



## Review

# Carbon materials for the electrochemical storage of energy in capacitors

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Received 17 February 2000; accepted 22 July 2000

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**Abstract**

The electrochemical storage of energy in various carbon materials (activated carbons, aerogels, xerogels, nanostructures) used as capacitor electrodes is considered. Different types of capacitors with a pure electrostatic attraction and/or pseudocapacitance effects are presented. Their performance in various electrolytes is studied taking into account the different range of operating voltage (1 V for aqueous and 3 V for aprotic solutions). Trials are undertaken for estimating the role of micro and mesopores during charging the electrical double layer in both kinds of electrolytic solutions for which the electrical conductivity and the size of solvated ions are different. The effect of pseudocapacitance for maximising the total capacitance is especially documented. Carbons chemically modified by a strong oxidation treatment represent a very well defined region of pseudocapacitance properties due to the Faradaic redox reactions of their rich surface functionality. Conducting polymers (polyaniline, polypyrrole, polythiophene derivatives) and oxidised metallic particles (Ru, Mn, Co, . . . ) deposited on the carbons also participate in the enhancement of the final capacity through fast faradaic pseudocapacitance effects. Evaluation of capacitor performance by different techniques, e.g. voltammetry, impedance spectroscopy, charge/discharge characteristics is also discussed. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. Activated carbon, Carbon aerogel, Carbon nanotubes, Carbon xerogel; D. Electrochemical properties

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**1. Introduction – why carbon?**

Carbon due to different allotropes (graphite, diamond, fullerenes/nanotubes), various microtextures (more or less ordered) owing to the degree of graphitization, a rich variety of dimensionality from 0 to 3D and ability for existence under different forms (from powders to fibres, foams, fabrics and composites) represents a very attractive material for electrochemical applications, especially for the storage of energy. Carbon electrode is well polarizable, however, its electrical conductivity strongly depends on the thermal treatment, microtexture, hybridization and content of heteroatoms. Additionally, the amphoteric character of carbon allows use of the rich electrochemical

properties of this element from donor to acceptor state. Apart from it, carbon materials are environmentally friendly.

During the last years a great interest has been focused on the application of carbons as electrode materials because of their accessibility, an easy processability and relatively low cost. They are chemically stable in different solutions (from strongly acidic to basic) and able for performance in a wide range of temperatures. Already well established chemical and physical methods of activation allow to produce materials with a developed surface area and a controlled distribution of pores that determine the electrode/electrolyte interface for electrochemical applications. The possibility of using the activated carbon without binding substance, e.g. fibrous fabrics or felts, gives an additional profit from the construction point of view.

Taking into account all the mentioned characteristics, carbon as a material for the storage of energy in electrochemical capacitors seems to be extremely attractive.

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### 1.1. Capacitors and supercapacitors

During the last years, electrode materials for electrochemical capacitors (EC) have been extensively developed [1–3] due to the increasing demand for a new kind of accumulators of electrical energy with a high specific power of more than 10 kW/kg and a long durability (over  $10^6$  cycles). The main advantage of this storage device is the ability of a high dynamic of charge propagation (short-term pulse) that can be useful in the hybrid power sources for electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers and pulse laser technique. The other profits of the EC system is a possibility of full discharge, and a short-circuit between the two electrodes is also not harmful.

The typical electrochemical accumulators cannot fulfil such demands due to the physicochemical processes and electrode polarisation accompanying the conversion of chemical into electrical energy. Charges can be admitted or withdrawn from the electrodes to the external circuit when electrochemical faradaic reactions take place, by charge transfer across an interface, involving changes of oxidation state of the chemical materials of the cell. Hence, a high power and a long cycle life is not available for this kind of power sources. The energy stored in an accumulator can be expressed by the following Eq. (1) and depends on the Gibbs energy (enthalpy of formation) of the chemical substances taking part in the total redox reaction:

$$\Delta G = -nFE \quad (1)$$

Contrarily, in the electrochemical capacitors, the electrical charge is accumulated in the double layer mainly by electrostatic forces without phase transformation in the electrode materials. The stored electrical energy is based on the separation of charged species in an electrical double layer across the electrode/solution interface (Fig. 1). The maximal charge density is accumulated at the distance of outer Helmholtz plane, i.e. at the centre of electrostatically attracted solvated ions. The electrochemical capacitor contains one positive electrode with electron deficiency and the second one negative with electron excess, both electrodes being built from the same material (Fig. 2). The amount of electrical energy  $W$  accumulated in such capacitors is proportional to capacitance  $C$  and voltage  $U$  according to the formula:

$$W = 1/2CU^2 \quad (2)$$

The electrochemical withdrawing of energy from these two types of power sources differs significantly. It is clear that in a typical accumulator a charge/discharge plateau is observed for the dependence  $U = f(t)$ , and for an electrochemical capacitor we have almost a linear decay of voltage with time. As a consequence, the energy stored in the capacitor ( $1/2 qU$ ) is half that for the equivalent battery cell ( $qU$ ).

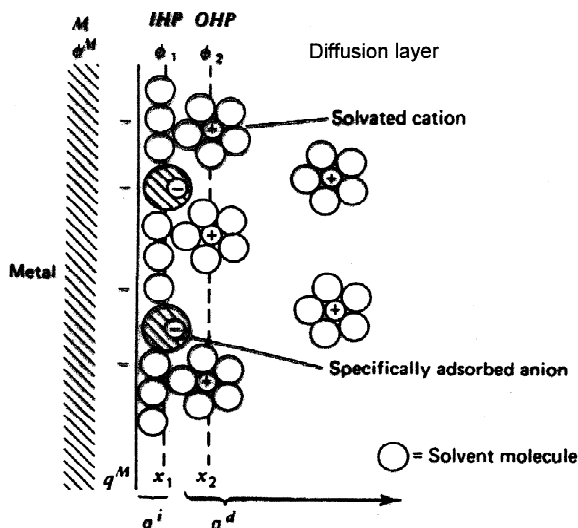


Fig. 1. Scheme of the electrical double layer.

The electrode materials in all the work voltage of the capacitor should be electrochemically inert that is the case of non-functionalized carbon. The stability of the electrolytic medium must be also carefully considered, especially in the aqueous solutions for which the maximum voltage is restricted to ca. 1 V due to the thermodynamic electrochemical window of water (1.23 V). The operating voltage of the capacitor is determined by the decomposition voltage of the electrolyte. Hence, the electrical energy accumulated in EC can be significantly enhanced by the selection of an aprotic medium where the decomposition potential of the electrolyte varies from 3 V to 5 V. Unfortunately due to the low conductivity of such a solution (20 mS/cm against 1 S/cm for water medium) this profit can be quite doubtful in the case of the high specific power demanded. Additionally for practical applications (e.g. supply of electrical car), the use of an aprotic medium can meet certain technological, economical and safety barriers. However, the possibility of reaching 3 V or

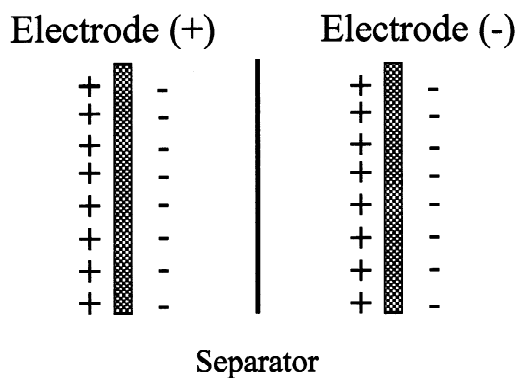


Fig. 2. Scheme of an electrochemical capacitor.

more, is still very attractive and a lot of research is performed especially for applications with a low specific power. Finally the choice of the electrolyte depends on the demanded specific power and energy values.

Presently, the development of electrochemical capacitors is connected with a seeking of optimal electrode materials able to a high, efficient accumulating of electrical energy with a simultaneous long durability. In the simplest model, an electrochemical capacitor is formed by two polarizable electrodes, a separator and the electrolytic solution (Fig. 2). The overall capacitance  $C$  is determined by the series equivalent circuit consisting of anode capacitance  $C_a$  and cathode capacitance  $C_c$  according to the equation

$$1/C = 1/C_a + 1/C_c \quad (3)$$

In the case of capacitors being built from materials with a significantly different surface, the component of smaller capacitance will contribute more in the total capacitance due to reciprocal dependence.

The electrochemical capacitors from carbon are of two types depending on the kind of accumulated energy: the electrical double layer capacitors (EDLC), where only a pure electrostatic attraction between ions and the charged surface of an electrode takes place, and supercapacitors (SC) based additionally on faradaic pseudocapacitance reactions [1,2]. The common criterion for a comparison and estimation of utilisability of electrode materials for electrochemical capacitors is the value of electrical capacitance. The amount of electrical charge accumulated by pure electrostatic forces that is typical for EDLC depends on the surface of the electrode/electrolyte interface and on an easy access of the charge carriers to this interface. The capacitance is proportional to the surface area  $S$  of the material and to the relative permittivity of the solution  $\epsilon$ , and reciprocally dependent on the thickness  $d$  of the double layer.

$$C = S\epsilon/d \quad (4)$$

In the concentrated electrolytic solutions, the charge separation is of the order of a few Å (for diluted solutions the diffusive part of double layer is ca. 1000 Å). Theoretically, the higher surface area and the concentration of electrolyte, the higher values of capacitance. In the case of carbon, the double layer capacitance is associated with the electrode/solution interface which varies with the type of carbon and its conditions of preparation and has a value of 15–50  $\mu\text{F}/\text{cm}^2$ . Taking an average value of 25  $\mu\text{F}/\text{cm}^2$  and a specific area of 1000  $\text{m}^2/\text{g}$  for carbon, the ideal attainable capacitance would be 250 F/g. The practically obtained values are of a few tens of F/g in EDLC due to the limited accessibility of carbon surface to electrolyte. The developed surface area of carbon is essentially consisting of micropores (<2 nm) often hardly or non-accessible for ions. In practice, the real surface area estimated by gas

adsorption differs significantly from the electrochemically active surface available for charged species.

Another way for increasing the capacitance values is the usage of the pseudocapacitance effects (see paragraph below) which depends on the surface functionality of carbon and/or on the presence of electroactive species, e.g. oxides of transition metals such as Ru, Ir, W, Mo, Mn, Ni, Co as well as nitrides e.g.  $\text{MoN}_x$  or conducting polymers deposited on the carbon surface [1–6]. In SC, electrosorption or redox processes can enhance the value of capacitance for the carbon material ca. 10–100 times.

However, for being competitive, modified carbons must fulfil the requirements of long cycle-life, good charge/discharge efficiency, high specific peak power, good retention of charge, low self-discharge, adequate operating voltage determining the energy and power density of the storage device.

## 2. Pseudocapacitance

Performance of a supercapacitor (or ultracapacitor) combines simultaneously two kinds of energy storage, i.e. an electrostatic attraction as in EDLC capacitors and faradaic reactions similar to processes proceeding in accumulators. Pseudocapacitance arises when, for thermodynamic reasons, the charge  $q$  required for the progression of an electrode process is a continuously changing function of potential  $U$  [1,2]. Then, the derivative  $C = dq/dU$  corresponds to a faradaic kind of capacitance. The term 'pseudo' originates from the fact that the double-layer capacitance arises from quick faradaic charge transfer reactions and not only from electrostatic charging. Pseudocapacitance effects (electrosorption of  $H$  or metal adatoms, redox reactions of electroactive species) strongly depend on the chemical affinity of carbon materials to the ions sorbed on the electrode surface.

An ideal double layer capacitance behaviour of an electrode material is expressed in the form of a rectangular shape of the voltammetry characteristics presented in Fig. 3. The sign of current is immediately reversed upon reversal of the potential sweep. In this type of energy storage, the phenomenon is purely electrostatic and current is independent on potential. On the other hand, electrode materials with pseudocapacitance properties point out a deviation from such a rectangular shape and reversible redox peaks connected with pseudofaradaic reactions are remarkable (Fig. 3). In this case the charge accumulated in the capacitor is strongly dependent on the electrode potential. The observed delay of potential during reversing the potential sweep is connected with a kinetically slow process involved during charging the pseudocapacitance.

A good example of material giving pseudocapacitance properties are conducting polymers called also synthetic metals [7,8]. They can be doped and dedoped rapidly to high charge density, hence, they can be applied as active

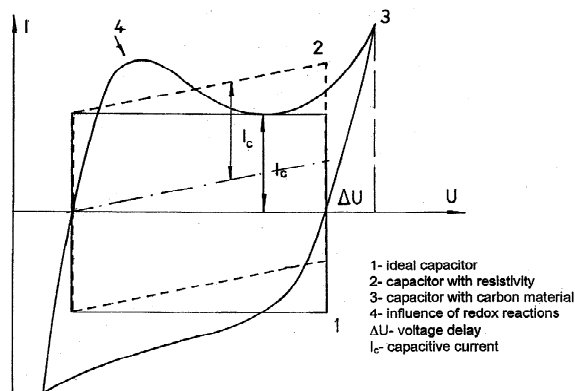


Fig. 3. Typical charge/discharge voltammetry characteristics of an electrochemical capacitor.

materials for supercapacitors. Higher energy densities can be achieved because charging occurs through the volume of material. Comparison of the charge density for conducting polymers, e.g. polyaniline (PANI), with a high surface area carbon electrode gives values of 500 C/g and 50 C/g, respectively. Taking into account the cost and compatibility of these two materials, the modification of carbon by conducting polymers for capacitor application seems to be a very attractive method [4–6].

Generally, the enhancement of specific capacitance for the carbon materials by quick faradaic reactions can be realized by the following modifications:

1. a special oxidation of carbon for increasing the surface functionality (through chemical treatment [5], electrochemical polarization [9], plasma treatment [10]).
2. the formation of carbon/conducting polymers composites by electropolymerization of a suitable monomer (aniline, pyrrole) on the carbon surface [4–6] or using a chemical method for polymerization.
3. insertion of electroactive particles of transition metals oxides such  $\text{RuO}_2$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Co}_2\text{O}_3 \dots$  into the carbon material [1,11–14].

Chemical treatment of carbons, e.g. by hot nitric acid, significantly enriches the surface functionality often with enhancing the surface area, but in some cases the resistivity can be also simultaneously increased excluding such a material from practical usage for capacitors. Electrochemical polarization gives also possibility of surface modification, however, these changes are reversible and they disappear with capacitor cycling (Fig. 4).

Modification of carbon materials by electroconducting polymers (ECPs) supplied an interesting feature of such composites [4–6]. ECPs have ability for the storage of charges and this process depends on the conditions of preparation, the state of oxidation but also on the solvent [15]. The values of specific capacitance of carbon fabrics

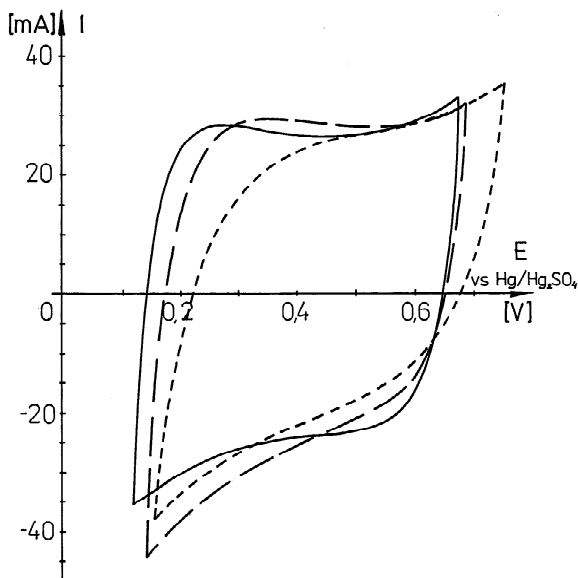
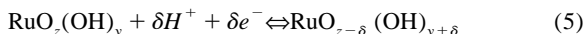


Fig. 4. Voltammetry characteristics of a capacitor from carbon fabrics; 10 M  $\text{H}_2\text{SO}_4$ , 2 mV/s; — non-modified, - - - electrochem. modified, - · - electrochem. modified after cycling [5].

modified by polyaniline can be significantly enhanced from 30 F/g to 150 F/g, however a gradual degradation of such composites takes place during cycling that aggravates the capacitor performance. The charge storage in the ECP depends on many parameters, hence, the shape of voltammograms is not stable. Fig. 5 represents the voltammetry characteristics of carbon fabrics modified by electrodeposition of polyaniline. It shows separately the various redox processes taking part on anode and cathode. Reversible reactions connected with the electrochemical behaviour of PANI are especially remarkable on the anode of capacitor.

Capacitance enhancement of carbon materials by electroactive species is extremely attractive but not always from an economical point of view. For example, carbon after modification by hydrous ruthenium oxides points out a higher value of specific capacitance [11–14] through the pseudocapacitance effect. However, the increase of capacitance is proportional to the amount of very expensive oxide. Pure  $\text{RuO}_x\text{H}_y$  is a mixed electron-proton conductor with a high specific capacitance from 720 F/g to 900 F/g [12,16].  $\text{RuO}_x\text{H}_y$  surface sites are reversibly oxidized and reduced with a simultaneous exchange of protons with the contacting solution according to the reaction



It is noteworthy that the faradaic nature of  $\text{RuO}_x$  solids is very sensitive to their degree of hydration and crystallinity [16]. For example the capacitance of amorphous

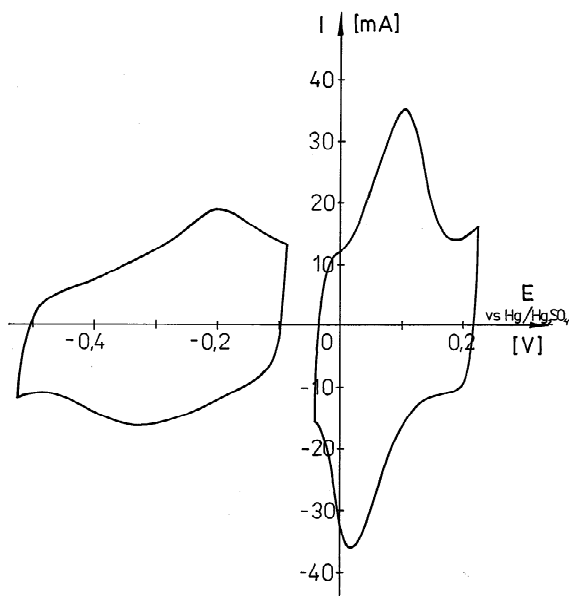


Fig. 5. Voltammetry characteristics of both electrodes of a capacitor from carbon fabric modified by polyaniline; 1 M  $\text{H}_2\text{SO}_4$ , 2 mV/s [5].

$\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$  is equal to 900 F/g whereas the highly crystalline anhydrous  $\text{RuO}_2$  presents only a low value of 0.75 F/g. Upon insertion of electroactive  $\text{RuO}_x\text{H}_y$  particles into the carbon capacitor electrodes, the rate of electrochemical protonation becomes limited by the diffusion process of the proton donating species to the electroactive sites. It is important to mention that the BET surface area of such pseudofaradaic active  $\text{RuO}_x\text{H}_y$  particles does not exceed  $100 \text{ m}^2/\text{g}$ , hence, after the deposition of oxide particles into the carbon matrix the total surface area of the material will diminish. Fig. 6 presents the effect of modification of carbon aerogel material by ruthenium oxide particles where untreated sample presents 95 F/g and after  $\text{RuO}_x$  treatment reaches 206 F/g [13]. An unique

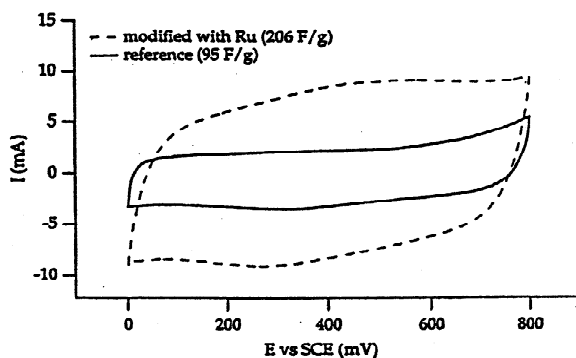


Fig. 6. Voltammetry of Ru/carbon aerogel composite electrodes for supercapacitor; 1 M  $\text{H}_2\text{SO}_4$ , 2 mV/s [13].

increase of capacitive current is observed in all the scan range of potential.

During the modification of carbon materials by electroactive species or conducting polymers, all the mentioned parameters (degree of hydration and crystallinity of transition metal oxides, possibility of degradation of ECPs, decrease of surface area of composites) should be taken into account for the preparation of optimal composite electrodes for capacitor.

### 3. Capacitor performance and determination of the capacitance values

The capacitor performance is strongly affected by all the components that can be represented in the form of the equivalent circuit. The circuit of an ECDL capacitor consists of a capacitance  $C$ , a parallel resistance  $R_F$  responsible for the self-discharge (in the presence of surface functional groups), an inductance  $L$ , and an equivalent series resistance  $R_s$  representing the internal resistance of the capacitor (Fig. 7). The key factors determining a high energy and power density are a maximum value of  $C$  and a minimum value of  $R_s$ . The time constant of the charging and discharging circuits is equal to  $R_s C$ , while the time constant of the self-discharge is equal to  $R_F C$ . In order to minimize the self-discharge,  $R_F$  should be as large as possible.

The choice of the electrolyte will determine the series resistance of the capacitor. A comparison between aqueous and organic electrolytes was done by Tanahashi et al. [17]. The organic electrolytes can operate at high voltages (up to 3 V) desirable for high energy and power densities, while the aqueous electrolytes reveal a higher capacitance and  $R_s$  lower by a factor 10. A very intensive research is devoted to seeking a polymer gel electrolyte for activated carbon electrodes, with reasonable conductivity. Gel electrolytes for capacitors based on such polymers as poly(vinylidene fluoride-hexafluoropropylene) and poly(methyl methacrylate) have been developed [6,18]. Lithium perchlorate, tetraalkylammonium or imidazolium salts were proposed as the electrolytic support [19].

Apart from the kind of electrolyte, the density of the electrode material will affect significantly the capacitor performance and such parameters as gravimetric and volumetric energy of the device. For a high volumetric

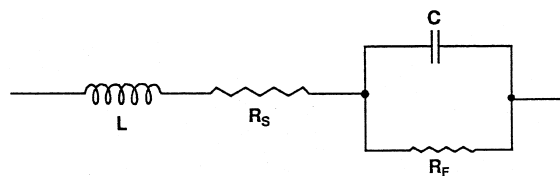


Fig. 7. Equivalent circuit of a practical capacitor.

energy of a capacitor, the carbon electrode materials should have a high density that is often in contradiction with a very developed surface area. Generally, values of capacitance of the order of 60 F/cc are demanded for practical applications. However, most of the authors express the capacitance mainly in F/g even if it would be convenient especially from a practical point of view to relate these values to F/cc.

The values of specific capacitance reported in literature are sometimes not consistent due to the different experimental methods used for their determination. The calculation of specific capacitance differs also depending on the cell used (2 or 3 electrodes). Especially, a two electrode cell represents a real supercapacitor device, however, without controlling the participation of the single electrodes in the total charge accumulation. The most common techniques for estimating the capacitance are the following: cyclic voltammetry ( $I = f(E)$ ), galvanostatic charge/discharge ( $I = \text{const.}$ ), external resistor discharge ( $R = \text{const.}$ ) and impedance spectroscopy. Each technique supplies different peculiar performance of the capacitor. For instance, the voltammetry experiments, at moderate scan rates of potential from 1 to 5 mV/s seem to be especially useful at the preliminary step to estimate the presence or lack of pseudocapacitance effects of the carbon electrode materials. The average capacitive current estimated from the dependence  $I = f(E)$  allows also to predict the optimal current for galvanostatic charge/discharge experiments. The time constant  $\tau$  expressed as  $R_s C$  gives another important characteristic of the capacitor performance. Carbon materials with an extremely developed micropore surface area will present the highest values of  $\tau$  for the charge/discharge of the capacitor.

It is important to mention that the real electroactive area of porous carbon electrodes takes part in the charging of the electrical double layer only with highly conducting electrolytes and at low frequencies. For example the full impedance response is not supplied unless the solution is enough conducting.

From the theoretical predictions and practical application it is clearly proved [1] that a capacitor built from two different materials that separately point out good characteristics will present always worse total performance.

#### 4. Activated carbons as electrodes

Among the different carbon materials, activated carbons are especially attractive as electrodes for capacitors from the economical point of view. In this case, a very developed surface area of the order of 2000 m<sup>2</sup>/g, with a controlled distribution of pores during the activation process, can be reached. Theoretically, the higher the specific surface area of an activated carbon, the higher the specific capacitance should be expected. Practically, the situation is more complicated, some activated carbons with

Table 1

Comparison of specific capacities, surface area, pore volume and average pore size of activated carbons [21]

Carbon	Specific capacity [F/g]	Specific capacity [F/cm <sup>2</sup> ]	BET [m <sup>2</sup> /g]	Pore volume [cc/g]	Pore size [Å]
M-10	55.95	0.041	1370	0.500	9.12
M-14	57.20	0.0047	1223	0.561	9.60
M-15A	78.10	0.043	1800	0.629	9.17
M-15B	55.80	0.034	1624	0.563	9.37
M-15C	63.34	0.042	1518	0.600	9.79
M-20	100.0	0.046	2130	0.709	14.73
M-30	62.9	0.024	2571	1.230	14.95
A-10	35.3	0.031	1150	0.424	–
A-20	41.20	0.020	2012	0.902	14.23
SACF-20	48.8	0.027	1839	0.699	9.74
SACF-25	27.9	0.011	2371	0.977	11.93

smaller surface area give a larger specific capacitance than those with a larger surface area (Table 1). The relationships between the BET surface area, the total pore volume, the average pore size and the pore size distribution of activated carbons and their electrochemical performance as electrodes for supercapacitors have been discussed in detail by Shi et al. [20–22].

There are few reasons for the absence of proportionality between specific capacitance and surface area: the double layer capacitance ( $\mu\text{F}/\text{cm}^2$ ) varies with different types of carbons prepared from various precursors through different processes and subsequent treatments (Table 1); the important factor is also the accessibility of micropores to aqueous solutions. Therefore, it has been concluded that since the size of a single nitrogen molecule is similar to that of hydrated  $\text{OH}^-$  or  $\text{K}^+$  ions, hence, those micropores that can adsorb nitrogen molecules at 77 K are also available for the electro-adsorption of simple hydrated ions at low concentration dependent rate [20,21]. In principle, the pores larger than 0.5 nm could be accessible electrochemically for aqueous solutions. On the other hand in aprotic medium, taking into account the size of bigger solvated ions (e.g. the order of 2 nm for  $\text{BF}_4^-$  in propylene carbonate or 5 nm for  $(\text{C}_2\text{H}_5)_4\text{N}^+$ ), the smaller, non-accessible pores will not contribute to the total double-layer capacitance of the material. Depending on the electrolytic medium, the convenient porous carbon material should be selected for a capacitor electrode.

It should be emphasised that the porous texture of carbon determines the ionic conductivity which relates to the mobility of ions inside the pores. This mobility different than in the bulk of electrolyte is responsible for the rate of electrochemical accessibility. Obviously, the movement of ions is more difficult in the small pores than in the large pores. Hence, in the equivalent circuit model, instead of one resistor, the total conductivity should be considered as a network of many resistors because the resistance distributes throughout the whole material.

As it was already mentioned, the electric conductivity of carbon materials is closely related to their morphology. The higher the surface area, the smaller the particle size, the more poor the conductivity should be. The electric conductivity which determines the flow of electrical carriers is another limiting factor for the power density of a capacitor, however it will not drastically influence the energy density. Among all the physical properties, it was also proved that the electronic properties of activated carbons affect very strongly the electrical double layer of the material [23,24].

For the practical applications, activated carbons with a large percentage of big pores are found to be more convenient as capacitor electrodes for high power supercapacitors because they can deliver high energy at high rate, although they can store less total energy. The selection of activated carbon materials for capacitor application can be helped by the impedance spectroscopy technique combined with the pore size analysis. The time of electrochemical accessibility to pores of various sizes was obtained from the fitting of impedance spectroscopy data using the transmission line equivalent circuit model [21].

Taking into account the resistance  $R$  and capacitance  $C$  of certain pores, we can obtain the time constant in seconds which indicates how fast the pores of certain size can be charged:

$$RC = (V/I)(It/V) = \tau \quad (6)$$

For example, pores with size larger than 1.1 nm, which represent 25% of the total surface of the activated carbon, can be electrochemically accessed in less than 0.1 s, while pores with about 0.6 nm representing 70% of the total surface area can only be reached for about 5 s [21]. The difference is mainly due to the change of diffusion rate of the electrolyte in the pores with different size and also due to the network connection between large and small pores.

Wettability of the carbon surface determined by the kind of surface functionality is another parameter that will also affect the capacitance properties depending on the used medium (organic or aqueous). In practice, the measurement of capacitance of porous carbon materials should be done after the complete soaking of the electrodes.

Apart from the physicochemical characteristics of carbon, as well the technological parameters such as the composition of the electrodes, i.e. the kind and amount of binding substance and the type of construction affect the final performance of the capacitor [25–33]. The conductivity of the carbon electrode plays a crucial role for the capacitance behaviour, hence, the amount of binding substance should be limited (5–10%). Carbon materials with developed surface area, in the form of powders or cloth, have been widely used in electrochemical capacitors designed for different usage, from the backup systems, hybrid supply for electrical vehicles to space applications [25–33].

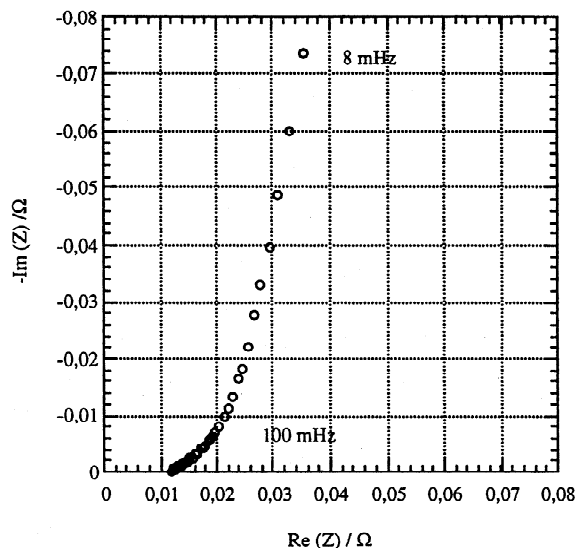


Fig. 8. Impedance spectrum of a real 20 electrodes capacitor [30].

Impedance spectroscopy is a very useful technique for the measurements of capacitance giving complementary results, e.g. the frequency dependence  $C = f(\nu)$ . Fig. 8 presents the impedance spectrum between 2 kHz and 8 mHz of a real 20 electrodes capacitor made from activated carbon [30]. At 100 mHz, the so-called knee frequency [1] appears which limits two different behaviours of the supercapacitor, i.e. above the knee frequency the real part of the impedance is frequency dependent, while below this value, the resistance changes weakly with frequency and the capacitor behaviour tends to approach that of a pure capacitance. The character of the impedance spectrum changed significantly with the number of electrodes and their thickness.

## 5. Carbon aerogels and xerogels as electrodes for capacitors

Carbon aerogels, i.e. a monolithic three-dimensional mesoporous network of carbon nanoparticles, are considered as promising materials for electrochemical capacitors. They are obtained by the pyrolysis of organic aerogels based on resorcinol-formaldehyde (RF) or phenol-furfural (PF) precursors via a sol–gel process. The gel composition (catalyst, precursor, solid ratio) and the pyrolysis temperature determine the microtexture of the final product, especially the particle size and the pore distribution. In order to simplify their production, a supercritical drying of the RF gels is favoured with a very low catalyst concentration, it means with high molar resorcinol to catalyst ( $R/C$ ) ratios. The catalyst concentration controls the particle sizes, and the degree of dilution determines the density of the material.

The advantages of carbon aerogels for capacitor application are their high surface area, low density, good electrical conductivity and the possibility of their usage without binding substances [34–40]. The special porosity of aerogels is based on the interconnection of carbon nanoparticles of the same size that is at the origin of a uniform mesoporous microtexture with a specific surface area between 500 and 900 m<sup>2</sup>/g and a high pore volume (0.4–2.6 cm<sup>3</sup>/g). The pore size distribution of the material affects strongly the nitrogen adsorption data and the electrochemical behaviour. It was proved [36] that carbon aerogels with a diameter of pores in the range from 3 to 13 nm pointed out the best voltammetry characteristics and the highest capacitance values (70–150 F/g). The carbon aerogels obtained at temperatures over 900°C showed an aggravation of specific capacitance. On the other hand, the functionalization of the carbon surface by a heat treatment at 500°C in air environment, caused an improvement of the specific capacitance through the pseudocapacitance effects [36]. After this oxidative treatment, symmetric peaks appeared on the cyclic voltammetry plots that revealed the existence of faradaic type reactions taking place on the surface. In this case the charge stored in the electrode/electrolyte interface depends on the potential of the electrodes.

The performance of carbon aerogels for supercapacitor applications depends strongly on the preparation process, i.e. the starting reactant concentration and the *R/C* ratio. Carbon aerogels with small particles have a large mesopore surface area which is easily accessible. Contrarily for the carbon aerogels with big particles, a large part of the total surface area is located in the micropores, hence not completely accessible for charging the electrical double layer.

Carbon aerogels obtained from a precursor prepared by a conventional drying, i.e. not by the supercritical method in CO<sub>2</sub>, are called xerogels [39,40]. It has been proved that the elaboration method and the final temperature of pyrolysis affect the pore structure of carbon aerogels and xerogels. Investigations demonstrate the competing effects of particle size and bulk density on the specific capacitance. Capacitance increases almost linearly with the surface area. However, for pore volumes of aerogels/xerogels over the value of 0.5 cm<sup>3</sup>/g capacitance maintains constant. The obtained values of capacitance varied from 60 F/g to 180 F/g (per single electrode of capacitor).

## 6. Carbon nanostructures for the storage of energy

Carbon nanotubes are of tremendous interest in view of a wide variety of applications from the fundamental research to applied perspectives. Apart from a potential use in molecular electronic devices, micromechanics, electron field emission, nanowires, they are also considered for some electrochemical applications such as membrane

support of catalyst for the electrocatalytic reduction of oxygen and the oxidation of methanol [41,42], storage of hydrogen [43], storage of lithium [44,45] and supercapacitors [46–50].

It has been proved [44,45] that the nanotube electrodes used for the storage of lithium in aprotic medium showed a high divergence between the characteristics for lithium insertion and extraction. The lack of potential plateau during de-insertion precludes this material from application in lithium-ion batteries, even if the amount of lithium reversibly stored reached in some cases a capacity of 600 mAh/g (the stoichiometry of LiC<sub>6</sub> in graphite is equal to 372 mAh/g). On the other hand, the linear dependence of potential versus the charge in the region from 1.5 to 3.0 V vs. Li during de-insertion using a lithium/carbon cell, proved the pseudocapacitance properties of the nanotubular material. The similar phenomenon has been observed for flaky carbon from nanocomposites [51,52]. Such observations led us to check both materials for capacitors usage [46,47,52].

The application of different types of nanotubes for building capacitors proved the high ability of this material for the accumulation of charges [46,47]. Intentionally, extremely different nanotubes with open and close central canal as well as entangled and stiff were selected as our investigated capacitor electrodes [47]. Multiwall carbon nanotubes (MWNTs) with an open central hollow were obtained by the decomposition of acetylene at 700°C, using cobalt supported on silica as catalyst. A general Transmission Electron Microscopy (TEM) view of purified carbon nanotubes obtained after elimination of the catalyst is presented in Fig. 9 and the detailed microtexture is shown in Fig. 10. The sample obtained from the same method but at 900°C was characterized by a fishbone morphology with an ill-defined central canal (Fig. 11). Both types of catalytic MWNTs have a sinuous shape and are extremely entangled; their internal diameter varied from 4 to 6 nm whereas the external diameter was from 15 to 30 nm. It is important to mention that for the purification hydrofluoric and nitric acids were used for removing silica and cobalt particles. Nitric acid treatment caused a modification of the carbon nanotubes, i.e. the formation of oxygenated surface groups, with amount of oxygen varying from 2 to 10 wt%. Diametrically different, i.e. straight and rigid nanotubes (Fig. 12) were obtained by chemical vapour deposition (CVD) of propylene at 800°C within the pores of an alumina template [53]. For these nanotubes, a wide central canal was remarkable of the order of 10 nm but only a few concentric, non-continuous graphitic layers formed the nanotube walls.

The capacitance properties of MWNTs were studied in two-electrode carbon/carbon cells. The electrodes were prepared in the form of pellets of ca. 10 mg from a mixture of carbon MWNTs (85%), acetylene black (10%) and binding substance (5% of polyvinylidene fluoride, PVDF). The accumulation of charges in the electrical double layer



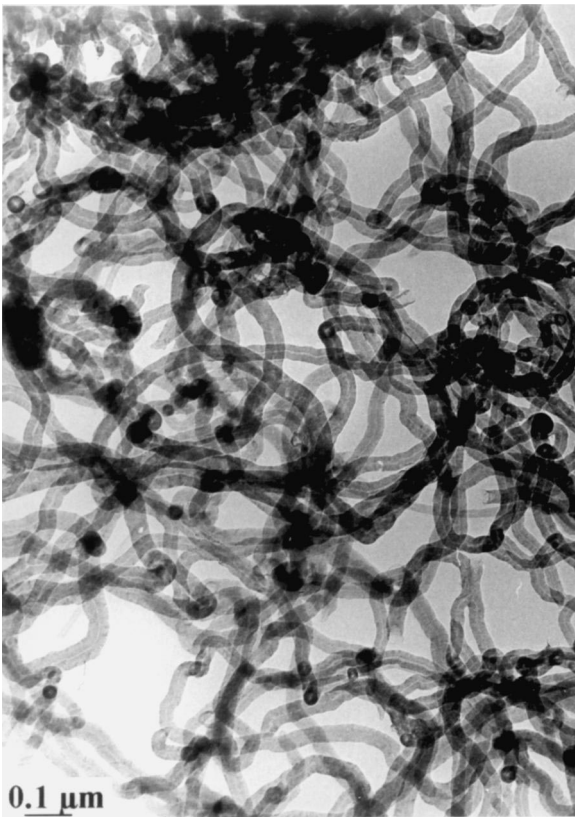


Fig. 9. General view of purified multiwalled carbon nanotubes obtained by catalytic decomposition of acetylene at 700°C [45].

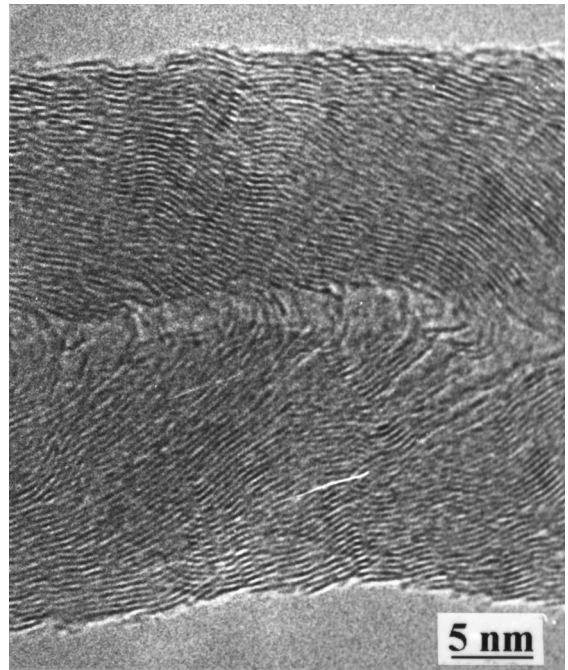


Fig. 11. TEM image of a carbon nanotube obtained at 900°C [47].

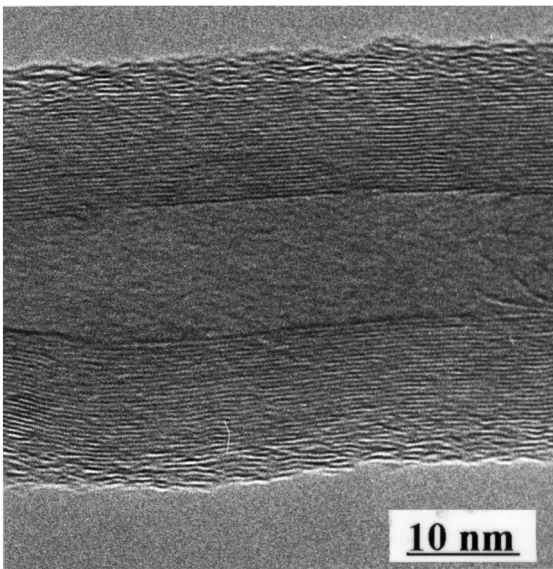


Fig. 10. TEM image of a carbon nanotube obtained at 700°C [47].

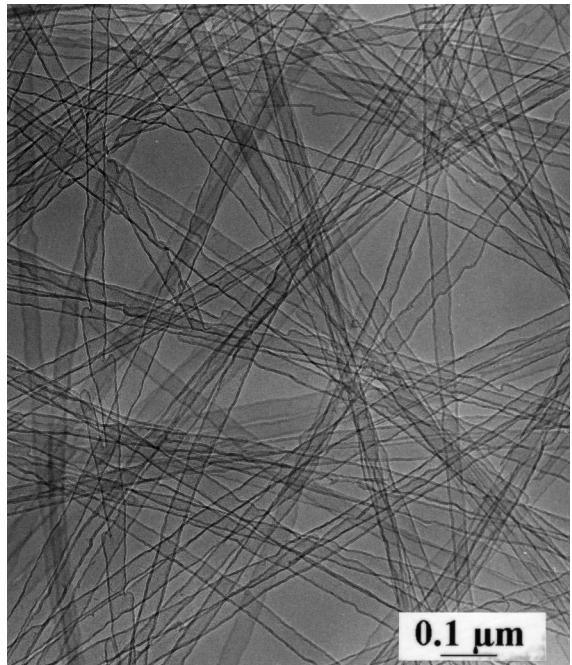


Fig. 12. General view of carbon nanotubes obtained through the decomposition of propylene at 800°C by a template method [53].

has been investigated by the voltammetry technique. An example is given in Fig. 13 for nanotubes prepared at 700°C with cobalt supported on silica. A regular, almost

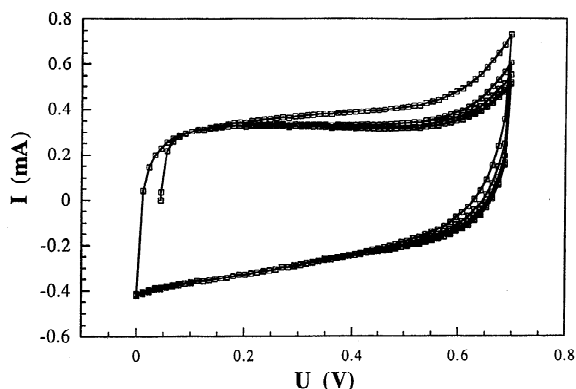


Fig. 13. Voltammetry characteristics of a capacitor built from carbon nanotubes obtained by decomposition of acetylene at 700°C on Co/SiO<sub>2</sub> 6 M KOH, 1 mV/s [54].

box-like shape of the curve has been observed from which the specific capacitance has been estimated of 70 F/g.

The values of capacitance could be enhanced from 70 to 120 F/g through an additional treatment of carbon nanotubes by nitric acid (69.5%) at 80°C for 1 h. In this case the voltammetry characteristics of the capacitor are definitively changed. Instead of a typical rectangular shape, a well remarkable region of reversible pseudofaradaic reactions is observed at ca. 0.2 V (Fig. 14). The galvanostatic charge/discharge characteristics for such modified nanotubes present a typical correct shape (Fig. 15).

These strongly oxidised nanotubes were also investigated by impedance spectroscopy technique, and measurements of capacitance in the ‘pseudo’ region (0.2 V)

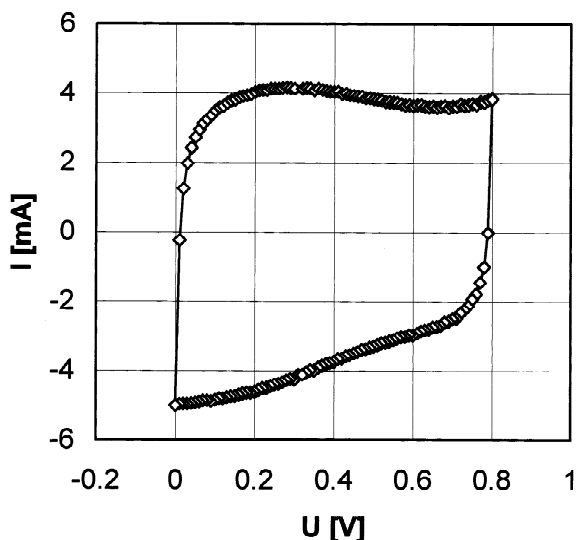
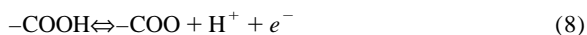
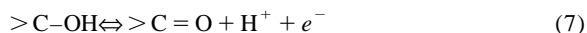


Fig. 14. Voltammetry characteristics of a supercapacitor built from carbon nanotubes obtained at 700°C and modified by 69% nitric acid; 6 M KOH, 10 mV/s [54].

presented higher charge transfer resistance than at pure capacitance region (0.6 V). It proves additionally the faradaic character of the reactions of surface groups. The values of specific capacitance evaluated only at very low frequencies (1 mHz) correlated with the values obtained by voltammetry and galvanostatic discharge that is typical for an electrochemical capacitor with an accompanying diffusion phenomenon.

The following reactions of electroactive functional surface groups could be considered:



However, it is noteworthy that this type of reactions represents only a quasi-reversible character, especially in KOH medium, and during long cycling a gradual decreasing of pseudocapacitance region was observed.

A good correlation has been found between the values of capacitance and the microtextural characteristics of the carbon nanotubes (Table 2). High values of capacitance (70 F/g) were obtained for nanotubes with entangled network and open central canal. Nitrogen adsorption/desorption isotherms supplied additional information extremely useful for the elucidation of the capacitance properties. All the nanotubes possess a mesoporous character with a type IV isotherm connected to the entanglement and/or the presence of an accessible central canal (Fig. 16). The BET surface area of the nanotubes ranges from about 100 to 410 m<sup>2</sup>/g. The higher the surface area of the nanotubular material, the higher the specific capacitance (Table 2). It seems also that the larger hysteresis between adsorption and desorption of nitrogen indicates the better capacitance properties.

The capacitance is significantly enhanced by the activation of nanotubes. A value of 97 F/g has been obtained for activated nanotubes, whereas the non-activated material supplied only ca. 1 F/g [48].

Supercapacitors have been also realized with free-standing mats [49] of catalytically grown nanotubes. The diameters of the nanotubes were very uniform with an average of ca. 8 nm and multiple layers of graphitic carbon were arranged concentrically around the tube axis.

Scanning Electron Microscopy (SEM) revealed that they were formed as bundles of 2 μm diameter and length of 20 μm. For the preparation of the nanotube sheet electrodes, such aggregates were simultaneously disassembled and functionalized by nitric acid. The functionalised nanotubes after filtration, drying and thermal crosslinking formed a rigid electrode for supercapacitors without binding substance. The surface area of the nanotube material was 430 m<sup>2</sup>/g and the measured specific capacitance reached the value up to 113 F/g. This high value can be explained by

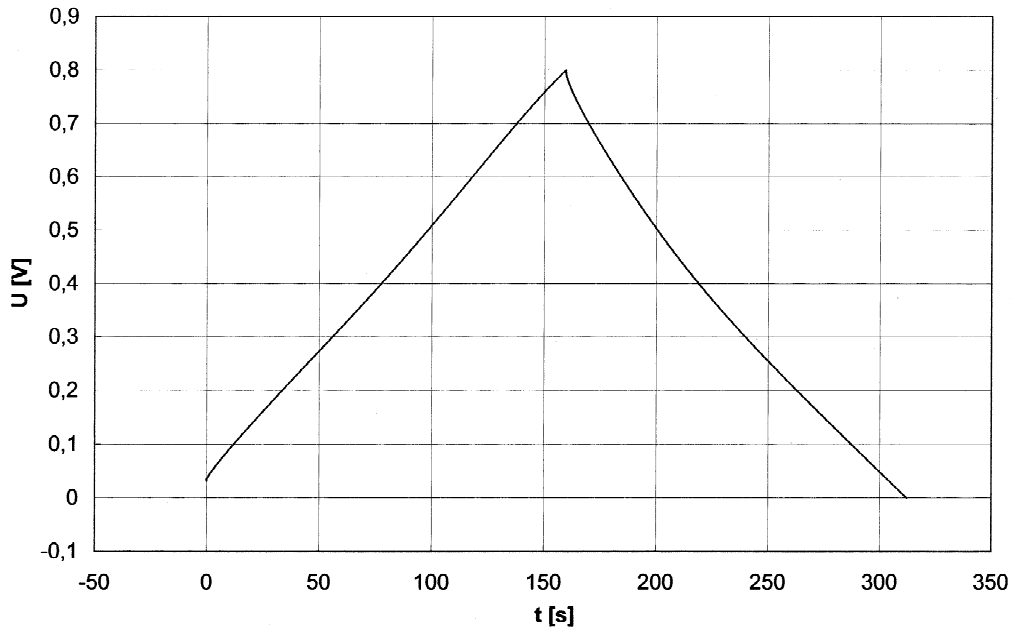


Fig. 15. Galvanostatic charge/discharge of a supercapacitor built from carbon nanotubes obtained at 700°C and modified by 69% nitric acid;  $i = 2$  mA, 6 M KOH.

Table 2

Specific capacitance of carbon nanotubes with their BET surface area, meso and micropore volumes

Sample		ACo/Si7 <sup>a</sup>	ACo/Si9 <sup>b</sup>	ACo/NaY6 <sup>c</sup>	PTemp8 <sup>d</sup>
6 M KOH	[F/g]	68	45	3	31
1 M LiPF <sub>6</sub>	[F/g]	–	36	–	17
BET	[m <sup>2</sup> /g]	411	396	128	311
$V_{\text{meso}}$	[cm <sup>3</sup> /g]	0.76	0.66	0.43	1.04
$V_{\text{micro}}$	[cm <sup>3</sup> /g]	0.003	0	0.004	0.014

<sup>a</sup> ACo/Si7: decomposition of acetylene on Co/SiO<sub>2</sub> at 700°C.

<sup>b</sup> ACo/Si9: decomposition of acetylene on Co/SiO<sub>2</sub> at 900°C.

<sup>c</sup> ACo/NaY6: decomposition of acetylene on Co/NaY at 600°C.

<sup>d</sup> PTemp8: CVD of propylene on alumina template at 800°C.

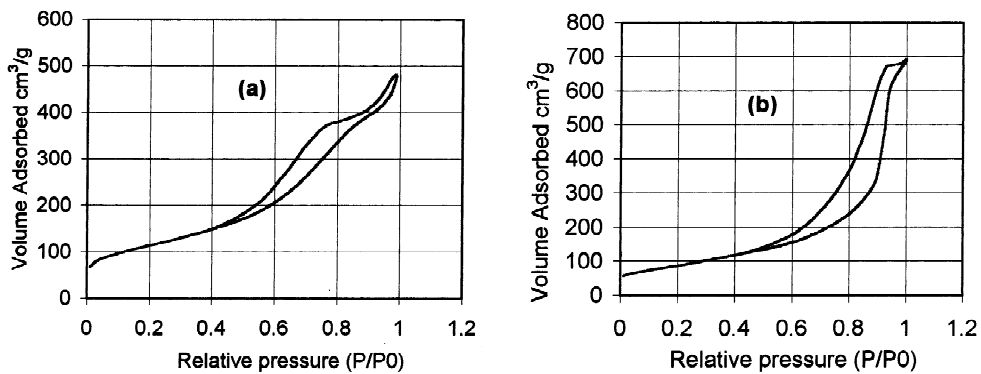


Fig. 16. Nitrogen adsorption/desorption at 77 K on multiwalled carbon nanotubes (a) MWNTs obtained at 700°C; (b) MWNTs obtained at 800°C by template method.

the unusual architecture of such a mat, i.e. an entirely mesoporous entangled nanotubes network providing an easily available electrode/electrolyte interface for forming an electrical double layer. For these carbon nanotubes, the impedance spectroscopy supplied important characteristics  $c = f(\nu)$ . The perfect accessibility of the ions to the carbon/electrolyte interphase, caused by the mesoporous network, gives a high value of capacitance at relatively high frequencies, i.e. 102 F/g at 1 Hz [49]. Additionally for the frequencies up to 1 Hz the phase angle is very close to  $-90^\circ$  what suggests that such a device built from carbon nanotubes functions like an ideal capacitor. The high value of power density  $>8$  kW/kg obtainable with carbon nanotubes proves also the exceptional properties of this material. In this case, the only hindrance for an industrial development is the cost of carbon nanotubes.

Another form of nanostructured material that has been considered for capacitor electrodes was a carbon film grown at room temperature by supersonic cluster-beam deposition [50]. The low-density granular structure of the material with a grain size of a few tens of nanometers was proved by atomic force microscopy (AFM). Aggregated clusters were at the origin of porosity on two different scales, i.e. single grains and grain network. The porosity of the grain network could be favourable for the formation of the electrical double layer. The nanostructured electrodes, with a density of  $1 \text{ g/cm}^3$ , deposited on an aluminium substrate as current collector were impregnated by a quaternary ammonium salt dissolved in propylene carbonate (PC). Hence, the nominal voltage of the capacitor in the dc regime was 2.7 V. Due to the highly accessible surface area of the film, the specific capacitance per electrode was of 75 F/g. The authors plan to develop a wide industrial production of this nanostructured material.

## 7. Conclusion

The key factors that dictate the selection of carbon materials for capacitor electrodes are the following: developed surface area, pore geometry and size distribution, average pore size, conductivity, wettability, presence of electroactive species. At the carbon surface apart from the electrostatic double layer capacitance, a significant pseudo-capacitance is often manifested. This can be due to anions chemisorption with a partial charge transfer or due to redox processes, e.g. involving quinone-hydroquinone functional groups at the carbon interface. Pseudo-capacitance effects connected with the faradaic reactions of surface groups enhance the value of capacitance. However these groups are not always stable and they often contribute to increase the self-discharge of the capacitor (in the equivalent circuit they represent the resistor  $R_F$ , connected in a parallel way). An increase of capacitance by pseudo-faradaic reactions of electroactive species such Ru, Ir, W, Mo, Mn, Co . . . oxides seems to be more efficient. Here, the seeking of the cheapest materials is actual. The

modification of carbon materials by conducting polymers is another promising way. However, this improvement of capacitance by electroactive species often decreases the total surface area and the access to the bulk of the electrode.

It is well known that highly porous activated carbons have distributed values of capacitance and resistance, hence, the evaluation of specific capacitance is more complicated owing to the spectrum of RC time constants. The micropores participate in the charge storage processes but wide pathways, i.e. mesopores are necessary for a fast accessibility of ions. Due to the presence of mesopores, a carbon material can deliver a high energy at a high rate. The formation of mesopores can be achieved by activation procedures which also introduce surface active groups. In such a case, an enhancement of capacitance is caused also due to pseudocapacitance redox reactions of oxygenated groups.

Considering their relatively moderate surface area, MWNTs are quite efficient for the accumulation of charges. The best materials are those which possess accessible mesopores formed by entanglement and by the central canal. Activation of MWNTs should allow to get higher values of capacitance through the development of micropores.

Most of the surface area of carbon materials resides in micropores which are incapable of supporting an electrical double layer. Partly the surface can be accessed by the ions migration into the pores, accompanied by an increasing electrolyte resistance. Hence, the energy stored can be withdrawn only at low frequencies or by dc technique. The performance of capacitor devices based on three-dimensional pseudo-faradaic reactions are determined by the kinetics of these reactions that depends on the activation energy of the charge transfer processes. Therefore, the rate capability for such capacitors is limited. The values of capacitance for a real capacitor are always at least twice smaller than for the single separate electrode materials. The high specific capacitance obtained for electrodes from different carbon materials opens new promising commercial applications from power back up systems to hybrid configuration for electric vehicles as well as for ignition and lighting in regular combustion engine powered vehicles, or even for very special space targets.

## Acknowledgements

The authors wish to acknowledge Dr. Krzysztof Jurewicz for fruitful discussions.

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