Polish J. Chem., **78**, 1345–1356 (2004)

Development of New Supercapacitor Electrodes Based on Carbon Nanotubes*

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(Received March 16th, 2004; revised manuscript April 19th, 2004)

Carbon nanotubes (CNTs) are essentially a mesoporous material with very limited microporosity, hence, they supply only moderate capacitance values. After KOH activation their capacitance values increase significantly from 15 F/g to *ca*. 100 F/g. CNTs are especially adapted as component of supercapacitor electrodes due to their exceptional conducting and mechanical properties. They play a perfect role of backbone for materials with pseudocapacitance properties. In this work a profitable role of nanotubes in nanocomposites with polypyrrole and polyaniline is demonstrated. High capacitance values from 200 to 360 F/g were obtained for such composites with a good cycling behavior, however, strongly affected by the operating voltage range of supercapacitor.

Key words: supercapacitor, carbon nanotubes, pseudocapacitance, polypyrrole

The exponential growth of the portable electronic devices market has created an increasing demand for light-weight and compact electric power sources of high energy and power density. Among the high performance systems which are considered, lithium-ion batteries, nickel/hydride batteries, fuel cells and supercapacitors are particularly promising because their technology can still benefit from scientific developments and they have the potential to trigger a cascade of technological breakthroughs. Additionally, the possibility of using battery-supercapacitor hybrid power systems has prompted the academic and industrial interest in the field of electric vehicle applications during the last years. Future developments depend in a decisive way on advanced electrode materials with good electrochemical characteristics.

Due to their tuneable microtexture, surface functionality and different forms (powders, fibres, foams, felts, tissues, composites, …), carbon materials offer a wide range of possibilities for electrochemical energy storage. Additionally, due its amphoteric character, carbon can be doped as well by donor and acceptor species, allowing to broaden the electrochemical properties. An intense research effort is devoted to develop functional carbon materials with optimized electrochemical characteristics and also to use them as a support for enhancing the performance of electrochemically active materials.

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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Among various carbon materials, carbon nanotubes (CNTs) due to their unique morphology (*e.g.* helical arrangement of graphitic layers, presence of central canal, entanglement, bundle formation) as well as exceptional conducting and mechanical properties are of great interest for some electrochemical applications, *e.g.* supercapacitors.

In this paper, the capacitance properties of carbon nanotubes based electrodes will be discussed, taking into account the microtexture, structure and surface functionality. A special attention will be paid to define strategies for an optimization of the electrode materials with some opening to future perspectives.

General properties of supercapacitors. The electrochemical capacitors, also called supercapacitors, are an intermediate energy system between the classical dielectric capacitors and batteries. At comparable volume, their storage capacity is roughly one hundred times that of dielectric capacitors, their specific power one hundred times that of batteries, but the specific energy stored is about one hundred times less than in batteries. The high power density of supercapacitors can be adapted for uninterruptible power sources (UPS), pulse laser technique and hybrid energy sources for electrical vehicles.

When a voltage is imposed between two parallel plates connected to an external circuit, the surfaces become oppositely charged, with a capacitance C_n in farads (F) expressed by equation (1):

$$C_n = \frac{\varepsilon S}{d} \tag{1}$$

where ε is the permittivity or dielectric constant of the material used to separate the plates, S is the area of the charged plates and d is the separation distance. The capacity of these systems is mainly limited by the surface area of the plates.

One way of overcoming this dimensionality problem is to use a material with an extremely large surface area, such as an activated carbon, and to take advantage of the electrical double layer which forms at the interface between an electrode and an electrolyte in all electrochemical systems [1,2]. The electrolyte contains ions which are able to freely move throughout a matrix, such as a liquid or a polymer, and respond to the charge developed on the electrode surface as demonstrated in Figure 1.

The double layer capacitance of each electrode is determined by equation (1), where the distance d is provided by the thickness of the compact layer, which is generally less than one nanometer. This is where the technological advantage of supercapacitors over conventional capacitors lies, as charge storage in the extremely thin compact layer gives rise to specific capacitances of approximately $0.1\ \mathrm{F \cdot m^{-2}}$. It gives an increase by several hundred thousand-fold over conventional film capacitors. Taking into account that the specific surface area of activated carbons is in the range of $1000\ \mathrm{m^2/g}$, a capacitance of 100 F per gram of carbon is easily reached.

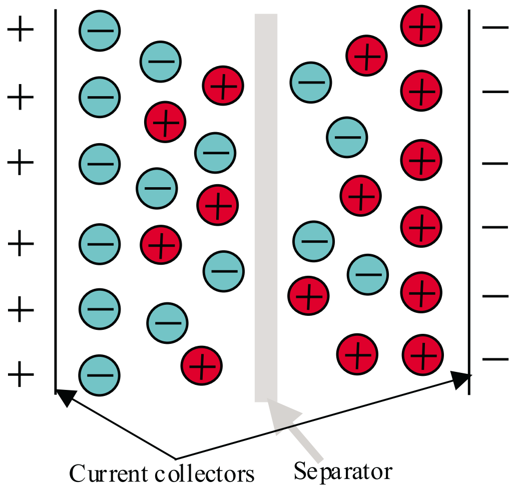

Figure 1. Schematic representation of an electrochemical capacitor. ⊕ cations of the electrolyte; ⊖ anions of the electrolyte.

Figure 1 shows that an electrochemical capacitor is equivalent to two capacitors in series, therefore the overall capacitance is given by equation (2):

$$\frac{1}{C_n} = \frac{1}{C_1} + \frac{1}{C_2} \tag{2}$$

where C_1 and C_2 denote the capacitance of each electrode. The energy E in joules stored in an electrochemical capacitor is given by equation (3):

$$E = \tfrac{1}{2}\mathrm{CV}^2 \tag{3}$$

where V is the operating voltage. Apart the size of the electrode/electrolyte interface for supercapacitor electrodes, the amount of energy stored is controlled by the electrolyte voltage window. In aqueous medium, this window is generally less than 1 V, whereas it can reach 3 V in organic electrolytes. Hence, the energy stored in supercapacitors working in organic electrolyte is about one order of magnitude higher than in aqueous medium.

Another parameter that describes a supercapacitor performance is the ability to store and release the energy rapidly, *i.e.* the power, P, which is given by equation (4):

$$P = \frac{V^2}{4R} \tag{4}$$

where R is the internal resistance of the supercapacitor, *i.e.* commonly the equivalent series resistance (ESR) R_S. The ESR of the entire device is the sum of the resistances of all the materials between the external contacts, *i.e.* substrate, carbon, binder, separator and electrolyte. The product R_SC determines the rate at which the device can be charged or discharged, and consequently its power limit. The power can be optimised through an understanding of the nanostructure/texture of the materials and of the processes which dictate the supercapacitor performance.

Equation (1) indicates that the capacitance value is determined by the surface area S of the electrode/electrolyte interface, which is strongly dependent on the amount of micropores. The dimensions of the latter should be adapted to the size of solvated anions and cations, that is crucial for a high performance of the capacitor. Nevertheless, the presence of mesopores is essential for ions transportation to the active surface of the micropores. A quick transportation of ions in the bulk of the electrodes is certainly the key criterion to lower R_s and to reach high power values. Multiwalled carbon nanotubes (MWNTs) and single wall nanotubes (SWNTs) are very promising for this function of electrochemical capacitors, because owing to their entanglement they form a well-developed network of open mesopores almost impossible to obtain with activated carbons [2,3]. Additionally, due to their well-extended graphitic type layers, their intrinsic electric conductivity is quite high, that is also profitable for lowering R_s. Figure 2 presents an example of mesoporous network of multiwalled carbon nanotubes obtained by a catalytic method.
Figure 2.

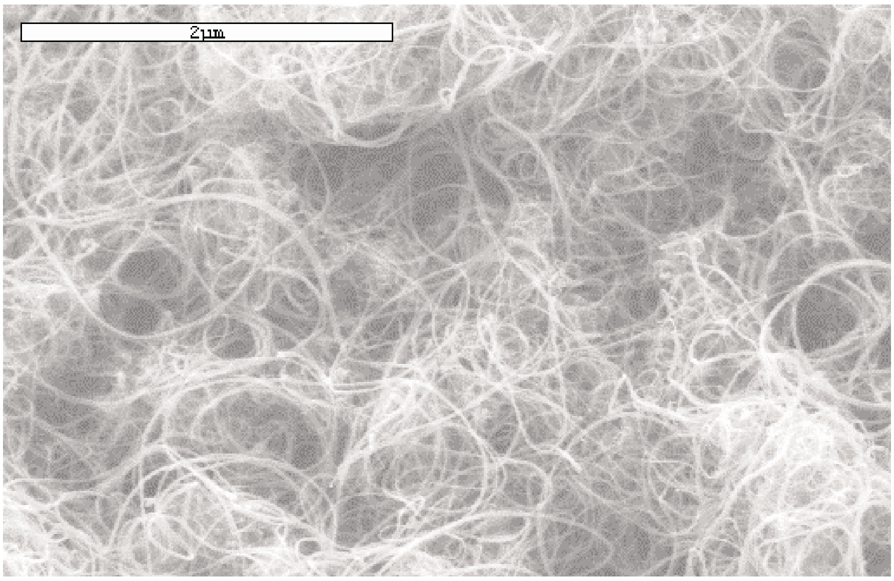

Figure 2. SEM micrograph of the purified nanotubes produced by the catalytic decomposition of acetylene at 600°C.

Capacitance properties of nanotubes. The electrochemical characteristics of supercapacitors built with pellets from various kinds of MWNTs have been investigated in 6 mol$\cdot$L^{-1} KOH medium, and correlated with the microtexture and elemental composition of the materials [2,4,5]. Most of the nanotube based capacitors give a regular box-like shape of the voltammograms, which denotes an entirely electrostatic attraction. In general, the higher the BET specific surface area and oxygen content of the nanotubes, the higher the capacitance values. Values as high as 80 F/g of carbon have been found with MWNTs prepared by decomposition of acetylene at 700°C on a Co supported catalyst, although the BET specific surface area of these MWNTs is only 411 m^2/g [5]. Beside the open mesopores which favour the ions access to the active surface, the surface functionality may also contribute to the capacitance value. However, after few cycles, the capacitance of nanotubular materials rich in surface groups noticeably decreases.

Another kind of effect has been demonstrated by Hyperion^{TM} catalytically grown nanotubes, depending on the electrolytic solution. The capacitance value is 14 F/g in 6 mol$\cdot$L^{-1} KOH and 78 F/g in 1 mol$\cdot$ L^{-1} H_2SO_4 [6]. A value of 104 F/g is even measured in 38 wt% H_2SO_4 on a free-standing mat of these nanotubes [3]. Well visible humps on the voltammetry curves clearly show that this behaviour is not strictly connected with the charging of an electrical double layer. Redox pseudo-capacitive reactions, related with iron from the catalyst (1.2 wt%) trapped in the material, contribute noticeably to the observed values [6].

The SWNTs prepared by laser ablation (Rice University) or by the HiPco^{TM} process (Carbon Nanotechnologies) supply capacitance values of 40–45 F/g [6,7]. Taking into account their BET specific surface area of 500 m^2/g, the specific capacitance per unit surface area is around 9 μF$\cdot$cm^{-2}, that is rather less than the value given by activated carbons. After annealing at 1650°C, capacitance of SWNTs from Rice diminishes to 18 F/g due to a better arrangement of the tubes in the bundles, that hinders the diffusion of solvated ions towards the active surface [6]. Interestingly, the capacitance of the HiPco SWNTs does not decrease at a current density of 150 mA$\cdot$g^{-1}. This is attributed to the large external surface area of this material (~400 m^2/g) on which ions adsorption /desorption proceeds quickly due to the absence of sieving effect [7].

We already mentioned that the good electrical conductivity of carbon nanotubes, together with the open mesoporous network provided by entanglement, are highly desirable properties for high power capacitors. Supercapacitors built with electrodes from self-standing mats of Hyperion^{TM} MWNTs have been investigated by impedance spectroscopy, showing a frequency "knee" at about 100 Hz, which suggests that most of the energy stored is accessible at frequencies below 100 Hz [3]. This value, which is much higher than that reported for capacitors from activated carbon electrodes, confirms the advantages of the nanotubes backbone to provide a well accessible active surface. As a consequence, a power density as high as 8000 W/kg of total cell weight could be measured [3].

Capacitance properties of activated nanotubes. Although relatively high values of capacitance were claimed for as received nanotubes in some literature reports, often for materials with a high amount of impurities, most of the recent data agree on values in the range of 20–40 F/g during long term cycling. Such values are smaller than those obtained with activated carbons, mainly due to the absence of micropores in carbon nanotubes.

Taking into account that a well balanced micro-mesoporosity is always recommended for a good performance of supercapacitor electrodes, it has been suggested to use KOH activation of multi-walled nanotubes to produce micropores in the walls, while keeping the mesoporous character provided by the entangled network [8–10]. An example of multiwalled nanotube activated by KOH (Figure 3) presents a number of defects on the nanotube walls with a special attack of potassium on the tip. Generally, a specific surface area of activated nanotubes increases a few times with a simultaneous opening of central canal.

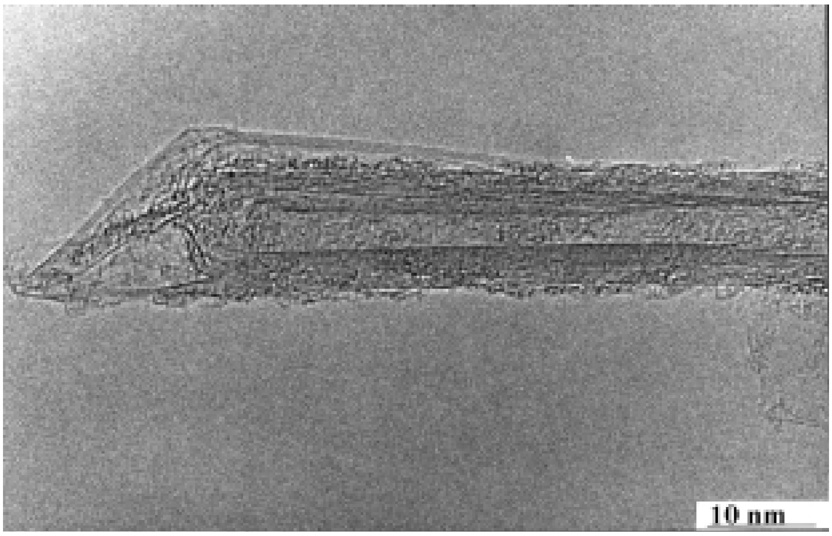

Figure 3. Transmission Electron Microscopy (TEM) image of a nanotube activated by KOH at 800°C.

Such activated MWNTs have been used as electrode material for supercapacitors in various aqueous and organic electrolytes (Figures 4, 5). Fig. 4 shows a galvanostatic charge/discharge characteristics of capacitor in 6 mol·L KOH and Fig. 5 presents a voltammetry dependences in 1 mol·L H_2SO_4 electrolytic solution.

In 6 mol·L KOH medium, the capacitance increased almost 7 times from *ca.* 15 F/g for non-activated nanotubes to 90 F/g after chemical activation. A similar capacitance enhancement is observed in acidic electrolytic solution. In organic electrolyte, the capacitance of the activated material reached 65 F/g with a box-like shape of the cyclic voltammograms [9,10].

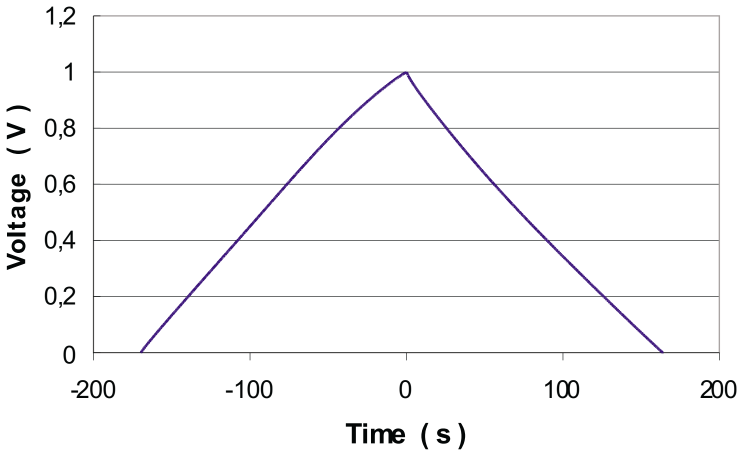

Figure 4. Galvanostatic charge/discharge of a supercapacitor built from activated nanotubes in 6 M KOH. Mass of electrode: 4.7 mg.

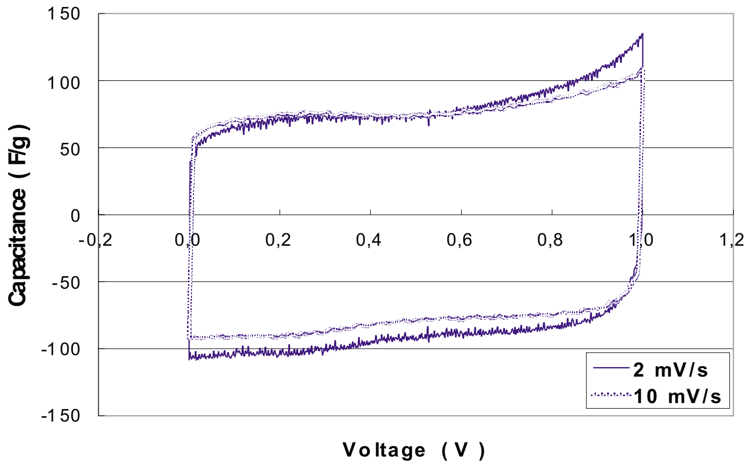

Figure 5. Characteristics of capacitor built from activated nanotubes at scan rate of 2 and 10 mV/s. Mass of electrode: 5.2 mg. Electrolyte: 1M H_2SO_4.

Although these values are interesting, they are lower than for the commercial activated carbons used in capacitors. On the other hand, due to the high cost of the pristine material, activated nanotubes cannot be produced at a competitive price. For these reasons, further developments should be oriented to the use of these materials as a component of composites.

Composites with a nanotube backbone. The structure of carbon nanotubes is generally characterized by extended graphitic type layers which provide them a high electrical conductivity. On the other hand, the high entanglement of the nanotubes creates an open network of mesopores. Hence, they are a perfect backbone for preparing nanocomposites with various electroactive materials. With nanotubes, the percolation of the active particles is more efficient than with the traditional carbon black which are generally used for the manufacture of electrodes [11]. On the other hand, the open mesoporous network allows the ions an easy diffusion to the active surface of the composite components. The two latter properties are essential to lower the equivalent series resistance (ESR) and consequently increase the power of the device.

The active components which are used in these composites are materials with pseudocapacitance properties such as oxides (RuO_2, a-MnO_2) and conducting polymers. Pseudocapacitance is an intermediate situation where a faradaic charge transfer occurs, but the potential changes are a continuous function of the charge passed, $dq = C\ dV$, as in a real capacitor [1]. High values of capacitance can be theoretically obtained with such materials which undergo quick pseudo-Faradaic reactions, as illustrated by polypyrrole (PPy) and ruthenium oxide:

$$[PPy^+ A^-] + e^- \Leftrightarrow [PPy] + A^- \tag{5}$$

$$RuO_a(OH)_b + \delta H^+ + \delta e^- \Leftrightarrow RuO_{a-\delta}(OH)_{b+\delta} \tag{6}$$

However, most of the literature reports are for three-electrode cell constructions and using very thin layers of the active material.

Real supercapacitors have been built from novel type of composite electrodes based on MWNTs with deposited conducting polymers. Chemical and electrochemical polymerization of the monomer has been considered in order to get a homogenous layer of the polymer on the nanotubular materials. The TEM micrograph presented in Fig. 6 for a material prepared by electrochemical deposition of polypyrrole (PPy) shows a very uniform polymer coating. The thickness of PPy layer (*ca*. 5 nm) was estimated from TEM image.

When the MWNTs are oxidized, their surface is covered with oxygen-containing groups, which can be used as anionic dopant of a PPy film electrodeposited on the MWNTs [12]. These films are notably less brittle and more adhesive to the electrode than those formed using and aqueous electrolyte as a source of counter ion.

The results reported in literature about capacitors using these kinds of composites concern mainly the coating by polypyrrole of MWNTs [12–16] and SWNTs [17]. Figure 7 shows the voltammogram obtained for such a composite. The square shape of the voltammogram demonstrates a typical capacitor behaviour, even if pure PPy usually gives more irregular characteristics, confirming a good synergy between PPy and MWNTs. This kind of capacitive behavior is confirmed by the linear discharge on the galvanostatic curve.

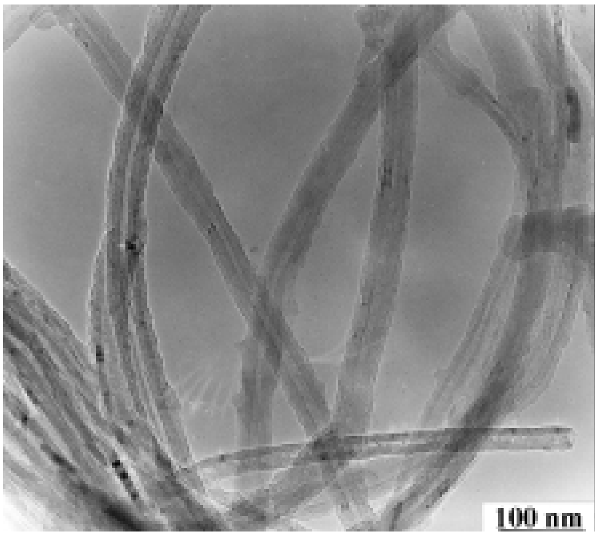

Figure 6. Multiwalled carbon nanotubes electrochemically coated by a thin layer of polypyrrole. The coating thickness is estimated to 5 nm.

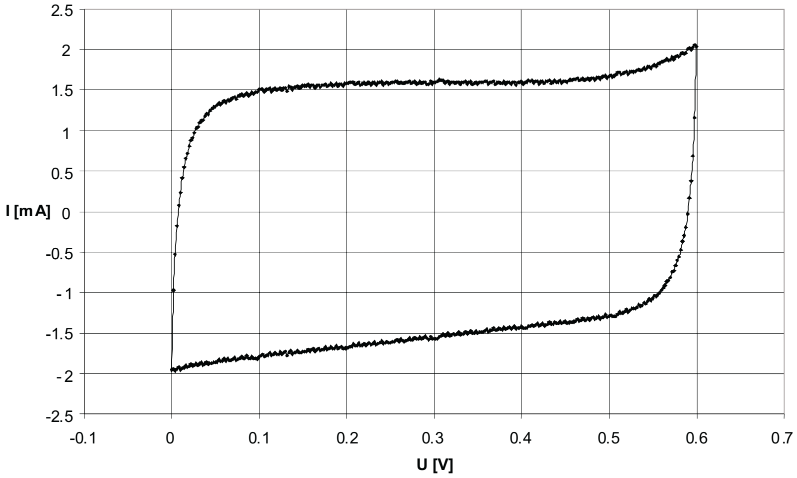

Figure 7. Voltammogram of a two electrode capacitor built with the PPy/MWNTs composite in H_2SO_4 electrolytic medium. Scan rate of potential 2 mV/s. Mass of electrode: 11.6 mg.

The maximum value of capacitance which was reached using a two electrode construction is 190 F/g for the PPy/MWNTs composite and 360 F/g for polyaniline composite PANI/MWNTs [18,19]. In fact, it has been demonstrated that the high values claimed in literature for very thin layers of pure conducting polymers in three electrode cells are valid only in a given potential range. For example, the

PPy/MWNTs composite investigated in a three electrode cell gives 250 F/g for the positive range of potential from 0.2 V to –0.3 V and 903 F/g for the negative range from –0.3 V to –0.6 V *vs* Hg/Hg_2SO_4. Taking into account these values, and the fact that the overall capacitance for a two electrode cell is given by the equation (2) for capacitors in series, the theoretical value cannot be higher than 196 F/g, that fits well with the maximum experimental value of 190 F/g. Such values were also confirmed by an impedance technique in a two electrode cell (Figure 8).

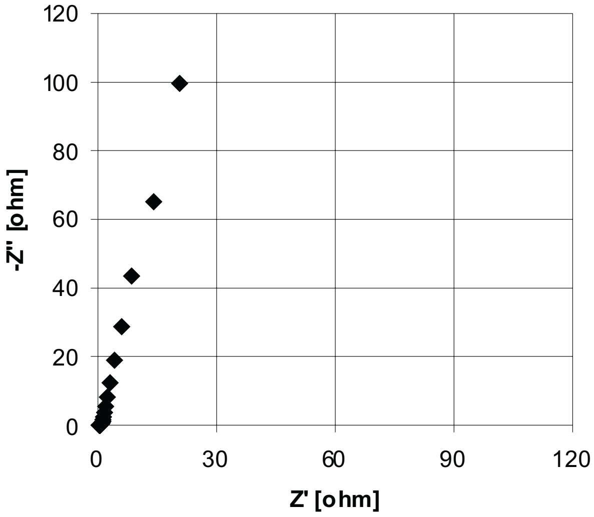

Figure 8. Impedance spectroscopy of a two-electrode capacitor built from composite electrodes MWNT/PPy with 25% of MWNTs.

Hence, it can be concluded that the bulk of the thin PPy layer coating the nanotubes is fully involved for quick pseudofaradaic processes, due to the open network of mesopores formed by the nanotubes, which allows a full doping of the polymer. This open web forms a volumetric electrochemical capacitor where the charge has a three dimensional distribution [20].

Apart of high capacitance values and a quick charge propagation, the cycleability of supercapacitor is an important demand. A long durability was obtained for capacitor built from MWNTs/PPy, however its cycleability is strongly affected by the range of operating voltage. The higher voltage range, the lower cycleability. Figure 9 presents such cycleability at the galvanostatic load of 350 mA/g with 0.8 V operating voltage. The loss of capacitance was observed only during first cycles.

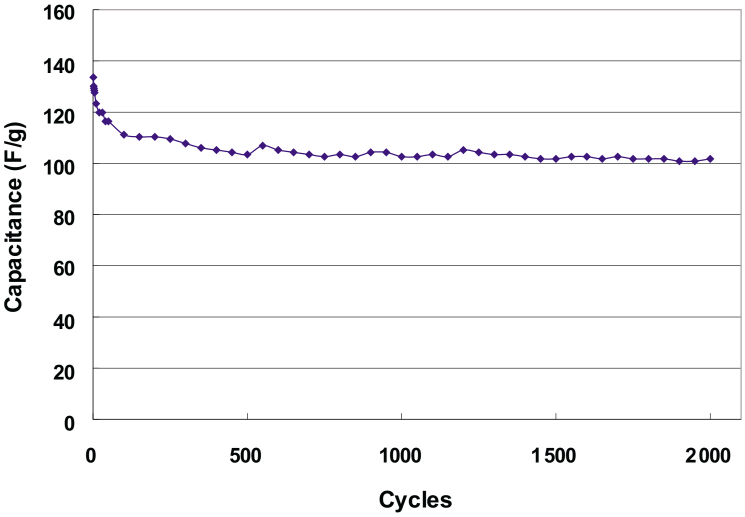

Figure 9. Cycling of two-electrode supercapacitor built from MWNTs/PPy composite. Current load of 350 mA/g.

Conclusions. The mesoporous character of nanotubular materials strongly influences their electrochemical properties, being somewhat a disadvantage in the case of lithium batteries and profitable for supercapacitors. Regarding the supercapacitors application, it is obvious that the nanotubes offer an interesting approach to reduce the ESR and to increase power. They are especially adapted as a backbone for a material with pseudocapacitance properties. Real capacitors with good electrochemical performance could be built using MWNTs/conducting polymer or MWNTs/a-MnO_2 composites. Taking into account that mainly results in three electrode cells were previously published for these materials, this in an important breakthrough. By using the two-electrode construction, it has been made possible to demonstrate that the performance of such systems is limited, due to the impossibility of controlling the potential of both electrodes. Therefore, the developments in progress of hybrid systems, with two different electrodes working in their optimal potential range, are very promising. In these systems, nanotubes are essential for the electrodes realization, not only for conductive and mechanical purpose, but also to allow a good access of ions to the active surface. Hybrid capacitors, with an activated carbon as negative electrode and MWNTs/a-MnO_2 or a MWNTs/conducting polymer composite as positive electrode, are actually demonstrating high capacitance values, while operating at a voltage of 2 V in aqueous medium [19]. Such systems allow to reach electrochemical performance comparable to organic electrolytes, without the environmental drawbacks of these media.

Acknowledgments

Authors would like to acknowledge the financial support of the Polish Ministry of Scientific Research and Information Technology (grant 4 T09B 107 24).

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