



Short communication

Supercapacitors based on conducting polymers/nanotubes composites

E. Frackowiak ^{a,*}, V. Khomenko ^{b,1}, K. Jurewicz ^a, K. Lota ^a, F. Béguin ^b^a Poznan University of Technology, 60-965 Poznan, ul. Piotrowo 3, Poland^b CRMD, CNRS-University, 1b rue de la Férollerie, 45071 Orléans, France

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Abstract

Three types of electrically conducting polymers (ECPs), i.e. polyaniline (PANI), polypyrrole (PPy) and poly-(3,4-ethylenedioxythiophene) (PEDOT) have been tested as supercapacitor electrode materials in the form of composites with multiwalled carbon nanotubes (CNTs). The energy storage in such a type of composite combines an electrostatic attraction as well as quick faradaic processes called pseudo-capacitance. It has been shown that carbon nanotubes play the role of a perfect backbone for a homogenous distribution of ECP in the composite. It is well known that pure conducting polymers are mechanically weak, hence, the carbon nanotubes preserve the ECP active material from mechanical changes (shrinkage and breaking) during long cycling. Apart of excellent conducting and mechanical properties, the presence of nanotubes improves also the charge transfer that enables a high charge/discharge rate. For an optimal use of ECPs in electrochemical capacitors, a special electrode composition with ca. 20 wt.% of CNTs and a careful selection of the potential range is necessary. The capacitance values ranging from 100 to 330 F g⁻¹ could be reached for different asymmetric configurations with a capacitor voltage from 0.6 to 1.8 V. It is also noteworthy that such a type of ECP/CNTs composite does not need any binding substance that is an important practical advantage.

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Keywords: Supercapacitor; Carbon nanotubes; Polyaniline; Polypyrrole; PEDOT**1. Introduction**

The growing demand for portable systems and electric vehicles which require high power in short term pulses have prompted a great interest in electrochemical capacitors, also known as supercapacitors [1–3]. Various carbon materials have been considered for supercapacitor electrodes and a great attention was also focused on conducting polymers. Electrically conducting polymers (ECPs) represent a very interesting family of synthetic metals due to a high doping level and a fast electrochemical switching. The possible application of ECPs in electrochemical capacitors is dictated by their significant capacitance values [4–11]. Contrarily to activated carbons where only the surface is used for charge accumulation, in the case of ECPs, the total mass and volume is involved in charge storage. Extremely high capacitance val-

ues can be obtained with a thin ECP film electrodeposited on a conducting support like Pt and/or glassy carbon. The values reported for different ECPs, e.g. PANI can easily reach values of 1000 F g⁻¹ when the electrochemical investigation is performed in a three electrode cell using a thin film that has a very limited use for a practical supercapacitor operating as a two-electrode system.

The main drawback of ECPs application as supercapacitor electrodes is connected with their poor stability during cycling. The ECP films, due to volumetric changes during the doping/dedoping process (insertion/deinsertion of counter ions), undergo swelling, shrinkage, cracks or breaking that in consequence gradually aggravates their conducting properties. Additionally, the electrochemical activity of each ECP is strictly determined by its working potential range limited by an isolating state and/or polymer degradation caused by overoxidation.

Our target is to overcome this stability problem of ECPs with cycling by using their composites with carbon nanotubes (CNTs) as mesoporous conducting network able to adapt to all the mechanical stress. The effect of the potential range

^{*} Corresponding author.

E-mail address: fracko@fct.put.poznan.pl (E. Frackowiak).

¹ On leave from the Kiev National University of Technology and Design, 2 Nemirovich-Danchenko str., 02011 Kiev, Ukraine.

during cycling will be especially emphasized. Different ECPs materials for the positive and negative electrodes will be also combined in order to optimize the voltage range of the supercapacitor.

2. Experimental

2.1. Materials preparation, characterization

The multiwalled carbon nanotubes used as composite backbone in this study were synthesized by acetylene decomposition on a $\text{Co}_x\text{Mg}_{(1-x)}\text{O}$ solid solution precursor of catalyst at 600°C according to reference [12]. The method allows an efficient production of high purity CNTs strongly entangled.

Polymerisation of conducting polymers was carried out mainly by a chemical method which appears definitively easier than the electrochemical one. For chemical polymerization of monomers, such oxidants as FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$ were used. Composites were prepared by immersion of multiwalled carbon nanotubes (0.1 g) into an aqueous solution of the monomer and by addition of an oxidant to this solution. Electroconducting PPy was deposited on CNTs by chemical polymerization of 0.5 ml pyrrole with 1.2 g of FeCl_3 in 50 ml of 0.1 mol L⁻¹ HCl. The PANI/CNTs nanocomposite was synthesized through oxidative polymerization of 0.4 ml aniline by 0.4 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 50 ml of 1 mol L⁻¹ HCl. The nanocomposites materials were then filtered and washed with a large amount of water and several times by ethanol to remove the residual oxidant. At the end, all composites were washed by acetone and dried at 60°C .

Because of a limited solubility of the EDOT monomer in aqueous medium, the polymerisation was performed in aprotic medium such as acetonitrile (AN) with Fe(III) playing the role of oxidant. The FeCl_3 or $\text{Fe}(\text{ClO}_4)_3$ oxidant (1.2 mol L⁻¹) was dissolved in AN and then EDOT (1 mol L⁻¹) was added drop by drop with an intensive stirring. The navy-blue PEDOT was carefully washed by AN and dried at 50°C . In the case of the direct polymerisation of PEDOT on carbon nanotubes, CNTs were dispersed in the reaction mixture using an ultrasonic bath. A two-component composite was also prepared by mechanical stirring of previously elaborated PEDOT with 20 wt.% of CNTs. In few cases instead of CNTs, acetylene black (AB) has been used for making the composite in order to determine if there is a beneficial effect of CNTs compared to AB. For all the composites the proportion of the components was estimated by weighing the final product in the dried state.

Scanning electron microscopy (SEM, HITACHI S 4200) has been used for the observation of the obtained composite materials and of the pellet electrodes.

2.2. Electrochemical characterization

The advantage of using the ECP/CNTs composite material is the possibility of manufacturing the electrodes without any

polymeric binder, while keeping enough good mechanical properties. The electrodes were pellets (5–20 mg) obtained by pressing the composite material. The capacitor is built from two pellets of composite separated with a glassy fibrous paper in a Swagelok® system. Two-electrode cells were most often applied but a three electrode configuration was also used. The electrochemical performance was determined in acidic (1 mol L⁻¹ H₂SO₄) and organic (1 mol L⁻¹ TEABF₄ in acetonitrile) solutions depending on the ECP composite, using galvanostatic, voltammetry and impedance spectroscopy techniques. For galvanostatic charge/discharge cycling, the current load ranged between 100 and 500 mA g⁻¹ and capacitance was estimated only from the discharging time. Cyclic voltammetry characteristics of the ECP/CNTs composites were recorded at different scan rates from 1 to 10 mV s⁻¹. The capacitance was calculated from the capacitive current and in the case of a non-rectangular shape, the curves were integrated. The formula $C = i\nu^{-1}$ was used, where i is the average current and ν the scan rate of voltage, whereas for galvanostatic measurements $C = itdU^{-1}$ was applied (t is the discharge time in the range of voltage dU). It is important to note that in our calculations the capacitance values are expressed per active material of one electrode. In the case of three-electrode cells, the capacitance value was immediately the capacitance per electrode, however, in the two-electrode cell we were multiplying the measured capacitance C by two to have specific capacitance per electrode. $C_{\text{spec}} = 2Cm^{-1}$ (m is the mass of one electrode). Obviously, for the full capacitor the capacitance values would be four times smaller.

The capacitance was also estimated from impedance spectroscopy using the following formula: $C = -(1/(2\pi fZ''))$. Impedance spectroscopy measurements were performed at open circuit voltage with $\pm 10\text{ mV}$ amplitude.

VMP (Biologic-France) and AUTOLAB potentiostat/galvanostats (ECOCHEMIE) were used for the electrochemical measurements.

3. Results and discussion

3.1. Microtextural characterization

The distribution of the conducting polymer in the composites was evaluated by SEM observation. Fig. 1 presents a general population of carbon nanotubes chemically coated by three types of conducting polymers: polyaniline (PANI), polypyrrole (PPy) and poly-(3,4-ethylenedioxythiophene), i.e. PEDOT. The composites contain 80 wt.% of ECP and 20 wt.% of CNTs. In the case of polyaniline (Fig. 1a), the nanocomposite is very homogenous and CNTs are equally coated by conducting polymer. The average diameter of the PANI coated nanotubes is up to 80 nm. For comparison it should be noted that the diameter of the pristine nanotubes is mainly ranging from 10 to 15 nm [12]. By contrast, for the PPy composite (Fig. 1b) a globular structure and irregular

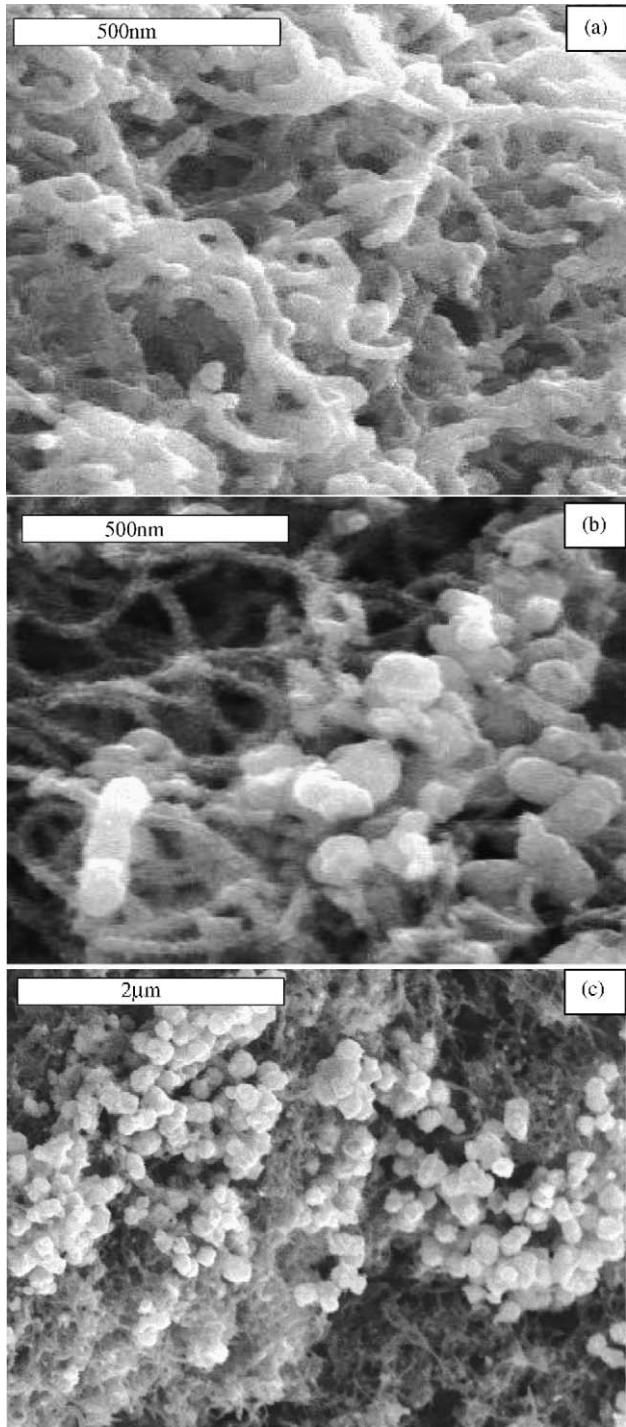


Fig. 1. SEM of composites from CNTs with PANI (a), PPy (b) and PEDOT (c) prepared by chemical polymerization.

deposits are observed. In the case of the PEDOT/CNTs composite a strong tendency for polymerization on the polymer itself appears.

From our previous experience with electrochemical coating of carbon nanotubes by PPy [13–16], it seems that chemical polymerization supplies a more porous morphology of the composite. Hence, even if the quality of the electrochem-

ical deposit is better, the higher porosity of the chemically polymerized product is more interesting on the point of view of capacitor application. Some SEM observations on cross sections of pellet electrodes from pure ECP showed a drastic loss of porosity, whereas the same polymer with CNTs preserved an accessible porous morphology.

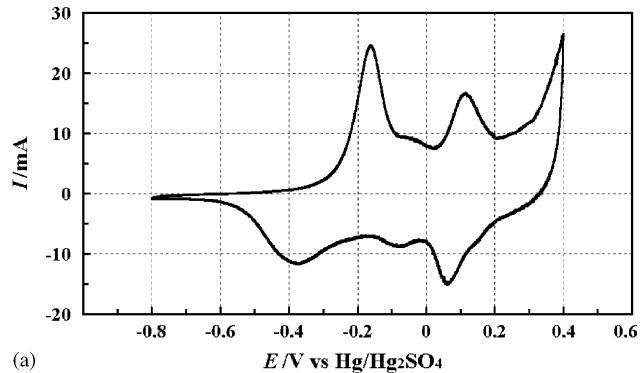
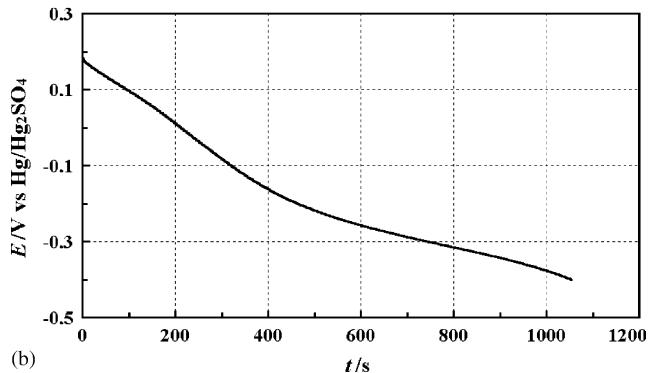
3.2. Capacitance properties

The novel composites based on chemically elaborated conducting polymers and CNTs were carefully investigated by the three electrochemical techniques and a good agreement was found between all the measurements. We proved that 20 wt.% of CNTs in the electrodes is sufficient to ensure a good permeability for the electrolyte and allow a high electrochemical performance. It is noteworthy that pure nanotubes pointed out very low capacitance values not exceeding 20 F g^{-1} . Hence, taking into account that the proportion of CNTs in the composite is only 20 wt.%, the total capacitance is mainly due to the conducting polymer. On the other hand, experiments carried out with acetylene black instead of CNTs showed definitively better performance for composites with CNTs due to a good dispersion of ECP in the nanometric scale and better conductivity of composite.

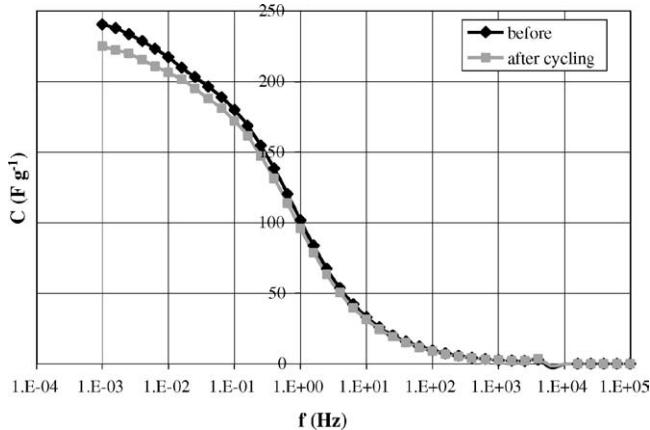
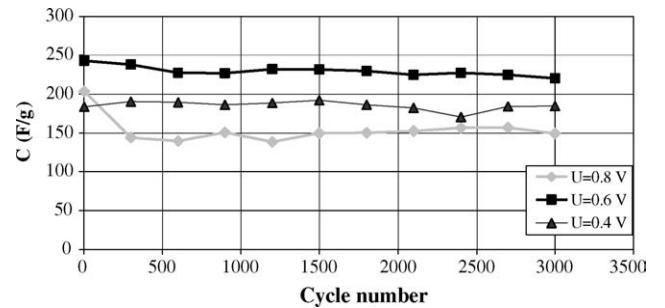
The capacitance values of the ECPs/CNTs composites are strongly depending on the cell configuration used for the electrochemical investigation, being always significantly higher for a three-electrode system. For example the average value for the PANI/CNTs composite estimated using a three electrode cell was 650 F g^{-1} , whereas in a two-electrode cell it diminished to 360 F g^{-1} or even lower. In both cases capacitance is expressed per active mass of one electrode. The electrochemical characteristics by the voltammetry technique (2 mV s^{-1}) and galvanostatic discharge at 2 mA are presented in Fig. 2. It is well seen (Fig. 2b) that depending on the selected potential range for calculation, the capacitance can greatly vary. However, one must remember that in a two-electrode system the lower capacitance value of both electrodes connected in series will determine the total capacitance according to the formula:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

It is noteworthy that well visible peaks typical for PANI are observed in a three-electrode cell whereas a rectangular shape voltammogram is recorded in a two-electrode configuration. The PANI/CNTs composite was systematically investigated by impedance spectroscopy before and after cycling in a two-electrode capacitor using different operating voltage (from 0.4 to 0.8 V). The capacitance (F g^{-1}) versus frequency (Hz) dependence is presented in Fig. 3 before and after 3000 cycles performed at 300 mA g^{-1} current load using 0.6 V operating voltage range. After cycling, only a slight decrease of capacitance in the low frequency region is observed, whereas the permeability of the composite bulk for ions at higher frequencies remains the same supplying still 100 F g^{-1} at 1 Hz in both

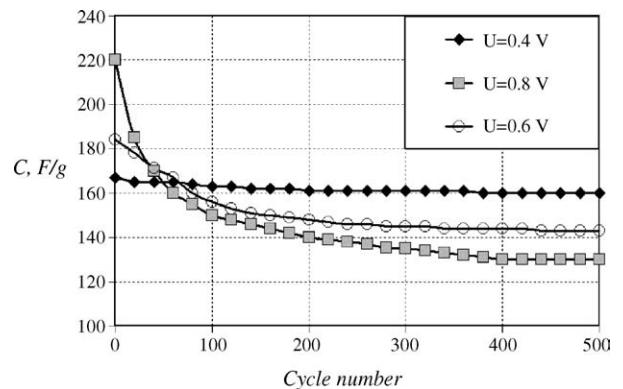
(a) E/V vs $\text{Hg}/\text{Hg}_2\text{SO}_4$ Fig. 2. Cyclic voltammogram at 2 mV s^{-1} (a) and galvanostatic discharge at 2 mA (b) of a PANI/CNTs pellet electrode; $m = 5.4 \text{ mg}$; $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte, three-electrode cell.

cases. Contrarily, an extension of operating voltage causes a rapid drop of capacitance already at 10 mHz . The loss of capacitance values during cycling for the PANI/CNTs composite for three different voltage ranges is shown in Fig. 4. The decrease of capacitance in the wider voltage range is caused by the operating of negative electrode on the border of the isolating state. It should be concluded that the cycling life of capacitor decreases dramatically after increasing the operating voltage as well for the PANI/CNTs and PPy/CNTs composites (Fig. 5). In the case of the PPy/CNTs

Fig. 3. Capacitance vs. frequency for the PANI/CNTs composite before and after 3000 cycles at 300 mA g^{-1} current load using a voltage range from 0 to 0.6 V . Two-electrode cell.Fig. 4. Cycleability of the PANI/CNTs composite at 300 mA g^{-1} current load with different operating voltage of supercapacitor. Electrolyte: $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

composite, capacitance values of 495 and 200 F g^{-1} were found in three- and two-electrode cell configurations, respectively. The cyclic performance of the two-electrode system is significantly dependent on the selection of the voltage range that is well demonstrated in Fig. 5. A very high cycleability > 3000 cycles, with stable capacitance values of 160 F g^{-1} , was observed using a narrow voltage range (0.4 V) for a capacitor based on the PPy composite. From experimental data obtained using lower operating voltage a total loss of about 15% for PPy/composite and 10% for PANI/composite of initial discharge capacitance is found after 100 cycles, but a fairly steady capacity is maintained thereafter. On the contrary, upon increasing the operating voltage, the decrease of capacity reaches about ca. 40% after 500 cycles performance.

Among the three investigated materials, the PEDOT/CNTs composite supplied lower capacitance values of 100 F g^{-1} , however, with a perfect stability during cycling. An example of electrochemical characteristics of a two-electrode capacitor based on this composite in organic medium is presented in Fig. 6. Fig. 6a shows an irregular shape of voltammetry characteristic taken at 10 mV s^{-1} , therefore a practical voltage of 1.5 V has been selected for the charge/discharge cycling shown in Fig. 6b. Additional advantage of the PEDOT/CNTs composite is a possibility of operating in acidic, alkaline and organic electrolytic solutions.

Fig. 5. Cycleability of the PPy/CNTs composite in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. $I = 2 \text{ mA}$.

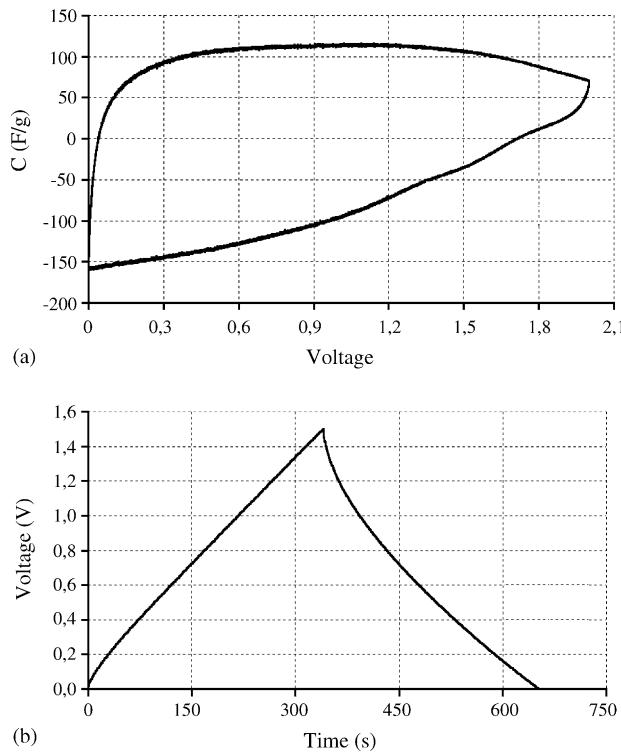


Fig. 6. Cyclic voltammogram at 10 mV s^{-1} (a) and galvanostatic charge/discharge at 2 mA (b) of a symmetric supercapacitor built from the PEDOT/CNTs nanocomposite; mass of each electrode 8.9 mg ; electrolytic solution, 1 mol L^{-1} TEABF₄ in acetonitrile.

In order to increase the capacitor operating voltage with enhanced capacitance values and durability, various combinations of ECPs composites working in their optimal potential range were also tested. Very interesting results were obtained when an asymmetric system was built with two different conducting polymer composites for the positive and negative electrodes. Electrochemical behaviour of PANI dictates its choice as a positive electrode because of a rapid loss of conductivity in the negative potential range (see Fig. 2). On the other hand PPy as well as PEDOT could serve as both electrodes (+) and (−) taking into account a suitable voltage range (Table 1). Fig. 7 shows the performance for a PANI/CNTs (+)/PPy/CNTs (−) capacitor which supplies 320 F g^{-1} . Both characteristics, i.e. voltammetry and galvanostatic charge/discharge are presented in Fig. 7a and b, respectively. Although pseudofaradaic charge transfer occurs

Table 1
Combination of different materials for positive and negative electrodes of supercapacitor

Positive (+)	Negative (−)	$C (\text{F g}^{-1})$	$U (\text{V})$
PANI	PPy	320	0.6
PANI	PEDOT	160	0.8
PANI	Carbon (PX21)	330	1.0
PPy	Carbon (PX21)	220	1.0
PEDOT	Carbon (PX21)	120	1.8

Electrolyte: 1 mol L^{-1} H₂SO₄; ECPs/CNTs composites (80 wt.-%/20 wt.-%).

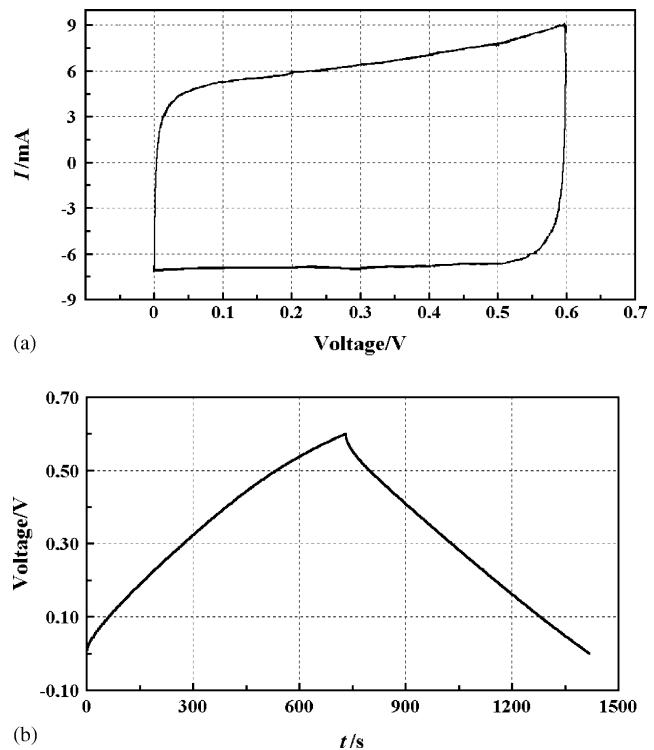


Fig. 7. Cyclic voltammogram at 5 mV s^{-1} (a) and charge/discharge at 1 mA (b) of an asymmetric capacitor based on PANI/CNTs (+) and PPy/CNTs (−) electrodes. Mass of each electrode 8.2 mg . Electrolyte: 1 mol L^{-1} H₂SO₄.

at both electrodes, an ideal capacitive behaviour is demonstrated from the voltammogram and the discharge curve for such an asymmetric capacitor with a good cycleability for 0.6 V voltage range.

An additional increase of the supercapacitor power and energy density through enhancement of the operating voltage can be easily realized by application of activated carbon as a negative electrode. In this case voltage can reach 1.8 V in aqueous medium with a very good cycleability over 10,000 cycles. Table 1 shows some examples of asymmetric configurations studied.

Instead of CNTs, acetylene black could be also used as carbon additive in such composites, however, nanotubes act as a more convenient backbone and allow a better dispersion of the conducting polymer.

4. Conclusions

Carbon nanotubes play a role of an excellent support for conducting polymers. Their unique microtextural, mechanical and conducting properties allow to form a supercapacitor with an accessible electrode/electrolyte interface for efficient charge propagation. Application of CNTs enables to extract fully the energy from the ECP, however, only if the operating voltage is optimally selected for the positive and negative electrode. This advanced type of composite from nanotubular material and conducting polymer in the doped state

allows to form a three dimensional volumetric supercapacitor using a synergic effect of complementary properties of both components.

Long-term charge/discharge tests at 300 mA g⁻¹ current load proved a good cycleability of ECP/CNTs composites. Good accessibility of ions into the ECP bulk after 3000 cycles was proved by impedance spectroscopy but only for composite with CNTs whereas pure PANI pointed out a dramatic resistive increase.

The development of hybrid systems, with two different electrodes working in their optimal potential range, is very promising. The applied potential was found to be the key factor influencing the specific capacitance of nanocomposites based on conducting polymers. For operating of each electrode in its optimal potential range, asymmetric capacitors have been built with MWNT/PPy and MWNT/PANI as negative and positive electrodes, respectively. High values of capacitance up to 320 F g⁻¹ of electrode material have been obtained with this construction. An additional extension of capacitor voltage was reached using activated carbon as a negative electrode and the ECP/CNTs composite as a positive one.

Acknowledgement

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