

Alternative Fuel Technologies

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Carbon materials for supercapacitor application†

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The most commonly used electrode materials for electrochemical capacitors are activated carbons, because they are commercially available and cheap, and they can be produced with large specific surface area. However, only the electrochemically available surface area is useful for charging the electrical double layer (EDL). The EDL formation is especially efficient in carbon pores of size below 1 nm because of the lack of space charge and a good attraction of ions along the pore walls. The pore size should ideally match the size of the ions. However, for good dynamic charge propagation, some small mesopores are useful. An asymmetric configuration, where the positive and negative electrodes are constructed from different materials, *e.g.*, activated carbon, transition metal oxide or conducting polymer, is of great interest because of an important extension of the operating voltage. In such a case, the energy as well as power is greatly increased. It appears that nanotubes are a perfect conducting additive and/or support for materials with pseudocapacitance properties, *e.g.* MnO₂, conducting polymers. Substitutional heteroatoms in the carbon network (nitrogen, oxygen) are a promising way to enhance the capacitance. Carbons obtained by one-step pyrolysis of organic precursors rich in heteroatoms (nitrogen and/or oxygen) are very interesting, because they are denser than activated carbons. The application of a novel type of electrolyte with a broad voltage window (ionic liquids) is considered, but the stability of this new generation of electrolyte during long term cycling of capacitors is not yet confirmed.

Introduction

Carbon materials are widely used for supercapacitor applications because of their low cost and versatile existing forms such as powders, fibers, felts, composites, mats, monoliths, and foils. An efficient charging of the electrical double layer requires materials with a high surface area and pores adapted to the size of ions, which is crucial for supercapacitor performance.^{1–3} Hence, activated carbons are the most often used electrode material. The pore size of carbon materials can be more or less controllable depending on the type of precursor and activation method (physical or chemical). The parameters of the activation process such as temperature, time, type of activating agent affect significantly the microporosity of the resultant carbons.^{4,5} An optimal choice of these conditions allows the amount of mesopores to be controlled to some extent. However, it will be shown that the most suitable method for controllable preparation of carbons with appropriately sized pores is the template method.^{6–8} Even though it is a relatively expensive technique, it has resulted in great progress in the development of capacitor performance. Notably, it confirms the role of small mesopores and their interconnectivity for rapid charge propagation, and also shows the significance of ultra-micropores for the accumulation of charges.^{9–13} Apart from the pure electrostatic attraction of

ions, very often the capacitance can be enhanced by the presence of heteroatoms in the carbon network. The most commonly present heteroatoms are obviously oxygen and nitrogen. It will be shown how advantageous the use of materials containing heteroatoms can be, which are at the origin of stable pseudo-Faradaic reactions.^{14–21} Another group of interesting materials for supercapacitors described in this review are nanotubes and their composites.^{22–31} It appears that nanotubes are a perfect conducting additive and/or support for materials with pseudocapacitance properties, *e.g.* transition metal oxides and, electrically conducting polymers (ECP). Special attention will be devoted to a C/C composite obtained by carbonization of a blend of carbon nanotubes with polyacrylonitrile.¹⁸ It is noteworthy that, even without activation, the composite shows interesting capacitance properties. In general, symmetric capacitors where both electrodes are built from the same material are described in the literature. However, an asymmetric configuration where the positive and negative electrodes are constituted from different materials have recently been shown to be of great interest because of a wide extension of the voltage range,^{32–34} leading to a significant enhancement of energy as well as power density.

Principle of a supercapacitor

An electrochemical capacitor, also called supercapacitor, golden capacitor or ultracapacitor, is a device able to store charges in the electrode/electrolyte interface.^{1–3} A schematic representation of porous electrodes and of the electrolytic solution is shown in Fig. 1. During the charging process, the negative

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† The HTML version of this article has been enhanced with colour images.

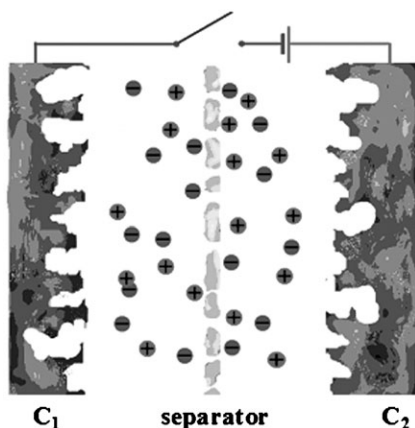


Fig. 1 Principle of an electrochemical capacitor.

plate attracts the positively charged cations, whereas the anions are accumulated in the pores of the positive electrode.

It is noteworthy that each electrode can be treated as a single capacitor of capacitance (C_1) or (C_2) with a value proportional to the surface area s of the electrode/electrolyte interface and to the electrolyte permittivity ϵ .

$$C_{dl} = \epsilon \cdot \frac{s}{d}$$

The total capacitance is controlled by the electrode with the smallest value according to the equation:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

An increase of the capacitor voltage (U) causes a significant enhancement of power (P) and energy (E) because of the following dependences (where R_S stands for the equivalent series resistance):

$$E = \frac{1}{2} CU^2 \text{ and } P = \frac{U^2}{4R_S}$$

Novel types of electrolyte for supercapacitors

Generally, in aqueous medium, the operating voltage of a capacitor does not exceed 0.8 V (even if the thermodynamic stability window of water is 1.23 V). On the other hand, an organic medium based on a salt, *e.g.* TEABF₄ (tetraethyl ammonium tetrafluoroborate) dissolved in acetonitrile (AN) allows the capacitor to be charged/discharged up to 2.0 V or 2.3 V. A further increase of capacitor voltage range can be achieved using ionic liquids (ILs).

ILs are defined as thermally stable salts synthesized by combining a bulky organic cation with different anions.^{35,36} They are generally liquid at room temperature (below 100 °C). ILs have a high thermal stability and negligible vapor pressure. They are often characterized by a high viscosity which complicates a good wetting of carbon materials with a developed microporosity. Hence, even if they permit an increase in the operating voltage, their viscosity and lower conductivity lead nonetheless to slightly reduced performance.

Fig. 2 shows a comparison of the electrochemical behavior of the same activated carbon AC (BET specific surface area of

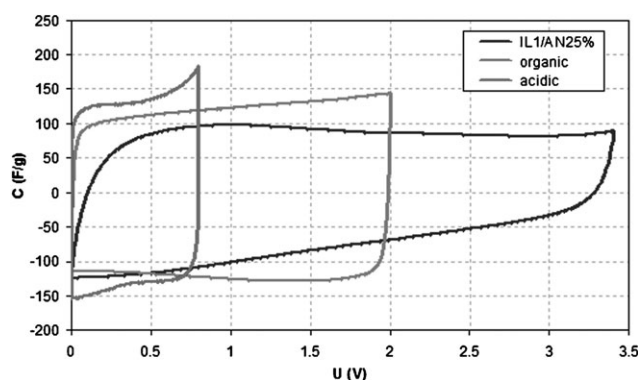


Fig. 2 Capacitance characteristics (voltammetry at 5 mV s⁻¹ scan rate) of the activated carbon AC in three electrolytic media. Reused with permission from Elzbieta Frackowiak, Grzegorz Lota and Juliusz Pernak, *Applied Physics Letters*, 2005, **86**, 164104. Copyright 2005, American Institute of Physics.³⁷

2070 m² g⁻¹ and external surface area of 374 m² g⁻¹) in three electrolytic media (1 mol L⁻¹ H₂SO₄, 1 mol L⁻¹ TEABF₄ in AN and an electrolyte prepared with an ionic liquid, IL1, based on a bulky phosphonium cation). IL1 stands for trihexyl(tetradecyl)phosphonium bis(trifluoromethyl-sulfonyl)imide.³⁷

It is clearly seen that the voltage range can be extended, especially using the IL1 solution containing 25% AN, although the voltammetry curve is worse than that of a commercial organic electrolyte. In the case of ILs, the capacitor performance is strongly affected by the type of anion and cation. For example, selecting an ethyl-methyl-imidazolium salt (EMI)⁺AlCl₄⁻ as electrolyte without any additional solvent, good capacitive characteristics can be obtained even at a high scan rate of 100 mV s⁻¹ or current load of 2 A g⁻¹. Galvanostatic charge/discharge curves of the activated carbon AC (2070 m² g⁻¹) in this IL are presented in Fig. 3.

The specific capacitance decreases only gradually from 130 F g⁻¹ to 115 F g⁻¹ for regimes varying from 100 mA g⁻¹ to 2000 mA g⁻¹.

One of the best way to overcome the viscosity of ILs and thus improve the capacitance behavior of such a system is a moderate temperature increase. Fig. 4 shows a linear dependence of the capacitance values with temperature for the same activated carbon AC (2070 m² g⁻¹) used as electrode material in a trigeminal tricationic ionic liquid, *e.g.* 1,2,3-propanetri [oxymethyl-1-(3-methylimidazolium)] bis(trifluoromethanesulfonyl)imide as electrolyte.³⁸

A significant increase (about threefold) of the capacitance values up to 140 F g⁻¹ at 75 °C is observed for the trigeminal tricationic ionic liquid whereas it gives only *ca.* 40 F g⁻¹ at room temperature. Similar successful trials have already been described by Mastragostino *et al.*³⁹ Typically, higher temperatures give rise to lower viscosity and higher conductivity, greatly improving the capacitor performance. Additionally, the less viscous IL improves wetting of the microporous carbon. On the other hand, performance of the capacitor at enhanced temperatures can be of little practical value.

It is noteworthy that ILs which are free of acetonitrile, although seen as an attractive generation of “green

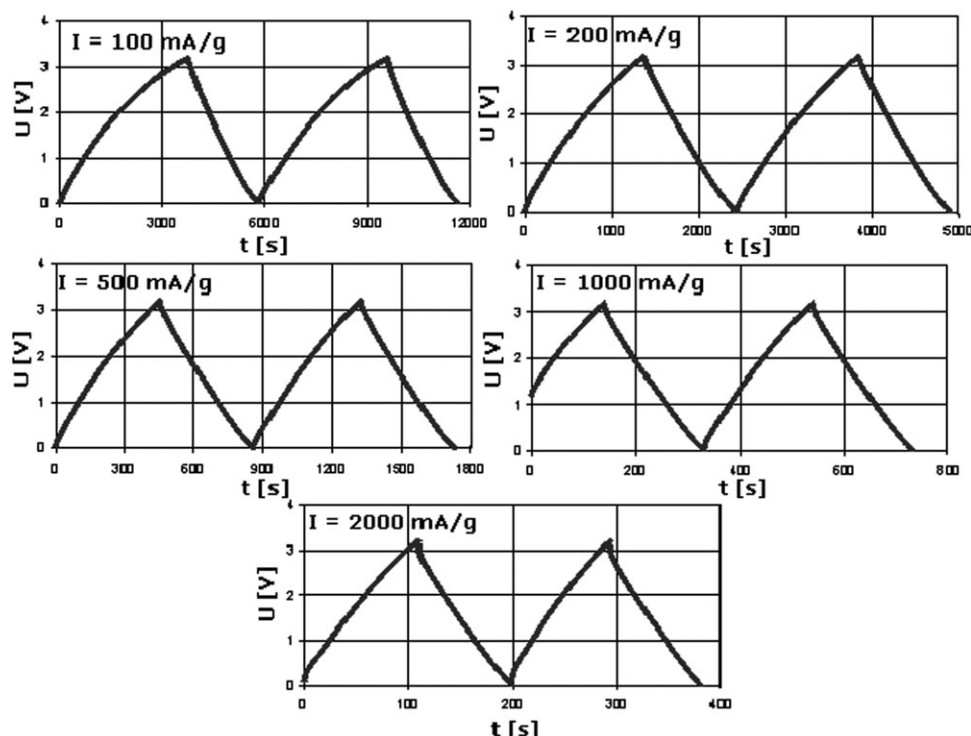


Fig. 3 Galvanostatic charge/discharge characteristics of the activated carbon AC operating in $\text{EMI}^+ \text{AlCl}_4^-$ at room temperature with current loads from 100 mA g^{-1} to 2000 mA g^{-1} .

electrolytes", are still very expensive. In addition to the high cost, the cyclability of capacitors in this novel type of electrolyte is not yet confirmed. Hence, the main electrolytic solutions considered for practical application are still aqueous and organic media based on TEABF_4 using activated carbons as capacitor electrodes.

Activated carbons as electrode materials

Generally, the larger the specific surface area of carbons, the higher the ability for charges accumulation in the electrode/electrolyte interface. It is well known that micropores (with diameters less than 2 nm) play an essential adsorption role for the formation of the electrical double layer. However, these

micropores must be electrochemically accessible for ions, therefore the presence of mesopores (diameters from 2–50 nm) is necessary for efficient charge propagation to the bulk of the electrode material, allowing the so called frequency response to be fulfilled, *i.e.* the energy to be extracted at higher frequencies (*e.g.*, 1 Hz). Hence, the availability and wettability of pores, with dimensions adapted to the size of solvated anions and cations which have to be transported from the electrolytic solution, is crucial for high capacitor performance.

For capacitor applications, activated carbons from different precursors and prepared by different activation processes have been widely used.^{40–50} It can often be found in the literature that the higher the BET specific surface area, the higher the capacitance values. However, for a wide variety of activated carbons, this trend is not perfectly followed. In fact, the narrow micropores may not contribute to the total double layer capacitance due to a sieving effect whose extent depends on the size of the electrolyte ions,^{51–53} which explains the absence of proportionality with BET surface area. This is confirmed by a recent study which shows that capacitance values as high as 175 F g^{-1} in aqueous medium can be reached using a carbon with a surface area of only $1300 \text{ m}^2 \text{ g}^{-1}$, if the pore size is optimized by chemical activation.⁵⁴ Usually, the capacitance values of activated carbons range from 100 to 200 F g^{-1} in aqueous medium, and from 50 to 150 F g^{-1} in organic medium. The larger values in aqueous electrolyte are essentially justified by a smaller size of solvated ions and a higher dielectric constant than in organic media. However, organic electrolytes are generally preferred for applications, due to their high potential window which allows more energy to be stored than in aqueous solution.

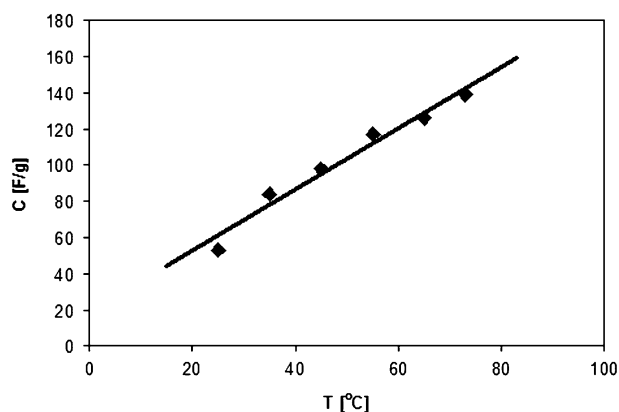


Fig. 4 Specific capacitance *versus* temperature for the activated carbon AC in trigeminal tricationic quat electrolyte.

Table 1 Effect of the pore size on the volumetric capacitance and the internal resistance of capacitors made from two carbons A and B. The pores of carbon B are smaller (an average pore diameter of 1.2 nm) than those of carbon A (1.6 nm)⁵⁵

	Negative electrode	Positive electrode	Volumetric capacity/ F cm ⁻³	Internal resistance/ mΩ
Capacitor 1	A	B	26.6	24
Capacitor 2	A	A	20.8	23
Capacitor 3	B	B	27.5	257
Capacitor 4	B	A	18.8	243

An interesting solution for optimizing the performance in an organic medium is the selection of activated carbons with pores adapted to the size of ions. Therefore, it has been suggested to use different carbons for the positive and the negative electrodes, taking into account that the ionic radii of the cations and anions are different.⁵⁵ Table 1 presents data obtained using tetraethylammonium tetrafluoroborate, (C₂H₅)₄N⁺ BF₄⁻ in acetonitrile. It demonstrates that capacitance is high and resistance is low when the pore size is smaller at the positive electrode than at the negative one.⁵⁵ Reversing the electrodes, capacitance decreases and resistance highly increases. It proves clearly that some compromise must be found between the size of ions and carbon pores.

For the preparation of attractive electrode materials for capacitors, KOH activation of cheap and available natural precursors, such as coals and pitch derived carbonaceous materials has often been used. This method efficiently develops the micropores, and allows various pore size distributions to be obtained depending on the kind of precursor and activation conditions.^{56,57} The nitrogen adsorption isotherms (Fig. 5) at

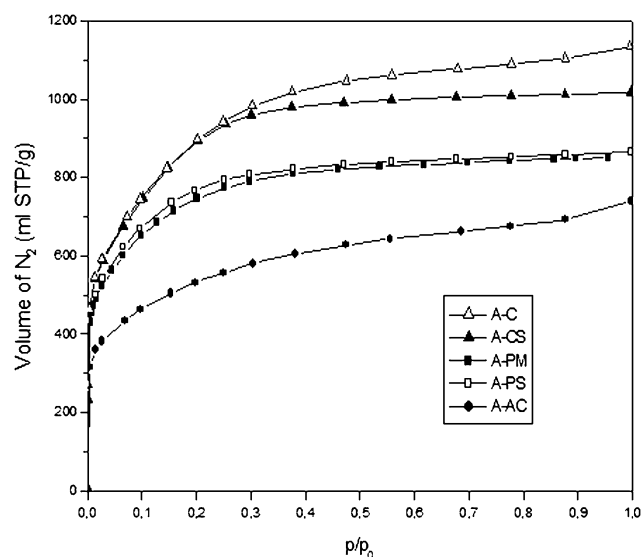


Fig. 5 Nitrogen adsorption isotherms at 77 K for KOH activated carbons (A) from various precursors. C = coal; CS = coal semi-coke; PM = pitch mesophase; PS = pitch semi-coke; AC = commercial activated carbon. Reprinted from *Electrochimica Acta*, **49**, K. Kierzek, E. Frackowiak, G. Lota, G. Gryglewicz and J. Machnikowski, Electrochemical capacitors based on highly porous carbons prepared by KOH activation, 515–523, Copyright 2004, with permission from Elsevier.⁴²

Table 2 Porosity parameters of KOH activated carbons prepared from various precursors and their capacitance values estimated by galvanostatic discharge in 1 mol L⁻¹ H₂SO₄ solution. The precursors are coal, coal semi-coke, pitch mesophase, pitch semi-coke and a commercial activated carbon for A-C, A-CS, A-PM, A-PS, A-AC, respectively⁴²

Sample	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{DR}}/\text{cm}^3 \text{g}^{-1}$	Capacitance/ F g ⁻¹	Specific capacitance/ $\mu\text{F cm}^{-2}$
A-C	3150	0.951	312	9.9
A-CS	3190	0.936	223	7.0
A-PM	2660	0.839	294	11.0
A-PS	2750	0.859	261	9.5
A-AC	1900	0.609	198	10.4

77 K of activated carbons obtained from coal (C), coal semi-coke (CS), pitch semi-coke (PS), pitch mesophase (PM) and a commercial activated carbon (AC), using potassium hydroxide and carbon in a 4 : 1 ratio, reveal that a wide distribution of micropores can be obtained by this method.⁴² A gradual step of the isotherm at low relative pressure ($p/p_0 < 0.3$) is the best proof for the existence of various sizes of micropores. The detailed porous characteristics for this series of activated carbons together with their average capacitance values in 1 mol L⁻¹ H₂SO₄ medium evaluated by three electrochemical techniques are shown in Table 2 and an example of galvanostatic charge/discharge curves is presented in Fig. 6.

In general, the results obtained on these kinds of activated carbons, in both organic and aqueous electrolyte, confirm that capacitance is not directly related to the BET specific surface area.^{41–43} Considering samples of comparable specific surface area, the wider the micropore size distribution, the higher the capacitance. Additionally, the existence of some mesopores favors the accessibility of narrow micropores by the electrolytic solution. It has also been shown that some large values of capacitance obtained with KOH activated carbons are related with important surface functionality. The presence of a large amount of oxygenated groups can be advantageous, either because they improve the wettability on the carbon surface or

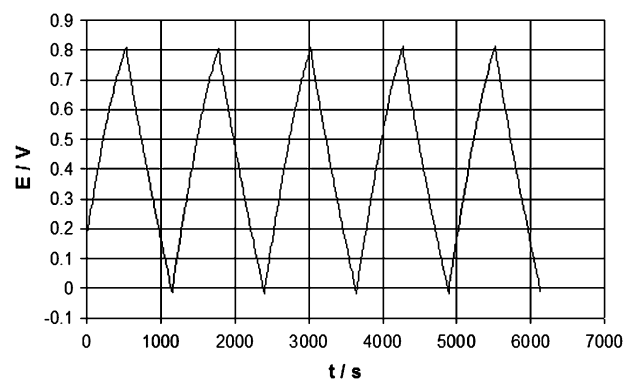


Fig. 6 Galvanostatic charge/discharge in 1 mol L⁻¹ H₂SO₄ of a supercapacitor built from the carbon A-PM obtained by KOH activation of pitch mesophase. $I = 2 \text{ mA}$. Reprinted from *Electrochimica Acta*, **49**, K. Kierzek, E. Frackowiak, G. Lota, G. Gryglewicz and J. Machnikowski, Electrochemical capacitors based on highly porous carbons prepared by KOH activation, 515–523, Copyright 2004, with permission from Elsevier.⁴²

they contribute to an additional pseudocapacitance. Finally, the microtextural/structural ordering of the activated carbon may also affect its electrochemical performance.⁴² For example, the high value of capacitance observed in Table 2 for the sample A-PM probably results from its good electrical conductivity directly connected with the precursor. One can also suspect that pores of well adapted size are produced as a consequence of potassium intercalation during KOH activation. All these contributions help explain why, even for materials obtained under identical conditions, the specific capacitances range from 7 to 11 $\mu\text{F cm}^{-2}$ (Table 2).

A typical galvanostatic charge–discharge profile, with a correct triangular shape and without significant ohmic drop, is shown in Fig. 6 for the activated carbon formed from pitch mesophase A-PM. Good cycling behaviour was also shown for this carbon over more than 3000 cycles.

An interesting study has recently been performed using a series of materials from a bituminous coal with progressively changing nanotextural characteristics.⁵⁸ The heat-treatment of coal was performed from 520 to 1000 $^{\circ}\text{C}$, followed by KOH activation at 700 $^{\circ}\text{C}$ or 800 $^{\circ}\text{C}$. For both series of activated carbons, the temperature of precursor heat treatment strongly affects the porosity development and the pore size distribution. The total micropore volume and the average pore diameter (L_o) decreases as the carbonization temperature increases. However, the volume of ultramicropores (<0.7 nm) is practically constant. The amount of oxygen functionalisation depends on the activation temperature. The ACs belonging to the series activated at 700 $^{\circ}\text{C}$ possess a higher amount of oxygen than those activated at 800 $^{\circ}\text{C}$. The relationship

between the pore size or surface chemistry and the capacitance performance in different electrolytes was investigated. For both series, the gravimetric capacitance in KOH electrolyte is almost proportional to S_{BET} , suggesting that the capacitance is controlled primarily by the surface area (Fig. 7). However, as far as the specific surface capacitance is considered, the highest values are observed for the low surface area and narrow pore carbons, *i.e.* samples treated at a high temperature, confirming the important role of ultramicropores. Additionally, higher gravimetric (and surface) capacitance values were observed for the activated carbons prepared at 700 $^{\circ}\text{C}$, rather than at 800 $^{\circ}\text{C}$, despite a lower BET surface area in the former material. It was shown that the higher oxygen content obtained when the activation is performed at 700 $^{\circ}\text{C}$ leads to a higher possibility of reversible redox reactions which can give rise to an additional pseudo-Faradaic contribution, especially at the negative electrode.

Analysis of the electrochemical performance in different electrolytes shows that an adequate pore size is more important than a high surface area for obtaining high values of capacitance. Pore filling seems to be optimal when the pore size is close to 0.7 nm and 0.8 nm in aqueous and organic medium, respectively. The saturation of gravimetric capacitance, observed in all the electrolytic media for the high surface area materials, is related to the increase of the average pore width L_o (Fig. 8). Although the pore volume of these carbons is very high, their pores are too wide for efficient participation in the formation of the double layer.

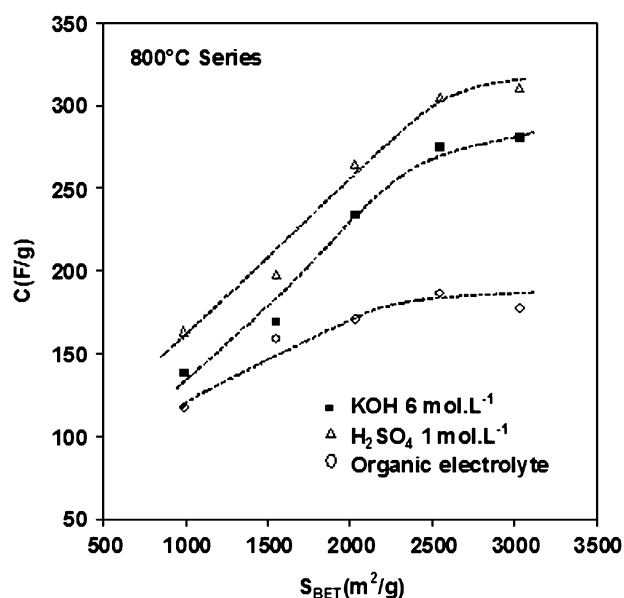


Fig. 7 Gravimetric capacitance in aqueous (6 mol L^{-1} KOH, 1 mol L^{-1} H_2SO_4) and organic (1 mol L^{-1} TEABF₄ in AN) media for the carbons activated at 800 $^{\circ}\text{C}$ vs. the BET surface area. Galvanostatic charge/discharge at 100 mA g^{-1} . Reprinted from *Carbon*, 44, E. Raymundo-Piñero, K. Kierzek, J. Machnikowski and F. Béguin, Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes, 2498–2507, Copyright 2006, with permission from Elsevier.⁵⁸

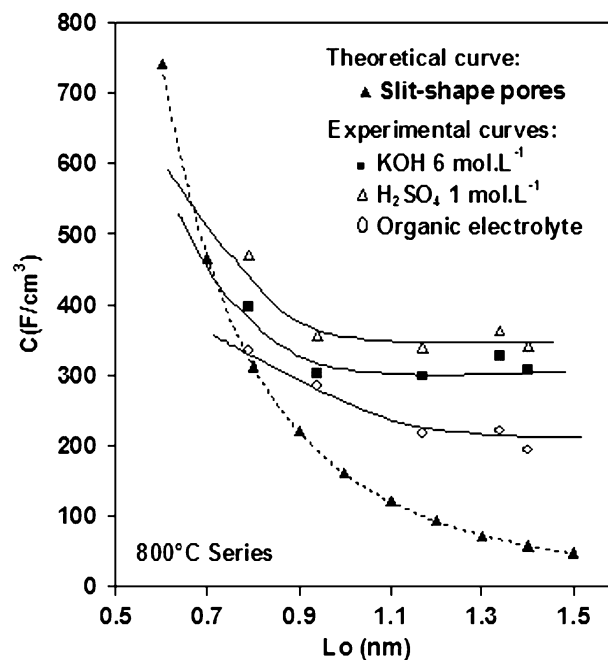


Fig. 8 Relation between the volumetric capacitance (theoretical and experimental) and the pore size in aqueous or organic medium for the 800 $^{\circ}\text{C}$ series activated carbons. Reprinted from *Carbon*, 44, E. Raymundo-Piñero, K. Kierzek, J. Machnikowski and F. Béguin, Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes, 2498–2507, Copyright 2006, with permission from Elsevier.⁵⁸

A significant increase in carbon capacitance has also been shown for pore sizes less than 1 nm using carbide-derived carbons.⁵⁹ This study focused on the pore size effect of carbon (pores from 0.6 to 2.25 nm) on charge storage in an electrolyte consisting of a 1.5 mol L⁻¹ solution of TEABF₄ in acetonitrile. A distortion of the solvation shells in pores below 1 nm was suggested that allows close approach of the ion center to the electrode surface. Pores with diameter close to the ion size were the most efficient, hence, an anomalous capacitance increase in extremely narrow pores (ultramicropores) was observed.

Apart from the kinetics parameters connected with the pore size distribution, the electrical conductivity of the carbon electrode mentioned above is another limiting factor of capacitor performance, especially power density.⁶⁰ The conductivity is strictly related to the porous texture of the material. Generally, higher porosity leads to poorer electrical conductivity. The conductivity of activated carbons varies from few tens of mS cm⁻¹ up to 100 mS cm⁻¹ depending on the kind of material.⁶¹ Hence, the addition of a conducting agent to the electrode material has crucial consequences on the electrochemical performance.

Apart from the gravimetric capacity, for practical application in all the energy sources, the volumetric value is of great importance. Hence, recent studies of carbon materials prepared without activation are of special interest because they provide materials of high density. For example, heat treatment of polyvinylidene chloride (PVDC) gives a carbon with a specific surface area of 700 m² g⁻¹,^{62–64} which provides for 30 nm size crystallites a high gravimetric specific capacitance of 370 F g⁻¹ when using a very low current density of 1 mA cm⁻². This material has a particularly narrow pore size distribution with a maximum pore diameter of 0.9 nm. This range of pore size, close to the size of solvated SO₄²⁻ ions⁶³ should be optimal for high electroadsorption because of the strong interactions of ions with the pore walls.

Microporous carbon nanospheres aggregates (MCNS) with a specific surface area as low as 245 m² g⁻¹, were prepared through the precipitation of an aromatic isotropic pitch in water without activation.⁶⁵ They supply a gravimetric capacitance of 154 F g⁻¹.

Due to their low porosity and a high density, both carbons possess a high capacitance per surface area (40–60 μF cm⁻² in comparison to 10–20 μF cm⁻² for activated carbons). This results in high volumetric capacitance, which offers another important advantage for supercapacitor applications, especially for design of highly compact electric power sources of high energy and power density.

In the MCNS, the microporous nanospheres are interlinked to form a three-dimensional mesoporous network. Their exceptional performance could also be related to the presence of mesopores which provide a rapid mass transport of ions within the electrode, facilitating the charging and discharging of the double layer. This effect has already been considered when studying activated carbons, whose surface capacitance was found to increase with the mesopore content. The optimal proportion of mesopores for using activated carbons in EDLCs was found to be between 20 and 50%.⁶⁶

Attractive materials of high density can also be obtained by one-step carbonization of biopolymers, *e.g.* sodium alginate at

600 °C under argon flow without any additional activation process.¹⁹ The carbonized material is moderately microporous ($S_{\text{BET}} = 273 \text{ m}^2 \text{ g}^{-1}$) but contains 15 at% oxygen in the carbon framework. Even if the specific surface area of this carbon is low, the capacitance in 1 mol L⁻¹ H₂SO₄ electrolyte reaches 200 F g⁻¹. Voltammetry curves of this material in a three electrode cell show reversible humps at around -0.1 V and 0.0 V vs. Hg/Hg₂SO₄.¹⁹ It is well known that peaks at such positions are connected with electrochemical reactions of oxygen surface functionalities such as the quinone/hydroquinone pair.⁶⁷ Lately, it has been shown that pyrone-like structures (combinations of non-neighboring carbonyl and ether oxygen atoms at the edge of the graphene layers) can effectively accept two protons and two electrons in the same range of electrochemical potential as the quinone/hydroquinone pair.⁶⁸ Consequently in the carbon obtained from sodium alginate, the high value of capacitance is related with charge transfer reactions on the quinone, phenol and ether groups.¹⁹ Apart from an attractive gravimetric capacitance, this weakly porous material has a high density and a high electrical conductivity, that allows a volumetric capacitance higher than that of typical activated carbons, and the capacitors can be charged at high regimes without any conductivity additive in the electrodes.¹⁹

In conclusion, the ultramicropores and micropores play an essential role for ion adsorption whereas the small mesopores are necessary for their rapid transportation to the bulk of the material. An optimal performance is expected with a carbon of high surface area with preferably narrow pores below 1 nm and well-balanced micro/mesoporosity. Hence, a strict control of the carbonization and activation processes is necessary for preparing optimized carbon materials. Even if the conventional carbons are characterized by a low cost and a large specific surface area, their EDLC application is rather limited, because their pore size has a wide distribution and the pores are randomly connected, limiting both charge storage capacity and rate capability. Closed or isolated pores may not be wetted by the electrolyte and an irregular pore connection makes ionic motion difficult. Hence, porous carbons should be designed with micropores of narrow pore size (to supply high capacitance values) interconnected with a regular network of small mesopores to assure a good charge propagation.

It must be pointed out that before backing carbon materials definitively, long-term capacitor performance should be investigated. In order to fulfil practical demand, only carbons with a small RC constant, low leakage current and limited self-discharge should be selected. Important research work performed recently, especially by the companies developing supercapacitors, seems to indicate that impurities, *e.g.* traces of water even at low level, or the presence of oxygenated acidic functional groups on carbon, may strongly affect the calendar life of these devices.

Templated carbons for capacitor applications

Charge storage and rate capability are strongly limited if the pores are randomly connected. Therefore, high surface area carbon materials containing regularly interconnected micro and mesopores are highly desirable for EDLCs electrodes.

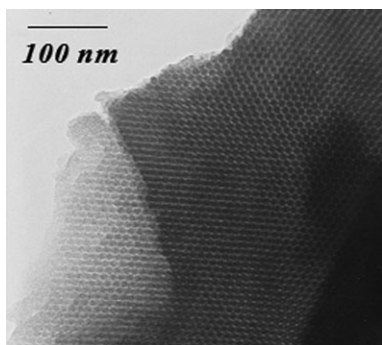


Fig. 9 TEM image of a template carbon prepared using SBA-15 silica as template and pitch as carbon source. Reprinted from *Carbon*, **43**, C. Vix-Guterl, E. Frackowiak, K. Jurewicz, M. Friebe, J. Parmentier and F. Béguin, Electrochemical energy storage in ordered porous carbon materials, 1293–1302, Copyright 2005, with permission from Elsevier.¹²

Recently many groups have synthesized ordered mesoporous silica, which can then be used as a template for the preparation of carbons with controlled pore sizes,^{69–72} meeting the above mentioned capacitor requirements. The templates are meso-structured silicas such as MCM48, MCM41, SBA15, whereas the carbon source is a liquid or gas phase, *e.g.*, a sucrose solution, polyfurfuryl alcohol, propylene or pitch.^{12,73–75} After its deposition inside the pores of the template, the carbon precursor is carbonized at temperatures close to 800 °C. The last step is the removal of the silica template by dissolution in hydrofluoric acid. An example of mesoporous material with a highly ordered structure obtained from SBA-15 silica and pitch is shown in Fig. 9.

In an attempt to correlate the electrochemical performance of template carbons with their nanotextural parameters, a perfect linear relationship has been found between the capacitance values in aqueous or organic media and the micropore volume determined by CO₂ adsorption at 273 K (Fig. 10).¹² It clearly proves that, with these kinds of porous carbons, the ions are essentially trapped in ultramicropores, *i.e.* pores with

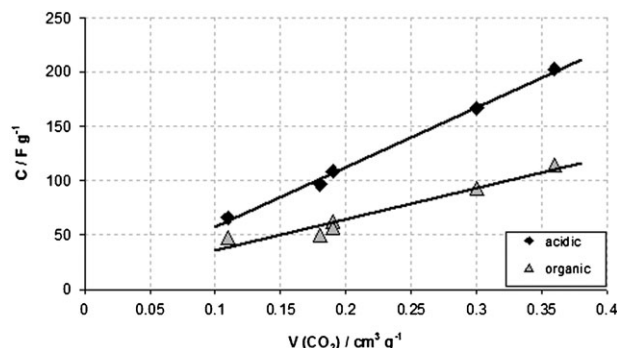


Fig. 10 Capacitance values in aqueous and organic media of the carbons synthesized with different carbon precursors and mesoporous silica matrices. Reprinted from *Carbon*, **43**, C. Vix-Guterl, E. Frackowiak, K. Jurewicz, M. Friebe, J. Parmentier and F. Béguin, Electrochemical energy storage in ordered porous carbon materials, 1293–1302, Copyright 2005, with permission from Elsevier.¹²

size below 0.7 nm. Comparing the measured value of capacitance in aqueous solution with the available volume of ultramicropores shows that most of them take part in trapping non-solvated ions in the electrical double layer. In these template carbons, micro and mesopores are perfectly interconnected, mesopores being the former walls of the silica matrix, whereas the carbonaceous walls are microporous. Under the application of an electrical polarization, the solvated ions easily diffuse into the mesopores, before becoming trapped as non-solvated in ultramicropores. In a typical microporous activated carbon, the situation is completely different. The pathway of solvated ions to reach the active surface is very tortuous and long, with several bottlenecks (gates). Therefore, the limiting pore size in this case is probably higher than the size of the pores where the ions are finally accumulated. Templated carbons, in spite of their difficulty of preparation and relatively high cost, are certainly a good material for supplying important information about pore size effects on the electrical double layer charging. The micro-textural data together with the capacitance performance for aqueous and organic media are reported in Table 3 for a series of template carbons prepared using MCM48 and SBA15.

Nanotubes and their composites for supercapacitors

Carbon nanotubes (CNTs), due to their unique morphology and extended graphitic layers, are characterized by exceptional conducting and mechanical properties which allow them to be used directly as three dimensional supports for active materials. With nanotubes, the percolation of the active particles is more efficient than with the traditional carbon blacks which are generally used for the manufacture of electrodes.³¹ On the other hand, the open mesoporous network formed by the entanglement of nanotubes allows the ions to diffuse easily 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. Finally, since the nanotubular materials are characterized by a high resiliency, the composite electrodes can easily adapt to the volumetric changes during charge and discharge, that improves drastically the cycling performance. For all these reasons, composites incorporating a nanotubular backbone coated by an active phase with pseudo-capacitive properties represent an important breakthrough for developing a new generation of supercapacitors.

Materials with pseudo-capacitance properties, such as oxides^{76,77} or electronically conducting polymers (ECPs)^{78,79} might be a promising alternative for the development of high performance supercapacitors. However, in most reports, a very thin layer of the active material coats a metallic current collector—very often platinum—that is far from the requirements for an industrial application. Moreover, swelling and shrinkage of ECPs may occur during doping/dedoping of the active film, that leads to mechanical degradation of the electrode and fading of the electrochemical performance during cycling. Adding carbon, especially carbon nanotubes, is the most effective solution which has been proposed to improve the mechanical and electrochemical properties of electrodes based on pseudo-capacitance materials.^{27–32}

Table 3 Characteristics of template carbons used as electrodes in supercapacitors. TSA: Total surface area determined by N_2 adsorption (BET method); $V(N_2)$ and $V(CO_2)$: micropore volumes calculated by the application of the Dubinin–Radushkevitch equation to N_2 adsorption at 77 K and CO_2 adsorption at 273 K; Pore size determined according to the BJH method—Maximum value of the BJH pore size distribution peak calculated from the adsorption branch of the N_2 isotherm; Capacitance values determined in 1 mol L^{-1} H_2SO_4 and 1.4 mol L^{-1} TEABF₄ in acetonitrile.¹²

Materials	TSA/m ² g ⁻¹	Elemental composition	$V(N_2)/cm^3$ g ⁻¹	$V(CO_2)/cm^3$ g ⁻¹	Pore size/nm	Capacitance/F g ⁻¹	
						in H_2SO_4	in TEABF ₄
CPr48	850	C ₁₀ H _{1.5} O _{0.1}	0.25	0.19	3.7	109	62
CS48	2000	C ₁₀ H _{1.9} O _{0.4}	0.58	0.36	2.7	202	115
CP48	1300	C ₁₀ H _{1.4} O _{0.25}	0.29	0.18	2.4	96	50
CPr15	713	C ₁₀ H _{1.3} O _{0.1}	0.21	0.11	3.4	66	48
CS15	1470	C ₁₀ H _{1.9} O _{0.4}	0.45	0.30	3.1	167	93
CP15	923	C ₁₀ H _{1.0} O _{0.2}	0.25	0.19	2.8	87	57

For the preparation of CNT composites with ECPs, the chemical or electrochemical polymerization of the monomer, *e.g.*, pyrrole, aniline, on the nanotubular materials was applied. The TEM micrograph presented in Fig. 11 for a material prepared by PPy electrochemical deposition shows a very uniform polymer coating.⁸⁰ Coating with a thin layer of polypyrrole has been achieved on MWNTs,^{24,25,80,81} well-aligned MWNTs⁸² and single wall nanotubes (SWNTs).⁸³ When MWNTs are oxidized, their surface is covered with oxygen-containing groups, which can be used as anionic dopants of a PPy film electrodeposited on the MWNTs.⁸⁴ These films are notably less brittle and more adhesive to the electrode than those formed using an aqueous electrolyte as a source of counter ion. The electrochemical behaviour of ECP/CNT composites has been studied either in two or three-electrode cells. A comparison of the redox performance of PPy films on aligned MWNTs and on flat Ti and Pt surfaces, shows a noticeable improvement for the case of the composites with MWNTs due to the high accessible surface area of the carbon nanotubes in the aligned arrays.⁸² By contrast, the results found with SWNT/PPy nanocomposites⁸³ are probably of limited application because: (1) the nickel foam used as current collector supplies an additional capacity in the alkaline solution used for the study; (2) PPy degrades quickly in alkaline solution. With the electrochemically obtained MWNTs/polypyrrole (PPy) composite, the values of capacitance reach *ca.* 170 F g⁻¹ with a good cyclic performance over 2000 cycles.³⁰

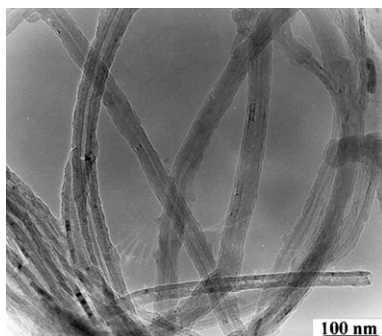


Fig. 11 TEM image of a PPy/nanotube composite obtained by an electrochemical method. E. Frackowiak, K. Jurewicz and F. Béguin, *Pol. J. Chem.*, 2004, **78**, 1345 – Reproduced by permission of the Polish Chemical Society.⁸⁰

It has been shown that the values of capacitance for the composites with polyaniline (PANI) and PPy strongly depend on the cell construction.⁸⁵ With chemically deposited ECPs, extremely high values of specific capacitance can be found—from 250 to 1100 F g⁻¹—using a three electrode cell, whereas smaller values of 190 F g⁻¹ for MWNTs/PPy and 360 F g⁻¹ for MWNTs/PANI have been measured in a two electrode cell. It highlights the fact that only two-electrode cells allow the material performance to be well estimated in electrochemical capacitors. The applied voltage was found to be the key factor influencing the specific capacitance of ECPs based nanocomposites. Generally, it cannot exceed 0.6–0.8V due to oxygen evolution in the positive range of potentials and switching to an insulating state in the negative values.⁸⁵ The high capacitances found with the MWNT/ECP composites are due to the unique property of the entangled nanotubes which supply a perfect three-dimensional volumetric charge distribution and a highly accessible electrode/electrolyte interface. Comparing the results of the two coating techniques, the non-homogeneous PPy layer deposited chemically is more porous and less compact than that electrochemically deposited. Consequently, the diffusion of ions proceeds more easily, giving a better efficiency for charge storage.⁸⁵

As mentioned previously, carbon nanotubes can also be a perfect support for cheap transition metal oxides of poor

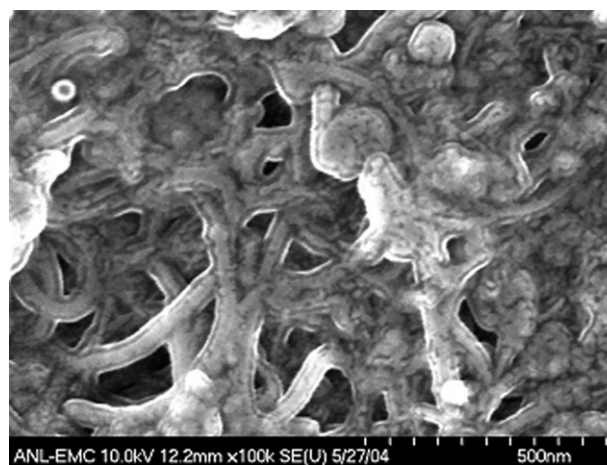


Fig. 12 SEM image of a a -MnO₂/MWNT composite containing 15 wt% of nanotubes (courtesy of M. Thackeray, Argonne National Laboratory, USA).

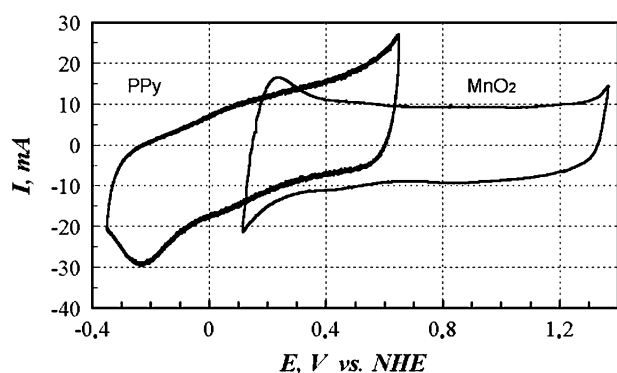


Fig. 13 Voltammetry characteristics of PPy/nanotube and MnO₂/nanotube composites in a three electrode system; 2 mol L⁻¹ KNO₃; scan rate of 10 mV s⁻¹.

electrical conductivity, such as amorphous manganese oxide (*a*-MnO₂ · *n*H₂O).^{31,86} The *a*-MnO₂/MWNT composite can be prepared by precipitation of *a*-MnO₂ from a KMnO₄ + Mn(OAc)₂ · 4H₂O mixture which contains a predetermined amount of carbon nanotubes. The SEM image presented in Fig. 12 for a *a*-MnO₂/MWNT composite containing 15 wt% of nanotubes shows a remarkable template effect of the entangled nanotubes framework. Consequently, the composite electrodes have a good resiliency, and their porosity is high enough to favor the access of ions to the bulk of the active material.

The *a*-MnO₂/MWNT has a capacitance of 140 F g⁻¹ with good cyclability and high dynamic of charge propagation. However, the voltage window of MnO₂ based capacitors is limited to 0.6 V, due to the irreversible conversion of Mn(IV) to Mn(II) at the negative electrode and Mn(IV) to Mn(VII) at the positive one.^{31,86} In order to circumvent this drawback, an asymmetric configuration has been proposed, where the positive electrode consists of *a*-MnO₂ and the negative is built from activated carbon.^{32,33,86} When the *a*-MnO₂/MWNT composite is used as the positive electrode, the supercapacitor demonstrates perfectly rectangular voltammograms and it can be operated up to 2 V in aqueous medium with an extremely good cyclability.⁸⁶

An asymmetric or hybrid configuration, with two electrodes of different nature, *e.g.*, conducting polymer, transition metal oxide and activated carbon,^{32,86} taking into account the optimal potential range of each electrode, is an excellent way

to reach a wide operating voltage. The most promising material for use as a negative electrode is activated carbon, whereas conducting polymers can easily operate as positive or negative electrodes. An example of optimal operating voltage for capacitor configuration with a PPy composite as negative electrode and the *a*-MnO₂ composite as positive electrode is shown in Fig. 13.

An interesting series of materials operating successfully in an asymmetric configuration is presented in Table 4. The advantage of the asymmetric combination over the symmetric one is clearly seen. A significant increase of energy and power can easily be obtained especially due to the extension of the supercapacitor voltage.

CNTs are effective for decreasing the resistance due to the fact that they enhance both ionic and electronic conductivity in the electrode network. Because of their higher electronic conductivity than activated carbons, one interesting approach is to use them as a conductivity additive for activated carbons. For the CNTs themselves, the conductivity varies from a few S cm⁻¹ up to 1000 S cm⁻¹, depending on the CNT types (single-wall, double-walled, multi-walled,...).⁸⁷ The evolution of the equivalent series resistance was studied for a supercapacitor constructed using electrodes obtained by adding CNTs to a commercial activated carbon. A nanotube content of 15 wt% seems to be the percolation threshold of such a system.⁸⁸

Carbons with heteroatoms present in their structure

Carbon materials depending on the type of precursor and/or the preparation conditions (atmosphere, temperature, activation procedure...) can possess a variable amount of foreign elements. The most commonly present heteroatoms in the carbon framework are oxygen, nitrogen, sulfur, hydrogen.

The functional groups present on the surface of carbons used as electrode can considerably enhance the capacitance through additional Faradaic reactions generally called pseudo-capacitance effects. Therefore, instead of developing the specific surface area, an alternative is to introduce pseudo-Faradaic properties by doping of carbon through foreign elements. The pseudo-capacitance induced by oxygen functionalities due to close association of oxygen with the carbon surface is the most frequent phenomenon.

The presence of different heteroatoms (oxygen, nitrogen) substituted for carbon in the graphene layers or occurring as functional groups has been considered in order to modify the

Table 4 Different configurations of asymmetric systems and their capacitor characteristics³²

Electrode materials		Supercapacitor characteristics			
Positive	Negative	U/V	E/Wh kg ⁻¹	ESR/Ω cm ²	P max/kW kg ⁻¹
PANI	PANI	0.5	3.13	0.36	10.9
PPy	PPy	0.6	2.38	0.32	19.7
PEDOT	PEDOT	0.6	1.13	0.27	23.8
Carbon Maxsorb	Carbon Maxsorb	0.7	3.74	0.44	22.4
PANI	Carbon Maxsorb	1.0	11.46	0.39	45.6
PPy	Carbon Maxsorb	1.0	7.64	0.37	48.3
PEDOT	Carbon Maxsorb	1.0	3.82	0.33	54.1
MnO ₂	MnO ₂	0.6	1.88	1.56	3.8
MnO ₂	PANI	1.2	5.86	0.57	42.1
MnO ₂	PPy	1.4	7.37	0.52	62.8
MnO ₂	PEDOT	1.8	13.5	0.48	120.1

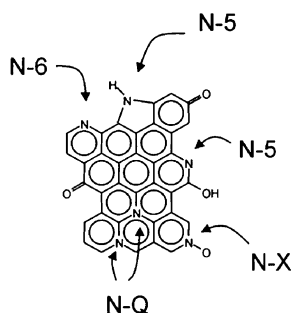


Fig. 14 Schematic representation of the possible nitrogenated functionalities in a carbon network.

electronic properties of the carbon, which can further influence the electrochemical performance. The foreign atoms modify the electron donor/acceptor properties of the graphene layers, and are consequently expected to affect the charging of the electrical double layer and to give pseudo-capacitance Faradaic reactions. The main dopant studied in the literature is nitrogen; some N substitutes for carbon ("lattice nitrogen"), and the rest is chemically bound to organic molecules ("chemical nitrogen"). Different types of nitrogenated functionalities are shown in Fig. 14.

Nitrogen enrichment in nitrogen has been reported as an interesting route for improvement in capacitance behavior.^{14–18,20,21,47,89} Nitrogen can be incorporated into the carbon network in different ways, for example it has been shown that ammoxidation of a carbon sample can improve its capacitance.^{14,47}

The effect of substitutional nitrogen in the graphitic network on the pseudo-capacitance properties has also been studied using carbon precursors in the form of polymers already rich in nitrogen. A series of nitrogen enriched carbons was prepared by carbonization of polyacrylonitrile (PAN) or oxidized poly(4-vinylpyridine) cross-linked with 25 wt% of divinylbenzene (PVPox) and their blends with pitch (*P*). They have then been activated by steam to give activated carbons which were tested in two electrode capacitors.^{16,17} The detailed nanotextural characteristics together with the elemental composition expressed by the N/C, O/C and N/O atomic ratios and the potential of zero charge were investigated. The voltammetry characteristics for the activated carbon from PAN shows a perfect rectangular shape at 2 mV s^{−1} and 20 mV s^{−1}. The capacitance values of the nitrogenated carbons are strongly affected by the nature of the electrolyte and the electronic structure induced by nitrogen. A careful analysis of the results obtained for samples with comparable nanotextural properties, *i.e.* $S_{\text{BET}} \approx 800 \text{ m}^2 \text{ g}^{-1}$ and comparable micropore volume, shows no remarkable differences in organic medium, whereas capacitance is proportional to the N content (Fig. 15) in alkaline and especially in acidic medium. It is noteworthy that the basic character of carbons is also proportional to the nitrogen content. For example, the carbon with 1.9 wt% of N has a $\text{pH}_{\text{pzc}} = 7.4$, whereas for 7.2 wt% of N the pH_{pzc} reaches a value of 9.3.

The enhancement of the capacitance values in a H_2SO_4 medium is interpreted by pseudo-Faradaic reactions due to the nitrogenated functionality, as illustrated in Fig. 16.

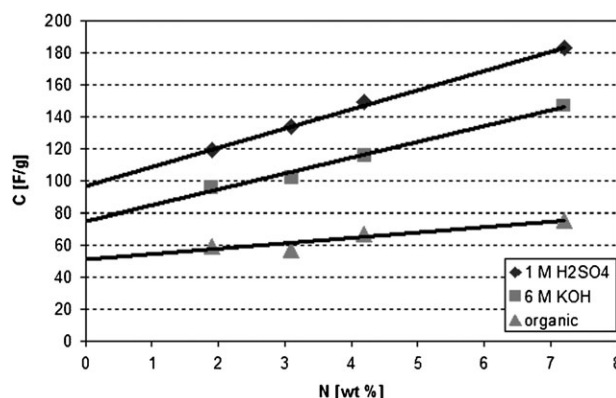
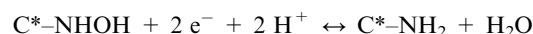
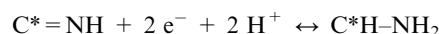


Fig. 15 Capacitance values for a series of activated carbon materials with a similar nanotexture and surface area but various nitrogen content.

The following reactions can also be taken into account:



where C^* stands for the carbon network.

Pseudo-capacitive properties connected with the nitrogen presence have also been shown in the case of C/C composites obtained by one step carbonization of a carbon nanotubes/polyacrylonitrile (30/70 wt%) blend at 700 °C.¹⁸ Whereas the specific surface area of polyacrylonitrile (PAN) carbonized at 700 °C is negligible ($S_{\text{BET}} = 6 \text{ m}^2 \text{ g}^{-1}$), the C/C pellets formed by pyrolysis of a CNT/PAN blend have a more developed porosity ($S_{\text{BET}} = 157 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{DR}} = 0.067 \text{ cm}^3 \text{ g}^{-1}$, $V_{\text{meso}} = 0.117 \text{ cm}^3 \text{ g}^{-1}$). The nitrogen content measured in this composite by XPS is 7.3 at%. Fig. 17 shows a perfect template effect of nanotubes during the carbonization process, which is at the origin of a well accessible electrode/electrolyte interface. A moderate capacitance value of 100 F g^{-1} was reached, whereas in the same conditions the capacitance value is 18 F g^{-1} for pristine CNTs and negligible for carbonized PAN. Moreover, the perfect charge propagation allowed a very high regime of 10 A g^{-1} to be used.

The main contribution to capacitance is due to pseudo-Faradaic charge transfer reactions, as for other nitrogenated carbons.^{14–18,20,21,47,89} The remarkable capacitance properties of this kind of composite are due to a synergy between the template effect of CNTs on nanotexture and the pseudo-Faradaic properties of the nitrogenated functionality of carbonized PAN. It is noteworthy that the lack of an additional activation process, similar to the case of carbonized biopolymers, is at the origin of a high volumetric density that improves the capacitor parameters.

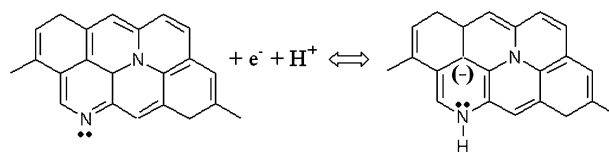


Fig. 16 Possible pseudo-Faradaic reaction of the pyridinic group in aqueous medium.

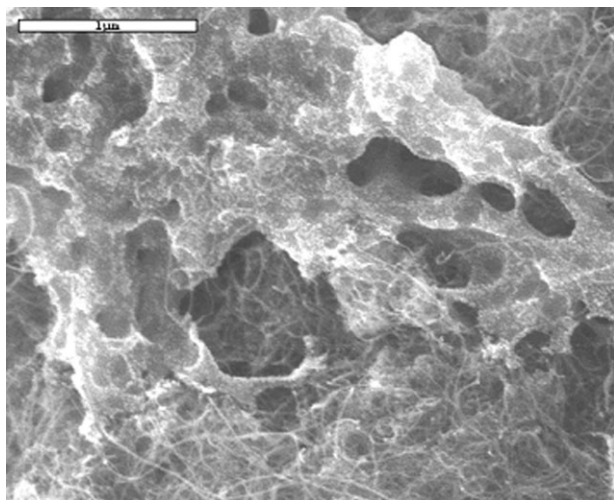


Fig. 17 C/C composite from a PAN/CNT blend carbonized at 700 °C without any activation process.

Conclusions and perspectives

Nanotextured carbons are the main materials for the realization of supercapacitor electrodes. Beside their reasonable cost and good electrical conductivity, they may be found in various forms with reasonably adaptable porosity and surface functionality. Supercapacitors can operate in aqueous and organic electrolytic solutions. When only the electrical double layer (EDL) is charged, the capacitance seems to be partly proportional to the surface area of the electrode/electrolyte interface. It has been found that the pore size must fit with the size of ions. Pores at the border of the ultramicropore region, *e.g.*, 0.7–0.9 nm, are the most useful for charging the electrical double layer. It is assumed that non-solvated ions can easily take part in charging of the electrical double layer. However, some additional mesopores interconnected with the micropores are also necessary to facilitate good dynamic charge propagation.

It has been shown that interesting composite electrodes can be obtained by using multi-walled carbon nanotubes as a three dimensional support of a material with pseudo-capacitive properties, *e.g.*, electronically conducting polymers or transition metal oxides. Due to a synergy between the high electronic conductivity of the graphitic type layers of nanotubes and the fast diffusion of ions to the bulk of the active material through mesopores, the electrical series resistance of these devices is very low. Moreover, due to the high resiliency of nanotubes, the electrodes can be charged/discharged over a large number of cycles without mechanical degradation of the active phase.

The capacitance of nanoporous carbons can be noticeably enhanced by an additional contribution related to quick Faradic reactions, the so-called pseudo-capacitance, due to the presence of heteroatoms. These processes generally involve nitrogenated or oxygenated functionalities incorporated into the carbon framework. In the case of nitrogen, the foreign atoms are either introduced by ammoxidation of an activated carbon or by pyrolysis of a nitrogen rich precursor followed by activation under steam or CO₂. Some interesting materials,

where the dominant contribution is of pseudo-capacitance type, were obtained by one-step carbonization of a seaweed biopolymer, *e.g.*, sodium alginate. Although only slightly developed, the porosity of this material is sufficient for a good access of ions to the functionality at the origin of the pseudo-Faradic charge transfer reactions. Similarly, a pseudo-capacitive C/C composite has been prepared by one-step pyrolysis of polyacrylonitrile/carbon nanotube blends. A templating effect of the nanotube framework creates mesopores during pyrolysis. The presence of multi-walled carbon nanotubes enhances considerably the electrical conductivity of the devices, allowing high charge/discharge rates to be reached while involving a pseudo-capacitive effect.

High voltage values can be achieved in an aqueous medium using an asymmetric configuration, with two different materials working in their optimal potential range for each electrode, *e.g.*, a nanoporous carbon at the negative electrode and a *a*-MnO₂/CNT composite at the positive electrode. Different asymmetric combinations were proposed using transition metal oxide, conducting polymers and activated carbon as electrode materials giving a significant increase of energy and power.

In the future, much attention should be devoted to cheap carbon materials obtained by simple carbonization processes without any activation. Such materials of high density and rich in heteroatoms giving stable pseudocapacitance effects seems to be the future for the development of high performance supercapacitors.

Supercapacitors can operate in aqueous and organic electrolytic solutions reaching a maximum voltage limit of 2.5 V. Further extension of the operating voltage can be achieved through application of ILs. However, their high viscosity and low conductivity should be overcome. Furthermore, the long term stability of such a type of electrolyte is yet to be confirmed.

Acknowledgements

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