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Nanotubular materials for supercapacitors

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Abstract

Different types of multi-walled (MWNTs) and single-walled nanotubes (SWNTs) have been considered as active electrode materials for the storage of energy in supercapacitors. Due to their unique mesoporosity, these materials have a high ability for the accumulation of charges in the electrode/electrolyte interface. MWNTs supply twice higher values of capacitance in comparison to SWNTs. The nanotubular materials of high purity point out a box-like shape of voltammetry characteristics that proves an entirely electrostatic attraction. Pseudocapacitance effects are observed if metallic particles are present and after additional functionalization of the nanotubes or deposition of conducting polypyrrole (PPy). The value of capacitance obtained from nanotubes modified by PPy reaches 170 F/g, about twice that given either by the nanotubes (ca. 80 F/g) or by pure PPy (ca. 90 F/g). The open entangled network of the nanocomposite seems to favour a better efficiency for the formation of the electrical layer in PPy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon nanotubes; Supercapacitor; Capacitance; Pseudocapacitance; Polypyrrole

1. Introduction

The electrochemical capacitors based on carbon electrodes represent attractive energy storage devices with a high power density and a long durability. A supercapacitor combines a pure electrostatic attraction of the ions in the electrical double layer and pseudocapacitance faradaic surface reactions. The enhancement of capacitance values by pseudocapacitance effects can be realised through a special introduction of electroactive metallic particles or electroconducting polymers [1–3]. The use of nanotubes for capacitor electrodes [4–6] proved the high ability of this material for the accumulation of charges in the electrode/electrolyte interface due to their special mesoporous microtexture.

2. Experimental

In this work, different types of multi-walled carbon nanotubes (MWNTs) have been used as electrodes for electrochemical capacitors. MWNTs with an open central canal and partly disorganised carbon on the outer layers were obtained from the decomposition of acetylene at 700°C using a cobalt catalyst supported on silica (MWNTs Co/700°C), whereas nanofilaments of fishbone morphology with a hardly defined central canal were elaborated at 900°C (MWNTs Co/900°C). Silica was eliminated with hydrofluoric acid (72%) and a subsequent treatment by 3 mol l^{-1} nitric acid allowed to remove a part of residual Co catalyst from the nanotubular material. MWNTs obtained by chemical vapour deposition from propylene at 800°C within the pores of an alumina template [7] presented a wide central canal of the order of 10 nm, but only a few concentric, non-continuous graphitic layers formed the nanotube walls (MWNTs templ/800°C). Commercially available nanotubes called Hyperion Graphite Fibrils™ have been also analysed without any purification. Electroconducting polypyrrole (PPy) was deposited on this material by chemical polymerisation of pyrrole with $(NH_4)_2S_2O_8$ as oxidant in acidic solution (0.1 mol l^{-1} HCl) [8]. All the MWNTs materials were characterised by Transmission Electron Microscopy (Philips CM 20) and nitrogen adsorption at 77 K (Micromeritics, ASAP 2000).

Two electrode swagelok type cells from teflon were applied using 6 mol l^{-1} KOH and 1 mol l^{-1} H_2SO_4 as electrolytic solution. The electrodes were prepared in the form of pellets with 85 wt.% content of MWNTs, 5 wt.% of acetylene black and 10 wt.% of binding substance (PVDF-Kynar flex, Atochem, France). For a comparison, bucky paper from single-walled nanotubes (SWNTs) (Rice

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University, USA) has been also used for the assembly of a capacitor.

The capacitor performance has been investigated by galvanostatic charge/discharge and voltammetry techniques (VMP-Biologic, France).

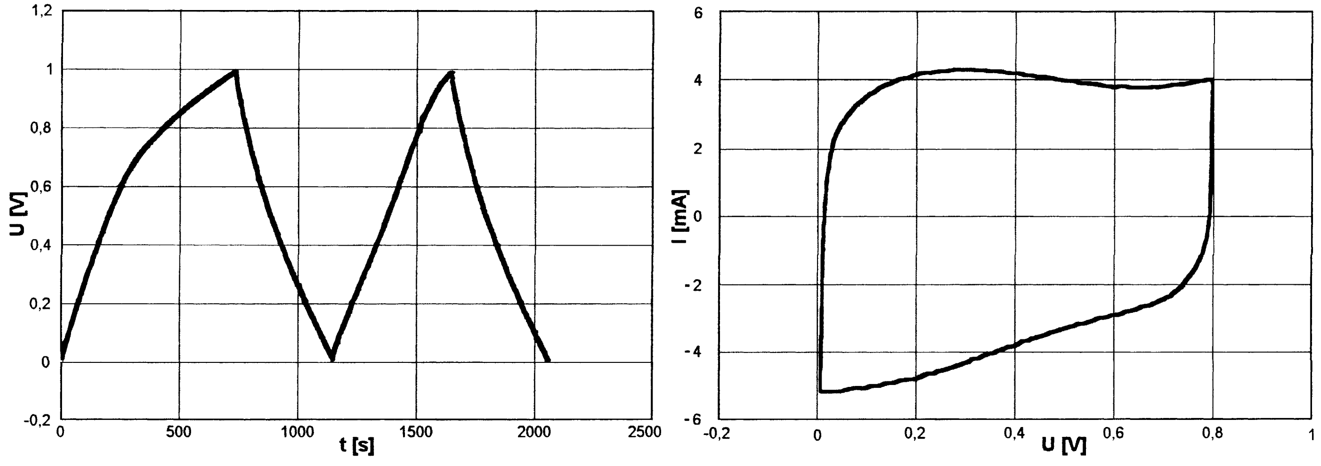
3. Results and discussion

The nanotubular materials of great variety due to the special modifications supplied different values of capacitance depending on their physicochemical parameters (Table 1). The capacitance (per active nanotubular material) was calculated mainly from the galvanostatic discharge curves and voltammetry characteristics at 2 mV/s scan rate. Our experiments prove that as-received SWNTs (Rice) supply a value of 40 F/g, i.e. twice smaller than for MWNTs Co/700°C. In the case of SWNTs thermally treated at 1650°C, a lower value of 18 F/g is obtained probably due to the more perfect arrangement of the tubes in the bundles after annealing. Additionally, the voltage for the capacitor performance diminishes due to a more easy decomposition of the electrolyte. MWNTs Co/700°C point out a capacitance of 80 F/g with a quite regular rectangular shape of the voltammograms. The highly mesoporous character of the material due to the open central canal and the accessible network of entangled nanotubes is confirmed by a type IV nitrogen adsorption/desorption isotherm. The presence of mesopores facilitates the transport of the ions from the solution to the charged interface. The galvanostatic charge/discharge characteristics (Fig. 1a) of a capacitor built from MWNTs Co/700°C treated by hot nitric acid (80°C, 1 h) show that the capacitance has some tendency to decrease during the first cycles typically of a surface modification. The irreversible reduction of some oxygenated groups is mainly responsible for this evolution. Therefore, the values of capacitance were always calculated from the electrochemical characteristics of stabilised capacitors. A well visible hump at ca. 0.2 V on the voltammogram of Fig. 1b which represents such a stabilised capacitor demonstrates the presence of a rich surface functionality. A pseudocapacitive effect due to the contribution of the surface groups noticeably enhances the measured value of capacitance which reaches 136 F/g even if the specific surface area remains almost unchanged (410 m^2/g) after the oxidative treatment of the sample.

For MWNTs Co/900°C with a comparable surface area (396 m^2/g) but a hardly accessible central canal, the smaller value of capacitance, i.e. 62 F/g, seems to confirm the role of the central canal in charging the electrical double layer. The lack of entanglement due to the rigid structure of MWNTs templ/800°C and the high purity of the material explains the low values of capacitance for this type of nanotubes.

Table 1
Specific capacitance of the carbon nanotubes in F/g

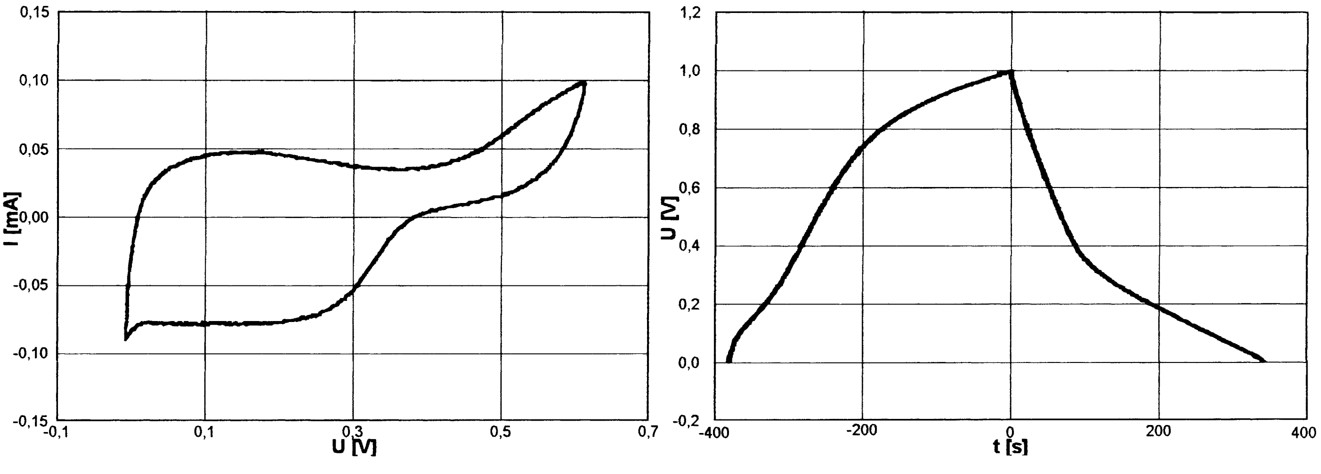
	SWNTs Rice	SWNTs Rice 1650°C	MWNTs templ/800°C	MWNTs Co/700°C	MWNTs Co/900°C	MWNTsCo/700°C mod. HNO_3	MWNTs Hyperion	MWNTs Hyperion mod. PPy
6 mol l^{-1} KOH	40	18	36	80	62	137	14	-
1 mol l^{-1} H_2SO_4	-	-	-	-	-	-	78	172



(a)

(b)

Fig. 1. Charge/discharge characteristics of a capacitor assembled in 6 mol l^{-1} KOH from MWNTs Co/700°C treated by hot HNO_3: (a) galvanostatic at $I = 1$ mA; (b) potentiodynamic at 10 mV/s. Mass of each electrode 8.5 mg.



(a) (b)

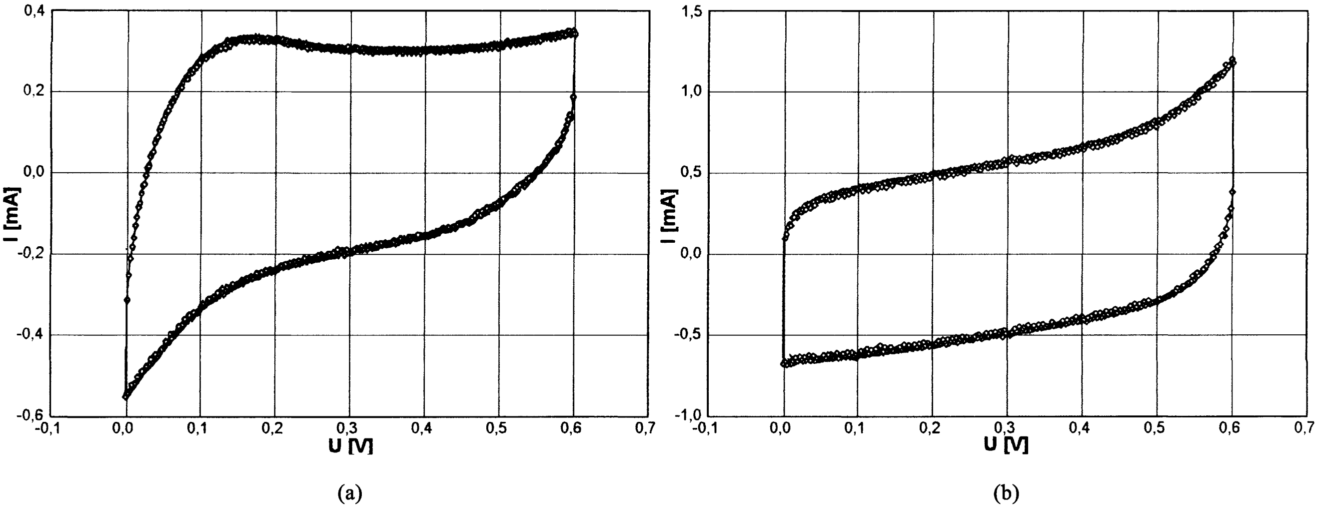
Fig. 2. Charge/discharge characteristics of a capacitor assembled in 6 mol l^{-1} KOH from Hyperion nanotubes: (a) potentiodynamic at 2 mV/s; (b) galvanostatic at $I = 0.1$ mA. Mass of each electrode 4 mg.

However, in this case the wide central canal can play some additional effect in charging the electrical double layer.

For the Hyperion sample, a two step charging/discharging is observed on both the potentiodynamic (Fig. 2a) and galvanostatic characteristics (Fig. 2b). The particular behaviour of this capacitor is probably connected with the electrochemical activity of the remaining iron catalyst (1.2 wt.% Fe from elemental analysis). This effect is especially pronounced in alkaline medium, whereas in acidic medium (1 mol l^{-1} H_2SO_4) the voltammetry curve has a more rectangular shape (Fig. 3a) because of a partial dissolution of iron. Simultaneously, a great difference is observed between the values of capacitance, i.e. 20 F/g for 6 mol l^{-1} KOH and 78 F/g for 1 mol l^{-1} H_2SO_4.

Trials were undertaken to increase the specific capacitance by deposition of PPy on the surface of Hyperion nanotubes. A square shape of the voltammograms is observed for Hyperion/PPy (Fig. 3b) and the capacitance reaches a value of 172 F/g. Taking into account the values given by the Hyperion nanotubes (78 F/g) and by pure PPy (ca. 90 F/g [1]), there is a considerable enhancement of the performance due to the association of these two materials in the nanocomposite. The open entangled network of this composite is probably responsible of a better efficiency for the formation of the three dimensional electrical double layer in PPy. The additional advantage of using a nanotube/PPy composite is an increase of the permissible voltage for the charge/discharge of the capacitor that has an important practical application.

The performed investigations proved that nanotubes represent a very attractive material as electrodes for capacitors even if they have a very moderate surface area from



(a) (b)

Fig. 3. Potentiodynamic characteristics (2 mV/s) of a capacitor assembled in 1 mol l^{-1} H_2SO_4 from Hyperion nanotubes: (a) without PPy; (b) with PPy. Mass of each electrode 3.5 mg.

200 to 410 m^2/g. A further treatment of the nanotubular materials, such as an oxidative treatment of the nanotubes or the deposition of PPy, is profitable for the enhancement of capacitance through pseudoeffects, however probably with a limited durability. For the three cases of pseudoeffects considered in this paper, the origin of pseudocapacitance is quite different depending if they involve the surface functionality, metallic particles or a conducting polymer.

Acknowledgements

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