charge/discharge cycling (VMP). The electrochemical impedance spectroscopy investigations have been performed in the frequency range from 100 kHz to 1 mHz at open circuit voltage with 10 mV amplitude (Solartron SI 1260, Schlumberger).

RESULTS AND DISCUSSION

The homogeneity and thickness of the PPy layer in the composites were carefully investigated by SEM and TEM observations. A typical population of the nanotubes A/CoNaY600 covered with a PPy film is presented in Figure 1. An image of one representative nanotube with a well visible homogeneous PPy outer layer of thickness 5 nm is shown in Figure 2. Due to the complexity of the system, it is difficult to say if the central canal is filled by PPy or not. In some cases, especially for thicker template PAl800 MWNTs we confirmed the presence of PPy inside of nanotubes.

Cyclic voltammetry and galvanostatic charge/discharge cycling from 0 to 0.8 V or up to 1.2 V were performed to estimate the values of capacitance. The voltammetry characteristics for all the cases of nanocomposites represent an almost ideal rectangular shape, and high values of capacitance (120–165 F/g) have been reached that is a proof of a synergy effect between nanotubes and PPy. Nanocomposites from the selected nanotube material (A/CoNaY600), but with different thickness of PPy layer (from 2 to 18 nm), have been prepared and it seems that 5 nm layer of PPy is optimal for capacitor performance. In the case of very thick PPy layer in nanocomposite (from 12 to 18 nm), it supplies the capacitance values of 120 F/g.

Impedance spectroscopy measurements have been used for observation of Nyquist plots to correlate the effect of PPy deposit on capacitance values and to study the frequency response. For example, the composite NT/PPy at frequency of 1 mHz supplied 117 F/g and at 1 Hz 57 F/g, whereas NTs without PPy gave 57 F/g and 21 F/g, respectively.

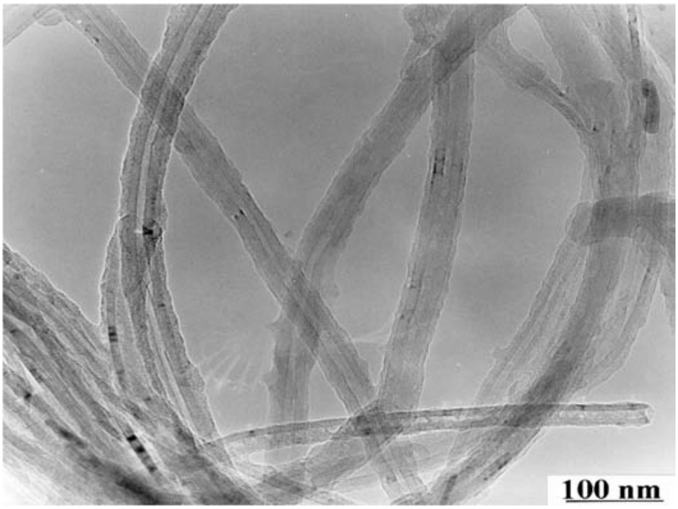

FIGURE 1 TEM image of nanotubes A/CoNaY600 coated by PPy film.

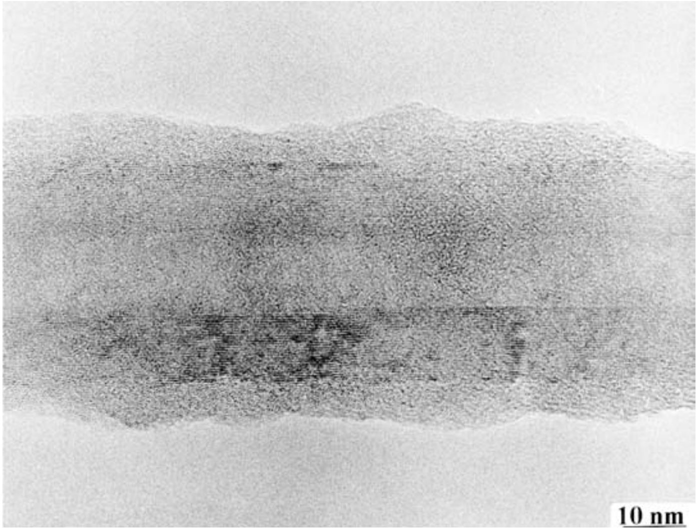

FIGURE 2 TEM image of one nanotube A/CoNaY600 showing PPy layer of 5 nm thickness.

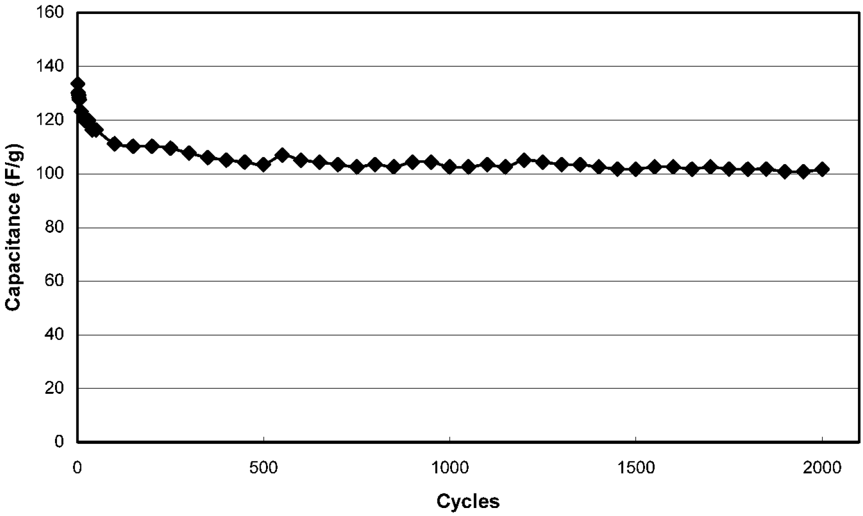

FIGURE 3 Cycleability of capacitor built from ACoNaY600/PPy composite material. Current density of 350 mA/g.

Some of the investigated capacitors have been cycled over 2000 cycles (Fig. 3) and the charge loss never exceeded 20%. Hence, coating of nanotubes by a thin layer of PPy seems to be efficient for a long durability.

The leakage current has been estimated from potentiostatic charging of capacitor until 1 V. After one hour, the leakage current was 4.9 mA/g and after two hours was 3.1 mA/g (Fig. 4). It shows that PPy redox reactions represent a high pseudocapacitive resistance connected in parallel to capacitance.

The homogeneous nanocomposite material used as capacitor electrodes combines the profit of the good electronic conductivity of PPy and an excellent ionic conductivity in the network of nanotubes demonstrating a synergy effect between the components. The open entangled web of the

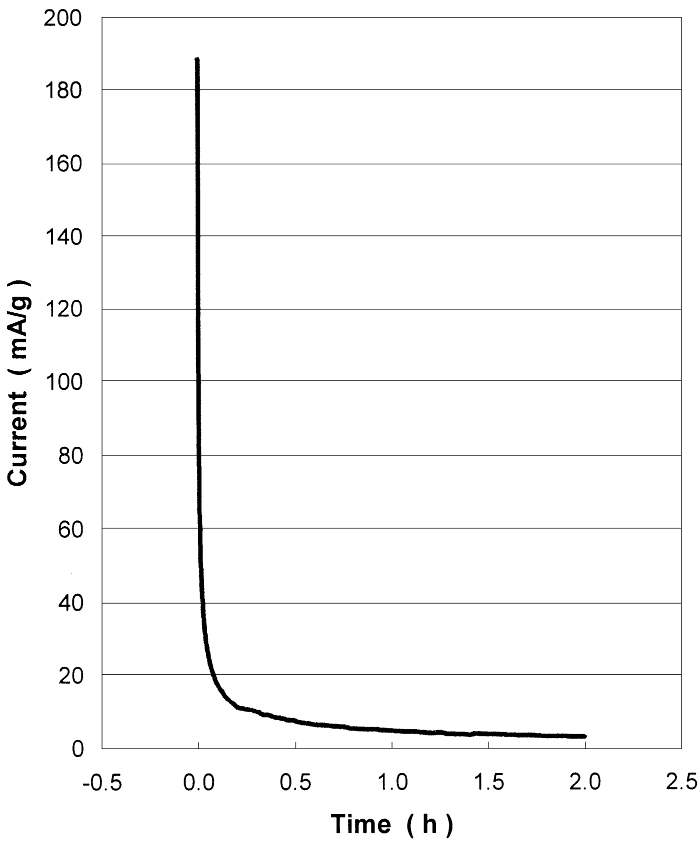

FIGURE 4 Leakage current of capacitor built from ACoNaY600/PPy material after charging to 1V.

nanotubular composite seems to form a volumetric electrochemical capacitor where the charge has a three dimensional distribution.

Capacitance values of 165 F/g (per active material of electrode) were reached and the demand of long durability is fulfilled with a moderate loss of charge at the beginning. Additional advantage of PPy coating is an increase of the permissible voltage for the charge/discharge of the capacitor that can give a higher amount of stored energy.

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