

SUPERCAPACITORS FROM NANOTUBES/CONDUCTING POLYMER NANOCOMPOSITES

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Introduction

Multiwalled carbon nanotubes (MWNTs) have been proposed as electrode materials for supercapacitors [1-4]. The capacitance values of the entangled MWNTs reach 80 F/g, even 130 F/g after functionalization by hot nitric acid [2], and energy can be withdrawn at relatively high frequency, ca. 1Hz [1], what can find a practical application. However, pseudocapacitance connected with the presence of surface groups diminishes with cycling. Since it has been demonstrated that electrically conducting polymers (ECP), enhance capacitance of carbon materials in aqueous medium [5, 6], our objective is to use PPy (polypyrrole) for the realization of optimized MWNTs/PPy composite capacitor materials, taking profit of the good electronic conductivity of PPy and an excellent ionic conductivity in the opened mesoporous network of nanotubes.

Experimental

The electrodes materials used in capacitors were Hyperion™ nanotubes, Pyrograph III fibers (Applied Science) and MWNTs prepared by catalytic decomposition of acetylene at 700°C using cobalt supported on silica (A/CoSi700) or on zeolite at 600°C [7] (A/CoNaY600). Chemical vapor deposition (CVD) within a perforated alumina film using propylene at 800°C [8] has been used to get a nanotubular product (P/Al800). The specific surface area of the nanotubular materials was measured by nitrogen adsorption at 77K (Micromeritics ASAP 2010).

The chemical polymerization of pyrrole on the nanotubes was performed with ammonium persulfate as an oxidant [9] while electrochemical polymerization was carried out through galvanostatic oxidation. The homogeneity and thickness of the PPy layer were checked using Scanning Electron Microscopy (Hitachi S 4200).

Electrodes 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 1M H₂SO₄ 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, Biologic). The electrochemical impedance spectroscopy investigations have been performed in the frequency range from 100kHz to 1 mHz at open circuit voltage with 10 mV amplitude (Solartron SI 1260, Schlumberger).

Results and Discussion

The nitrogen adsorption/desorption isotherm is of type IV for all the pristine MWNTs confirming the strongly mesoporous character of the material due to the central canal and/or entanglement. The catalytically produced nanotubular material forms a web of entangled tubes with an inner diameter (2 to 6 nm), and an outer diameter from 10 to 25 nm. Nanotubes A/CoSi700 possess an open central canal ($S_{\text{BET}} = 430 \text{ m}^2/\text{g}$) while the tips of A/CoNaY600 are closed ($S_{\text{BET}} = 130 \text{ m}^2/\text{g}$). The Hyperion™ nanotubes with a hollow core of 5 nm and an outer diameter typically of 10 nm are curved, forming intertwined entanglements ($S_{\text{BET}} = 290 \text{ m}^2/\text{g}$). A different type of MWNTs, i.e. straight and rigid (bamboo-like) is produced by the CVD method within an alumina membrane. In this case the diameter of the central canal (from 100 to 200 nm) as well as the number of cylindrical carbon layers is depending on the deposition time. The outer diameter of P/Al800 tubes determined by the pores of the alumina template is 250 nm. The BET specific surface area of this material is very low ca. 50 m²/g.

Chemical deposition of PPy on nanotubes or fibres led to aggregates-like polymer deposit while electrochemical method gave a homogeneous PPy film as indicated by the SEM micrograph of the nanotubes A/CoNaY600 with electrodeposited PPy (Figure1).

Cyclic voltammetry and galvanostatic charge/discharge cycling from 0 to 0.6 V (or up to 1.2V) were performed to estimate the values of capacitance. The effect of PPy on the capacitance properties of A/Co700 measured by

voltammetry is shown in Fig. 2 and using dc discharge in Fig. 3. The square shape of the voltammogram (Fig. 2) suggests a pure electrostatic attraction confirmed by a linear galvanostatic discharge (Fig. 3).

Electrochemical impedance spectroscopy, was used to check the ability of the novel composite carbon materials to store electrical energy. An example of the Nyquist plots for the material A/CoNaY600 and for the nanocomposite A/CoNaY600+PPy is shown in Fig. 4. The PPy composite exhibits a Warburg behaviour significant for electrolyte diffusive limitation. The Nyquist spectra revealed a capacitive behavior in the low frequency range with a quite vertical dependence of the imaginary part versus the real impedance part, and a small time constant related to the electrical charge transfer to the carbon material in the high frequency range. The capacitance of the cells was evaluated from the low-frequency data of the spectra according to the formula: $C = -1 / (2 \pi f Z_{im})$. A good correlation has been found between all the techniques (Tab.1). We can see that the nanotubular materials with electrochemically deposited polypyrrole give significantly higher values of capacitance than the pristine nanotubes which is a proof of a synergy effect between nanotubes and PPy. The open entangled web of the nanotubular composite seems to form a volumetric electrochemical capacitor where the charge has a three dimensional distribution. Thus, the pristine template nanotubes P/Al800 with an extremely low specific surface area (below 50 m²/g) demonstrate negligible values of capacitance (5 F/g). In this case mainly electrodeposited PPy is responsible for the value of capacitance given by the composite. The large diameter of central canal, ca. 100 – 200 nm, may suggest that a thin PPy film also covers the inner core accessible for the electrolyte. The high value of capacitance compared to pristine P/Al800 originates from inner and outer coating of the nanotubes.

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

Conclusions

For the first time carbon nanotubes modified by polypyrrole have been used as an active electrode material for a supercapacitor assembly. The

electrochemical deposition of PPy supplied a homogeneous nanocomposite demonstrating a synergy of capacitance between the components. Capacitance values of 163 F/g (per active material of electrode) were reached due to the three dimensional accumulation of charges in the PPy composite. The demand of long durability is fulfilled with a moderate loss of charge. Its additional advantage 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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Kind of nanotubes	C [F/g] without PPy	C [F/g] with PPy
A/CoSi700	65	141
Hyperion™	78	146
P/800Al	5	123
Pyrograf III	16	130
A/CoNaY600	50	163

Table 1. Capacitance values [F/g] of the nanotubular material in acidic medium (1M H₂SO₄) without and with PPy.

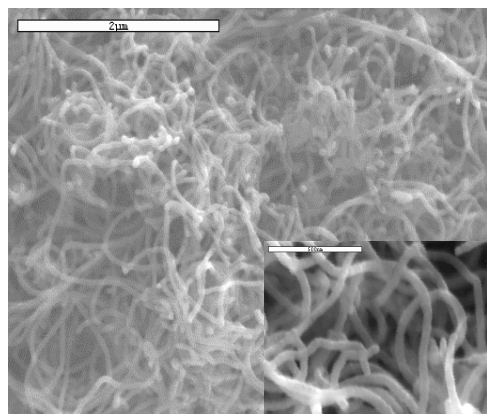


Figure 1. SEM micrograph of a homogeneous population of carbon nanotubes A/CoNaY600 with electrodeposited polypyrrole.

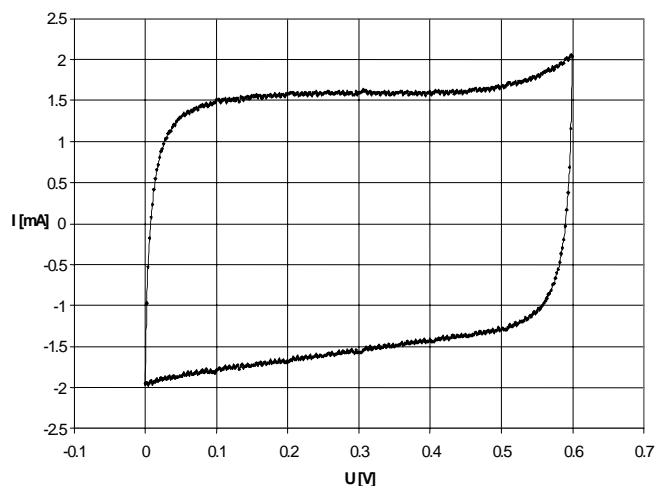


Figure 2. Voltammetry characteristics of a capacitor built from carbon nanotubes A/CoSi700 with electrodeposited PPy. Scan rate of potential 2 mV/s. Mass of each electrode: 11.6 mg.

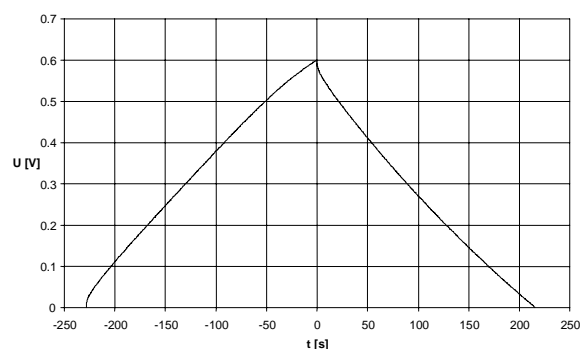


Figure 3. Galvanostatic charge/ discharge of a capacitor built from carbon nanotubes A/CoSi700 modified by electrodeposited PPy. Mass of each electrode: 11.6 mg. Current of 2 mA.

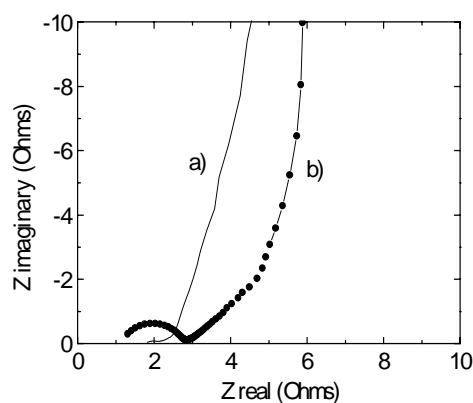


Figure 4. Impedance Nyquist plot of supercapacitors built: a) from carbon nanotubes A/CoNaY600 (mass of each electrode: 7.0 mg); b) from the nanocomposite A/CoNaY600 + PPy (mass of each electrode: 11.3 mg).