The role of the electric conductivity of carbons in the electrochemical capacitor performance

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Abstract

The interpretation of the performance of electrochemical capacitors based exclusively on the textural features and surface chemistry of carbons can be insufficient, or even misleading, in the case of materials prepared at low temperatures (typically below 800°C).

It is suggested that the gradual improvement of the electrochemical performances of carbon-based capacitors at high current densities, following heat treatments up to 900°C, is mainly a consequence of the simultaneous increase in conductivity. This is illustrated by a study of carbons based on a mesoporous carbon prepared at 550°C, which displays poor electrochemical performances and a low conductivity (4.6 10^{-6} S m^{-1}). A first heat treatment at 700°C leads to major structural, chemical and electrochemical changes, due to the collapse of the smaller mesopores and the formation of a microporous structure with average pore widths around 1.3 nm. One also observes a reduction in the surface oxygen density from 13 to approximately 5 µmol m^{-2}. Further heat treatments at 800 and 900°C do not modify significantly these

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characteristics, nor the surface-related capacitances at low current densities (1 mA cm^{-2}) in the aqueous (2M H$_2$SO$_4$) and organic (1M (C$_2$H$_5$)$_4$NBF$_4$/CH$_3$CN) electrolytes. On the other hand, one observes increasingly high rate capabilities which may be ascribed to the simultaneous increase in conductivity from 7.3 to 147.8 S m^{-1} between 700 and 900°C.

1. Introduction

Electrochemical double-layer capacitors (EDLC) have been an important development in the field of electric energy storage [1,2]. There are many industrial fields that can benefit from the unique combination of high reliability, power and energy provided by EDLC technology. Several applications have drawn considerable attention, including regenerative braking in hybrid vehicles, cold engine starting, ride-through backup power systems and digital electronic devices [1,2].

In view of the high potentiality of porous carbons for electrodes in EDLC, research efforts are presently being devoted to identify the key physico-chemical properties of these materials for high capacitance and high voltage devices [3,4]. Most studies focus on the effect of the textural features of carbons, such as specific surface area and pores size distribution, on their ability for energy storage and power release [3-6]. Additionally, the influence of surface functionalities on the electrochemical performance has also been analyzed [3,4,6]. Indeed, all these characteristics determine the behavior of carbon-based capacitors. It has been shown that for the aqueous H_2SO_4 electrolyte the specific capacitance of carbons at low current densities consists of a contribution from the electrochemical double layer formed at the accessible surface area and of an additional pseudo-capacitance arising from certain surface functional groups, such as oxygen- [7] and nitrogen-containing complexes [8]. The pseudo-capacitive effects in the aprotic electrolyte $(C_2H_5)_4NBF_4$ in acetonitrile seem to be much weaker than in the aqueous medium and the performance of the corresponding capacitors results basically from the double-layer mechanism [9].

Furthermore, it appears that the variation of the specific capacitance at high current densities in both aqueous and aprotic electrolytes is controlled by the average micropore width and the amount of CO_2 generating surface groups [7,9].

This study goes one step further by illustrating that the interpretation of the performance of EDLCs based exclusively on the textural and chemical features of carbons can be insufficient and other factors must be taken into account to get reliable conclusions. The systematic analysis of a series of carbons, based on the same precursor, with similar porosity and surface chemistry clearly shows that the complementary role of the electric conductivity of materials has to be added to the processes in the solution side of the double layer.

This work also illustrates that the poor suitability of a mesoporous activated carbon obtained at 550ºC is overcome by heating in N_2 at temperatures between 700 and 900ºC. This simple process allowed the preparation of interesting microporous carbon with high capacitances, as well as increasingly high rate capabilities in aqueous (2M H_2SO_4) and organic (1M $(C_2H_5)_4NBF_4/CH_3CN$) electrolytes. Such information can be further extended to the design of high performance electrochemical capacitors.

2. Experimental

2.1. Carbon materials

A commercial activated carbon, Norit® C-Granular (hereafter labelled C) was heat treated under N_2 at 700, 800 and 900ºC for 2 hours. This leads to carbons C700, C800 and C900, respectively.

2.2. Characterization of carbons

The solids have been characterized by N_2 adsorption at 77 K (*Micromeritics ASAP*

2010) and by immersion calorimetry at 293 K (*Tian-Calvet*-type calorimeter). These techniques have been described in detail elsewhere [10].

The microporosity characterization was based on Dubinin´s theory, where the linearization of the Dubinin-Radushkevich (DR) equation leads to the micropore volume W_o, the average width L_o of the locally slit-shaped micropores and the surface area of the micropore walls S_{mi} [10,11]. On the other hand, the classical comparison plot based on the N_2 adsorption on a non-porous reference (*Vulcan 3G*) provided the total pore volume V_p and the external surface area S_e of the carbons [11]. The combination of both approaches provided the total surface area based on the DR approach, $S_{totDR} = S_{mi} + S_e$. As summarized in Table 1, S_{DR} is in good agreement with the total surface area obtained from the analysis of N_2 isotherm by other methods such as the comparison plot (S_{comp}) and the Density Functional Theory (S_{DFT}) [11]. These areas and their averages $S_{av} = (S_{totDR}+S_{comp} +S_{DFT})/3$ are listed in Table 1.

The pore size distributions (PSD) of the mesopores were obtained by applying the Kruk-Jaroniec-Sayari (KJS) method to the adsorption branch [12].

The density of surface oxygenated functionalities has been estimated by the enthalpies of immersion into water and into benzene [13].

2.3. Supercapacitor performance of carbons

Two-electrode capacitors were assembled in a Swagelok® system with pellets of 8 mm in diameter and a thickness of ca. 300 μm. The electrode ($\sim$10 mg) was composed of 75 wt.% of carbon, 20 wt.% of polivinylidene fluoride and 5wt.% of carbon black. 2M H_2SO_4 aqueous solution and 1M $(C_2H_5)_4NBF_4$ in acetonitrile were used as electrolytes. A glassy fibrous material played the role of separator. The

electrochemical measurements involved cyclic voltammetry at scan rates from 1 to 50 mV s^{-1} and galvanostatic charging-discharging cycles at current densities between 1 and 70 mA cm^{-2} (potentiostat-galvanostat *Autolab-Ecochimie PGSTAT 30*). The cell voltage ranged from 0 to 0.8 V for the aqueous medium and between 0 and 2 V for the aprotic electrolyte.

The electrical conductivity of the carbons was measured at room temperature using a rig composed by a hollow glass cylinder and two brass pistons, as described in a previous work [14]. The sample was compressed at 2 MPa (*Shimadzu AG-IS*) and, simultaneously, the electrical resistance was determined by the four-probe method of impedance spectroscopy in the frequency range 0.1 Hz -1 MHz (*Solartron 1296/1255B*).

3. Results and discussion

Following Vinke *et al*. [15], the initial carbon C corresponds to a highly disorganized material with a large content of aliphatic hydrocarbon fragments and rather limited conjugated ring structures [15,16]. The value of E_o around 16 kJ mol^{-1} obtained from the analysis of the N_2 isotherm by the Dubinin equation [10], as well as the pore size distribution (PSD) derived by the KJS method [12], practically exclude the presence of classical micropores. This means that C is a mesoporous carbon with a broad porosity between 2 and 30 nm (Fig. 1). The analysis based on the nitrogen comparison plot leads to a total surface area S_{comp} of 739 m^{2}g^{-1}, in good agreement with the value of 715 m^{2}g^{-1} obtained by the DFT method. Therefore, the average area (S_{av}) of carbon C is 727 m^{2}g^{-1}.

The comparison of the enthalpies of immersion into water and into benzene [13] indicates a surface oxygen density of 9.6 mmol g^{-1} or 13.2 µmol m^{-2}, in agreement

with the significant presence of carboxylic acid groups reported by Vinke *et al.* [15].
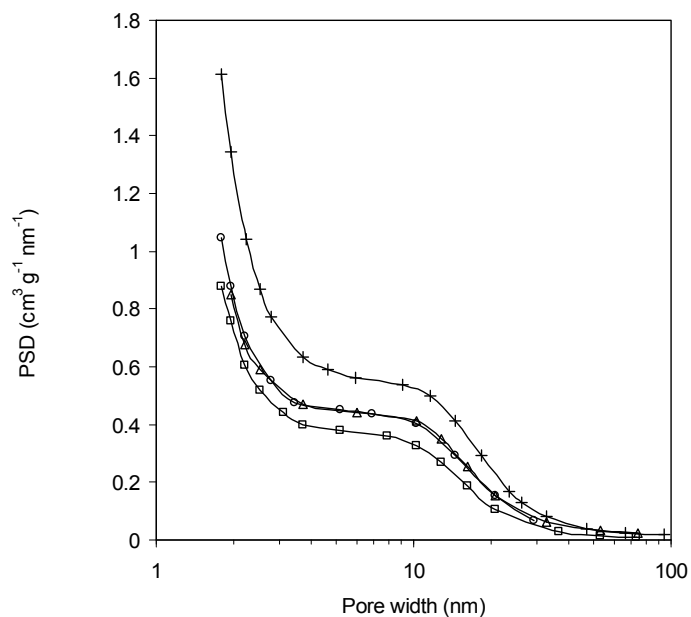
Figure 1. Pore size distributions for carbons: C (+), C 700 (○), C800 (□) and C900 (△) above 2 nm, following the KJS method.

The structural and chemical characteristics on their own (Table 1) suggest a potentiality for the use of carbon C and similar carbons as electrodes in electrochemical capacitors. Its relatively high-surface-area (727 m^2 g^{-1}) should allow a high energy density storage, whereas its porosity, consisting essentially of mesopores, should provide a high power density [3,4,9]. However, these expectations, based exclusively on textural properties, contrast with the poor performance displayed by the capacitor prepared with carbon C. Fig. 2 illustrates collapsed cyclic voltammograms in both aqueous and aprotic media. If, by contrast, one takes into account the low conductivity of the material this result is not surprising. Carbon C, prepared by chemical activation of wood with phosphoric acid at a relatively low temperature (550°C), has a large content of aliphatic hydrocarbon

fragments and carbon atoms with sp^3 configuration [15,16]. As a consequence, the electron mobility is highly limited [15-17] and only 4.6 10^{-6} S m^{-1} is obtained at 2 MPa. The importance of electric conductivity has been reflected in several studies based on carbon electrodes modified by the addition of carbon nanotubes [6].
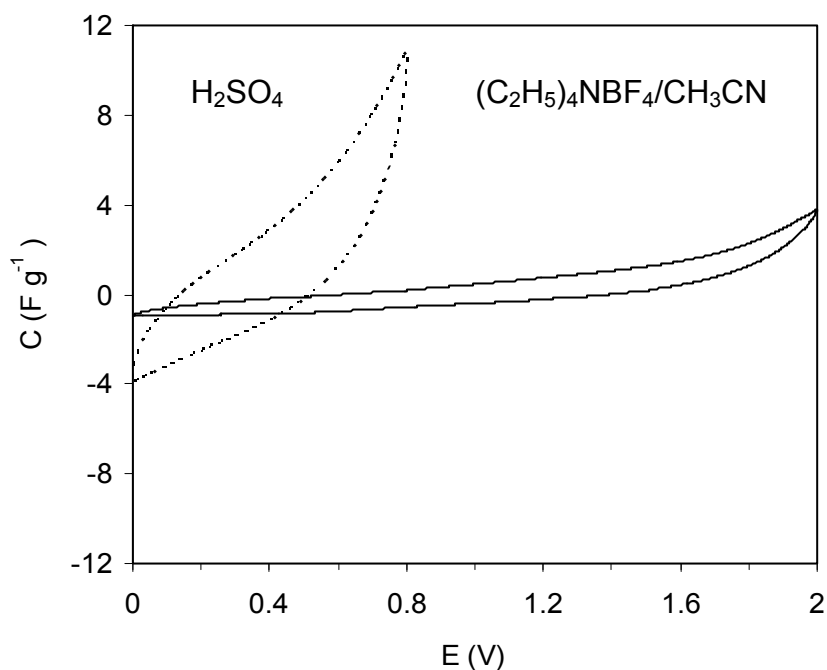
Figure 2. Cyclic voltammograms for carbon C at 5 mV s^{-1} in 2M H$_2$SO$_4$ (dotted line) and (C$_2$H$_5$)$_4$NBF$_4$/CH$_3$CN (solid line)

The success of a heat treatment under inert atmosphere near 1000ºC to enhance the suitability of porous carbons prepared at a high temperature (typically above 800ºC) has been noted in previous studies. For example, Ruiz et al. [18,19] reported that the heating in N$_2$ at 1000ºC of a mesophase-derived activated carbon induced changes in the texture and the surface chemistry. It was suggested that the reduction in specific capacitance in H$_2$SO$_4$ and KOH and the enhancement of life-cycle of the supercapacitor were due mainly to the elimination of surface functionalities. On the

other hand, templated mesoporous carbons obtained at 800°C required treatment at 1000 ° C for 11 h to be suitable as electrodes for aqueous supercapacitors [20]. Such a treatment did not change significantly the pore structure of carbons (modifications in surface chemistry were not analyzed), but the conductivity of the electrode prepared with the treated samples is about one order of magnitude higher than that of the as-synthesized carbons. Obviously, the effect of heat treatment on the electrochemical performance depends largely on the temperature at which the material has been prepared as well as the textural and chemical properties of the resulting carbon. For example, Table 2 shows the relatively small modification in $C(j)/C_o$ of sample derived by post-heating at 1000ºC of the pitch-based superactivated carbon microbeads M30 (Osaka Gas Chemicals Co., Ltd.). It has probably been prepared around 850ºC, like many pitch-based carbons.

In the case of carbon C obtained at 550°C, the subsequent heat treatments between 700° and 900ºC lead to an interesting pattern. Firstly, as illustrated by Table 1 and Fig.1, heating at 700ºC is a major step which induces a significant change in the porous structure. One observes a shift from the smaller mesopores towards a microporous stucture with average pore widths L_o of 1.38 nm. The further treatments at 800 and 900ºC reduce only slightly the micropore volume W_o and L_o, and the total surface areas are practically the same as observed for the initial carbon (727 m^2 g^{-1}). This clearly indicates a collapse in the structure around 700ºC. Simultaneously, it appears that the treatment at 700ºC leads to a strong reduction in the content of surface oxygenated-functionalities from 13.2 µmol m^{-2} to approximately 5 µmol m^{-2} for carbons C700 to C900 (Table 1).

Secondly, as seen in Figure 3, the capacitors based on carbons C700-C900 also show regular box-like voltammograms, with a steep current change at the switching

potential and characteristic for the behavior of an ideal capacitor. The rectangular shape is well preserved over a wide range of scan rates (1 to 50 mV s^{-1}), which indicates a quick charge propagation. Moreover, high gravimetric capacitances are obtained from galvanostatic charge-discharge cycling at 1 mA cm^{-2} (C$_o$, in Fg^{-1}). Table 2 reports values, expressed per carbon mass in a single electrode, ranging from 124 to 173 Fg^{-1} in the aqueous H$_2$SO$_4$ electrolyte and around 74-80 F g^{-1} in the aprotic medium. For both electrolytes, the surface related capacitances C$_o$/S$_{av}$ compare well with the values observed for typical activated carbons prepared at 800 to 900°C [7,9].
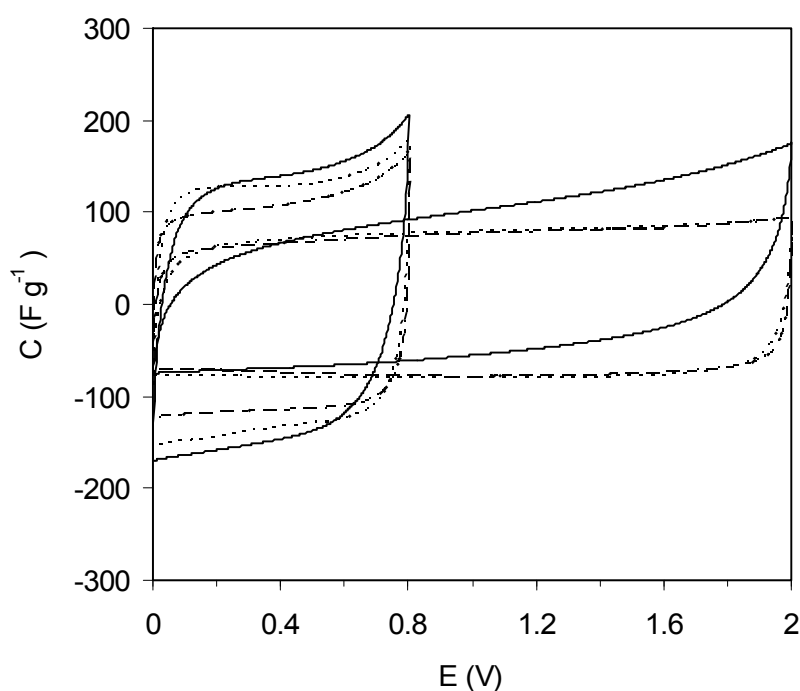
Figure 3. Cyclic voltammograms for carbons C700 (solid line), C800 (dotted line) and C900 (dashed line) at 5 mV s^{-1} in 2M H2SO4 and (C$_2$H$_5$)$_4$NBF$_4$/ CH$_3$CN.

Carbons C700 to C900 show structural and chemical similarities and their surface-related capacitances C$_o$/S$_{av}$ at j = 1 mA cm^{-2} in both electrolytes are similar, with one exception (C900 in 2 M H$_2$SO$_4$). However, in spite of the presence of carbon black in

the electrode, differences in their capacitance retention are found. As shown in Table 2, the decreases in the normalized capacitance $C(j)/C_o$ with increasing current density j show different profiles. For example, at 70 mA cm^{-2} C900 still delivers around 73% of the capacitance achieved at 1 mA cm^{-2} in both electrolytes, as opposed to only 37 % in the case of C700. It appears that the heat treatment has a retarding effect on the decrease of $C(j)/C_o$. Furthermore, the cyclic voltammogramms of Fig. 3 show differences in the steep current change at the switching potential.

In the absence of significant changes in porous and chemical characteristics, these differences must be related to another factor, likely to be the electric conductivity of the carbons [3,21,22]. As reported in Table 1, the heat treatment produces major changes in the electrical conductivity, characterized by an important jump between 550 (4.6 10^{-6} S m^{-1}) and 700°C (7.3 S m^{-1}), and followed by a further increase up to 900°C (147.8 S m^{-1}). Earlier investigations [23-25] reported that a transition between an insulating and a conducting state usually occurs when carbon materials are heated around 600-700°C. The removal of strong electron-withdrawing heteroatoms (primarily acidic functionalities) from the carbon surface favours the electron delocalization and the electrical conductivity is notably enhanced. In the case of carbon C, the conductivity rapidly increases by at least six orders of magnitude by heating at 700°C. This increment coincides with a drop in the content of surface oxygenated-functionalities [O] from 9.6 to 3.3 mmol g^{-1} (Table 1). Above 700°C, the much slower increase of the electrical conductivity is probably related to the enhancement in the structural order by thermal annealing of the pseudo-graphitic carbonaceous layers [23-25] rather than to the loss of further surface groups.

The increase in carbon conductivity is associated with a significant reduction in the equivalent series resistance (ESR) of the corresponding capacitor. In H_2SO_4, ESR of

the cell with electrodes made of carbon C700 is 11 Ω (1 mA cm^{-2}). It drops to 5 Ω for the capacitor with carbon C900 as electrodes. For the aprotic electrolyte, the device based on C900 displays an ESR of 18 Ω against 36 Ω for C700.

Figure 4 confirms that the textural and chemical characteristics are not the only factors controlling the performance of the electrochemical capacitor and the electronic properties of carbons have a prime importance, especially for achieving high power delivery. As illustrated by Figure 4 for aqueous and aprotic electrolytes, the increase in the carbon conductivity by heat treatment at 900ºC has a limited effect on the capacitor capacity for energy storage but results in power density almost 4 times higher than that of the device based on C700.
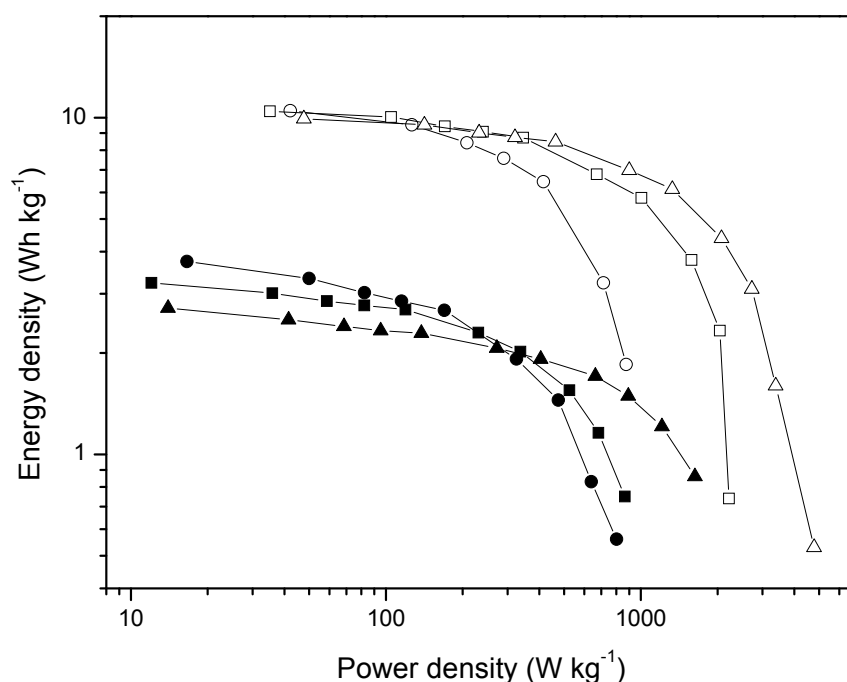
Figure 4. Energy density *vs* Power density for the supercapacitors based on carbons: C700 (○, ●), C800 (□, ■) and C900 (△, ▲). The data corresponds to the unit mass of carbon in the capacitor.
Open symbols for 2M H_2SO_4 aqueous solution.
Closed symbols for 1M $(C_2H_5)_4NBF_4/CH_3CN$.

4. Conclusions

Heat treatment in N_2 at 700, 800 and 900°C notably improves the poor electrochemical performance of a mesoporous carbon prepared at 550°C. The major step occurs around 700°C, which corresponds to a collapse in the porous structure and the removal of oxygen-containing surface complexes. The structural and the chemical properties the three carbons are similar, as well as their surface-related capacitances at low current density (1 mA cm^{-2}) in aqueous (2M H_2SO_4) and in organic (1M $(C_2H_5)_4NBF_4/CH_3CN$) electrolytes. On the other hand, it appears that the performance at higher current densities (5 to 70 mA cm^{-2}) increases considerably with the temperature of treatment. The ratio $C(j)/C_o$ and the energy storage performances (in particular for the aprotic electrolyte, which is independent of the surface oxygen) improve between C700 and C900. At the same time, the power density is multiplied by a factor of four. These improvements, observed in both electrolytes, are directly related to the increase in electric conductivity between 700 and 900°C. This is an additional factor leading to the optimization of carbons for electrochemical capacitors.

The performance of carbons in electrochemical capacitors should not be based exclusively on the suitability of pore structure for electrolyte wetting and rapid ionic motion. In order to get reliable conclusions from comparison of carbons with different origins, electric properties of materials have to be also considered.

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Table 1. Main physico-chemical characteristics of the carbons.

Carbon	V_p (cm^3 g^{-1})	W_o (cm^3 g^{-1})	E_o (kJ mol^{-1})	L_o (nm)	S_{mi} (m^2 g^{-1})	S_e (m^2 g^{-1})	Surface area (m^2 g^{-1})		$-\Delta_iH[C_6H_6]$ (J g^{-1})	$-\Delta_iH[H_2O]$ (J g^{-1})	[O] (mmol g^{-1})	[O] (μmol m^{-2})	Electric Conductivity (Sm^{-1})
C	0.86	0.50	16.4	~ 2.3	-	-	S_{totDR} S_{comp} S_{DFT}	- 739 715	144.4	126.1	9.6	13.2	4.6 10^{-6}
							S_{av}	727					
C700	0.67	0.40	19.2	1.38	580	162	S_{totDR} S_{comp} S_{DFT}	742 700 771	113.2	56.4	3.3	4.5	7.3
							S_{av}	738					
C800	0.58	0.34	19.8	1.28	531	142	S_{totDR} S_{comp} S_{DFT}	673 700 647	123.1	63.6	3.8	5.6	29.3
							S_{av}	673					
C900	0.64	0.38	20.1	1.25	608	122	S_{totDR} S_{comp} S_{DFT}	730 681 734	121.2	61.4	3.6	5.0	147.8
							S_{av}	715					

Table 2. Electrochemical properties of the heat-treated carbons C700 to C900. For comparison purposes, data for the pitch-based activated carbon M-30 and after heat treatment at 1000°C are also included.

Carbon	2 M H_2SO_4 electrolyte							1 M $(C_2H_5)_4NBF_4/CH_3CN$ electrolyte						
	C_o	C_o/S_{av}	Normalised capacitance for current densities of 5 to 70 mA cm^{-2}					C_o	C_o/S_{av}	Normalised capacitance for current densities of 5 to 70 mA cm^{-2}				
	(Fg^{-1})	(Fm^{-2})	C_5/C_o	C_{10}/C_o	C_{30}/C_o	C_{50}/C_o	C_{70}/C_o	(Fg^{-1})	(Fm^{-2})	C_5/C_o	C_{10}/C_o	C_{30}/C_o	C_{50}/C_o	C_{70}/C_o
C700	173	0.23	0.89	0.82	0.58	0.44	0.38	80	0.11	0.90	0.78	0.46	0.35	0.22
C800	148	0.22	0.93	0.90	0.82	0.74	0.67	78	0.11	0.96	0.92	0.80	0.72	0.63
C900	124	0.17	0.91	0.88	0.82	0.79	0.75	74	0.10	0.96	0.93	0.84	0.77	0.72
M30	201	0.18	0.93	0.90	0.84	0.81	0.78	121	0.11	0.97	0.94	0.90	0.88	0.82
M30-1000	131	0.14	0.98	0.96	0.94	0.92	0.90	102	0.11	0.97	0.95	0.94	0.92	0.92