The role of textural characteristics and oxygen-containing surface groups in the supercapacitor performances of activated carbons

T.A. Centeno [a], F. Stoeckli* [b]

[a] *Instituto Nacional del Carbón-CSIC. Apartado 73, E-33080 Oviedo, Spain*

[b] *Laboratoire de Chimie Physique des Surfaces, Institut de Microtechnique de l'Université, rue Emile Argand 11, CP 158, CH-2009 Neuchâtel, Switzerland*

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Abstract

It is suggested that the specific capacitance C_o of activated carbons at low current densities ($d \sim 1$ mA cm^{-2}) consists, to a good first approximation, of two contributions. For the H_2SO_4 electrolyte they correspond to approximately 0.080 F m^{-2} from the total accessible surface area and an additional pseudo-capacitance of 63 F mmol^{-1} from the surface species generating CO in thermally programmed desorption (TPD). The new correlation proposed here is an alternative to Shi´s earlier approach which considered contributions from the microporous and the external surface areas. Furthermore, it appears that the variation of the specific capacitance C at high current densities d (up to 100-150 mA cm^{-2}) depends essentially on the CO_2-generating surface groups and on $1/L_o$, the inverse of the average micropore width.

Keywords : Supercapacitor; Double-Layer; Carbon; Porosity; Chemical groups

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* Corresponding author. Tel.: +41 32 718 24 25

E-mail address: fritz.stoeckli@unine.ch

1. Introduction

Microporous carbons, and in particular activated carbons, are well known for their high sorptive capacities, but in recent years they have also found applications in electrical energy storage, as double-layer capacitors [1-4]. In the case of electrolytes such as concentrated aqueous solutions of H_2SO_4 or KOH, specific capacitances C as high as 300 F per gram of carbon have been reported for KOH activated materials. The origin of the high performances of certain carbons remains a matter of debate and an appropriate description can be of help for the preparation of materials with optimum properties.

The electrical double layer capacitance (EDLC) is essentially a surface property and various correlations have been proposed for the specific capacitance C. For example, some years ago Shi [5] suggested specific contributions c_e and c_{mi} from the external (non-microporous) surface area S_e and from the microporous surface area S_{mi}, respectively. This attempt appears to be successful in many cases, but one obtains different pairs of c_e and c_{mi} values, even for a given electrolyte such as aqueous H_2SO_4 or KOH [4-8]. Although the exact definition of the micropore surface area plays an important role [6,9,10], it appears that more parameters must be taken into account. It has been recognized, for example, that the chemistry of the surface also contributes to the electrical capacitance [1,11-19]. The role of basal planes and edges has also been pointed out (see for example the text-books by Conway [1] and Kinoshita [11]), which is not too surprising, since chemical groups are located mainly on edges. However, in view of the diversity of experimental conditions, it seems that no clear correlation has been proposed so far, which combines structural and chemical factors. The present study offers

relatively simple quantitative relations for both the specific capacitance C_o (F g^{-1}) at low current densities (typically $d\sim$1 mA cm^{-2}) as well as C (F g^{-1}) at higher current densities (up to 100-150 mA cm^{-2}). In order to gain a coherent picture, the study is based on our own work with H_2SO_4 electrolyte and on isolated data reported in the literature.

2. Experimental

The present study of supercapacitor performance is based on a total of 30 activated carbons used in our laboratories (Table 1), characterized by adsorption and immersion calorimetry techniques, as described in detail elsewhere [9,20]. In the present study, the relevant structural parameters are S_{mi} , the surface area of the micropore walls, S_e the surface area found in larger pores or on the outside of the carbon and L_o, the average micropore width. Micropores being locally slit-shaped, their volume W_o is related to L_o and S_{mi} through the simple geometrical relation W_o(cm^3 g^{-1}) = L_o(nm)$\cdot S_{mi}$(m^2 g^{-1})/2000 [9,20]. For comparison purposes, we also used a meso- and macroporus graphite, HSAG-300, which has an average surface area of 329 m^2 g^{-1}.

Twelve carbons, including HSAG-300, were also characterized by thermally programmed desorption (TPD) [21, 22], which led to the amounts of [CO] and [CO$_2$] released by the surface groups given in Table 2.

Following a technique described earlier [23], the distribution of oxygen-containing groups in the micropore system has been investigated for carbons UO3 and UO3-ox. The method consists in the pre-adsorption of variable amounts of n-undecane followed by immersion calorimetry into water. It confirms the distribution of oxygen over the entire micropore system.

For comparison purposes, the study also considers another 30 typical activated carbons reported in the literature [13-15,19,24], with known TPD data and surface areas (mainly S_{BET}), for which the electrochemical properties were determined with aqueous H_2SO_4 as electrolyte. The combined data provides enough information to establish correlations between supercapacitor performance, surface areas and chemical properties, using this particular electrolyte.

The electrochemical measurements were carried out in a potentiostat-galvanostat Autolab-Ecochimie PGSTAT30. Sandwich-type capacitors were prepared with two carbon pellets (8 mm in diameter) separated by glassy fibrous paper and placed inside a Swagelok-cell. The electrodes (11-12 mg) were obtained by pressing a mixture of 75 wt% of carbon, 20 wt% of polyvinylidene fluoride and 5 wt% of carbon black (Super P). 2M H_2SO_4 aqueous solution was used as electrolyte. The capacitance C was determined by galvanostatic charge-discharge voltage cycles (after a minimum of 40 cycles) from 0 to 0.8 V at current density d between 1 and 150 mA per cm^2 of electrode surface. The values of C are relative to the carbon mass in the electrode, like the other structural parameters of Tables 1 and 2.

The two-electrode configuration may be questioned as far as it does not provide information on the specific participation of positive and negative electrodes, but preliminary results obtained with a three-electrode cell [1] for a selection of carbons of the present series show a good agreement between the two configurations for the 2M H_2SO_4 electrolyte (Courtesy Dr. M. Hahn, *Paul Scherrer Institute Villigen*, Switzerland).

3. Results and discussion

3.1. Distribution of oxygen in the micropore system.

As discussed by different authors, and in particular by Figueiredo at al. [25], untreated and treated activated carbons contain, apart from hydrogen, a variety of chemical species such as carboxylic, lactonic, phenolic and quinonic groups. They can be titrated by classical techniques, such as Boehm's method [26] or immersion calorimetry into standard HCl, $NaHCO_3$ and NaOH solutions [27]. Thermally programmed desorption (TPD) [21, 22] also provides useful information on the surface complexes and a satisfactory agreement has been found between the different techniques. The data obtained for twelve standard and treated carbons of the present series, including a high surface area graphite, HSAG-300, is shown in Table 2. These carbons cover a wide range of structural and chemical properties and may be considered as being representative for the thirty carbons of Table 1. Moreover, as discussed below, the results obtained for HSAG-300 show that the concepts developed for micrporous carbons can be extended to meso- and macroporosity in carbons, which includes templated carbons.

Water has a low affinity for pure carbon, but it interacts strongly with oxygen-containing surface groups. It has been shown by a combined study of immersion calorimetry and TPD [28] that this interaction corresponds, on average, to -10 J per mmol of oxygen. Consequently, one may expect that in the case of aqueous electrolytes the strong affinity of water for the surface groups and the formation of clusters play an important role.

It has been argued that surface groups are found mainly on the external surface area [5], but there is strong evidence that they are distributed over the entire micropore

system. The first clue was provided some years ago by Stoeckli et al. [23], who determined the enthalpy of immersion of typical activated carbons into water, $-\Delta_iH(H_2O)$, following the pre-adsorption of increasing amounts of n-undecane. These molecules gradually fill the structure, starting with the smallest micropores, and they are not displaced by water during the calorimetric experiment lasting 30 to 45 minutes. Fig. 1 shows the cases of carbons U03 and U03-ox, where $-\Delta_iH(H_2O)$ decreases almost linearly with the available micropore volume. This indicates a relatively regular distribution of the oxygen-containing sites throughout the structure, which has been confirmed recently by the modelling of water adsorption in slit-shaped micropores [29]. The approach was similar to that used for CO_2 [30], but it also took into account the specific interactions of water with oxygen. The analysis of the water adsorption isotherm of well characterized carbons, based on the CO_2 pore size distribution, led to the conclusion that oxygen atoms must be located in all pores. Refined calculations even suggest slight variations in their distribution, but at this stage nothing can be said about the location of the different functional groups.

It follows that the presence of oxygen-containing groups in the entire microporous structure increases the complexity of the problem, since it must be added to the purely structural constraints imposed by the pore size distribution.

3.2. The influence of chemical groups on the capacitance at low current densities

A reasonable starting point is the study of C_o, the limiting capacitance at low current density d, by convention at 1 mA cm^{-2}. This property has been investigated by Shi [5] for more than 30 carbons (activated microbeads and fibers), using a 5 M KOH electrolyte. It

was shown that for these well activated carbons S_{BET} is often larger than $S_{mi} + S_e$, which is not surprising [9]. These different areas were obtained respectively from the analysis of the nitrogen isotherm with the BET model, the DFT technique and comparison plots. Shi's data for C_o expressed in F m^{-2} and given by the ratio

$$C_o(F\ m^{-2}) = C_o(F\ g^{-1}) / S_{BET}\ (m^2\ g^{-1}) \tag{1}$$

varies between 0.06 and 0.22 F m^{-2}.   On the other hand, the data of Kierzek et al. [31] obtained for highly activated carbon fibers with BET surface areas between 2700 and 3200 m^2 g^{-1} and a 6 M KOH electrolyte, leads to values as low as 0.08 F m^{-2}. These results are surprising, since it has been shown that for carbons without micropores this electrolyte leads to approximately 0.12 F m^{-2} [32]. One may conclude that the actual surface area is smaller than S_{BET}.

Since S_{BET} is often unreliable for carbons with high surface areas, it is not surprising that a better correlation can be obtained for C_o if one use the total surface area of the carbons, $S_{tot} = S_{mi} + S_e$. Shi's data leads to an average capacitance of (0.138 ± 0.038) F m^{-2} (standard deviation for 30 values). In the case of a series of carbons investigated by the present authors and based on 2 M H_2SO_4 [33], S_{tot} leads to (0.172 ± 0.038) F m^{-2}. The data of Gryglewicz et al. [7] for 1 M H_2SO_4 and 6 M KOH electrolytes leads respectively to (0.127 ± 0.028) F m^{-2} and (0.095 ± 0.024) F m^{-2}. These sets of data show some similarities, but in view of their scatter, they are only indicative for the whole range of industrial activated carbons and cannot be used for reliable predictions of C_o.

Such examples suggested that more refined approaches were needed, in order to obtain a better overall agreement between the different sets of experiments. It was first suggested by Shi [5] that C_o consists of separate contribution from S_{mi} and S_e,

$$C_o[F\ g^{-1}] = c_{mi}S_{mi} + c_{ext}S_{ext} \tag{2}$$

For his data, parameters c_{mi} and c_{ext} are respectively 0.195 and 0.74 F m^{-2} for activated microbeads and 0.145 and 0.075 F m^{-2} for activated fibers. However, the value of 0.74 F m^{-2} is unusually high, since the external surface areas of the two types of carbons are similar. The recent data of Centeno and Stoeckli [33] based on 2 M H_2SO_4, leads to c_{mi} = 0.20 F m^{-2} and c_{ext} = 0.043 F m^{-2} (correlation coefficient of 0.893).

These results show that Shi's Eq. (2) provides a better description for C_o than the use of S_{BET} or S_{tot} alone, but the sets of c_{mi} and c_{ext} values seem to differ between families of carbons. This means that a different approach must be found for a more general description.

An interesting clue is provided by the recent work of Bleda-Martinez et al.[19] who investigated a series of KOH-activated carbons with BET surface areas up to 3500 m^{2}g^{-1}, using a 1M H_2SO_4 electrolyte. Although these surface areas may be questioned, it was shown that there exists a good linear correlation between C_o/S_{BET} and [CO]/S_{BET}, where [CO] represents the amount of CO obtained from TPD. This suggests that the CO-generating surface species contribute to the EDLC at low current density, probably as a pseudo-capacitance. Furthermore, a regression analysis taking into account the amount of CO_2 released in TPD, also given by these authors, shows that the contribution of the latter

groups to C_o is small.

The contribution of certain types of surface groups to C is also suggested by the work of Okajima et al. [17] on the plasma treatment of a KF-1500 fiber monitored by TPD. Their study shows an increase in the specific capacitance C_o(F g^{-1}), using a H_2SO_4 electrolyte, with the number of oxygenated functional groups. Similar conclusions can be derived from the data of Hsieh et al. [13] and Nian et al. [14].

An overall assessment combining our data (Tables 1 and 2) with data reported in the literature for the H_2SO_4 electrolyte in two-electrode [13, 14], as well as three-electrode [19] cells leads to

$$C_o (Fg^{-1}) = (0.081 \pm 0.007) (F\ m^{-2})S_{tot}(m^2\ g^{-1}) + (63 \pm 5)(F\ mmol^{-1})[CO](mmolg^{-1}) \qquad (3)$$

As illustrated by Fig. 2, there is a good agreement between the data from 2- and 3-electrode configurations. This suggests that, in accordance with Oda et al. [34], the capacitance of both electrodes does not differ significantly in H_2SO_4. As mentioned in section 2, preliminary results obtained for a few carbons of Table 2, using three-electrode cells, also show a good agreement between the two techniques.

One obtains an interesting correlation, but there are exceptions, as observed for certain samples strongly oxidized with $(NH_4)_2S_2O_8$ and where the contribution to the pseudo-capacitance is well below 63 F $mmol^{-1}$. These exceptions, not shown here, require a detailed study of the CO-generating surface complexes formed by this agent.

It should be pointed out that the average specific contribution of the total surface area suggested by Eqn (3), 0.081 F m^{-2} is close to the value obtained for XC-72 (0.088 F m^{-2}),

a carbon which contains only 0.02 mmol of oxygen per gram. Moreover, it also appears that Eqn (3) includes the high surface area graphite HSAG-300, which means that the underlying description can be applied to predict the capacitance of meso- and macroporous carbons such as templated carbons.

At this stage, Eqn (3) may be regarded as an alternative to Eqn (2), the expression proposed by Shi [5]. Instead of variable contributions from the microporous and external surface areas, C_o seems to depend on contributions from S_{tot} and the CO-generating groups, with the reservation expressed above regarding oxidation by $(NH_4)_2S_2O_8$. Obviously, there may be numerical changes to Eqn (3) in the light of new data, but it appears that the chemical nature of the surface (in the present case oxygen-containing surface groups) plays a relatively important role in the capacitance at low current densities. Eqn (3) also applies to a wide range of activated carbons, whereas Eqn (2) leads to different sets of parameters c_{mi} and c_{ext} , often depending on the series of carbons and their origin [5, 7, 33, 35].

There is little doubt about the contribution of certain oxygen-containing groups to C_o, and it is likely, that other chemical surface groups or atoms may also contribute to C_o. For example, as shown recently by Kodama et al.[16] and Frackowiak et al.[36], the presence of residual nitrogen from the precursor in the surface structure can increase considerably the capacitance of the carbon in the H_2SO_4 electrolyte. Obviously, this avenue should be investigated, in particular if the performance/cost ratio is favourable.

It is interesting to note that the surface groups which generate CO in TPD and contribute significantly to C_o occupy only a small fraction of the total surface area of the carbons. This surface area is part of the accessible edges and of indentations created by a

strong chemical treatment (KOH). It corresponds to the so-called active surface area (ASA), a concept investigated some years ago by Ehrburger [37, 38]. If one assumes, a molecular surface area of 0.083 nm^2 per desorbed CO molecule, or 50 m^2 per mmol, the capacitance of the corresponding groups is approximately 63(F $mmol^{-1}$)/50(m^2 $mmol^{-1}$) = 1.3 F m^{-2}. It follows that the average capacitance of 0.14 F m^{-2} obtained by Centeno et al.[32] for the surface of templated mesoporous carbons and HSAG-300 corresponds to an extra contribution from (0.140-0.081)/1.3 = 0.045 or 4.5% of the surface. This corresponds essentially to edges. In the case of the internal surface area S_{mi} of the KOH-activated carbons Maxsorb, a similar calculation suggests that the CO-generating groups occupy approximately 13% the micropore walls. This is the direct result of KOH activation, which exposes existing edges and creates new edges by an attack perpendicular to the basal planes [39, 40].

According toY.-J. Kim et al.[40], the edges represent approximately 7% in activated carbons, whereas C.-H. Kim et al.[41] report values as high as 23%. However, edges and indentations may also contain [CO_2]-desorbing groups, which means that the real surface of the exposed edges is approximately one third higher for typical carbons. This is suggested by the fact that the ratio [CO]/([CO] + [CO_2]) is often around 0.7 to 0.9. [13, 14, 19, 21] (For our carbons, given in Table 2, one obtains 0.70, in good agreement with 0.75 derived from the data of ref. [19]).

At this stage, it is interesting to point out that, as shown by Ehrburger et al. [38], the active surface area (ASA) of various oxidized carbons, and consequently the amount CO-generating surface groups, tends to increase with their micropore volume W_o. His data suggests an upperbound given by

$$ASA(m^2g^{-1}) = 166(m^2 cm^{-3})W_o(cm^3 g^{-1}) \qquad (4)$$

Since ASA (m^2g^{-1}) = 50 $(m^2$ per mmol CO) [CO] $(mmol\ g^{-1})$, it follows that the amount of CO is equal to $166W_o/50$ $(mmol\ g^{-1})$. This correlation explains the empirical contribution of approximately 160 F cm^{-3} suggested earlier [33], to be added to the specific capacitances of S_{mi} and S_e. In the last analysis, this apparent volumic contribution corresponds effectively to the CO-generating surface groups and the corresponding exposed edges, which tend to increase with the micropore volume W_o .

3.3. Variation of C with the current density d

It is known [1,4] that the C generally decreases when the current d increases, typically up to 150-200 mA cm^{-2}. As illustrated for carbons U03, U03-ox and Maxsorb, as well as the non-microporous graphite HGSA-300 (Fig. 3), the relative decrease C/C_o varies from carbon to carbon and it appears again that the oxygen content of the surface plays an important role.

Recently, the following empirical correlation has been suggested for a series of 12 well characterized carbons [33]

$$C\ [F\ g^{-1}] = C_o \exp[\ -5.32^{\cdot}10^{-3}d\ (1 + 0.0158[O]^2\ )\ ] \qquad (5)$$

where [O] represents the total oxygen content and $d < 70$ mA cm^{-2}. However, one may expect that the mobility in the micropore system also depends, to some extent, on the

average pore width L_o. This effect should be added to the barriers created by the surface oxygen, which is present in the entire microporosity accessible to the 2 M H_2SO_4 electrolyte.

It has been suggested by different authors that oxygen-containing surface groups-in particular acids-may reduce the mobility of ions [13, 14, 42, 43]. This means that the variation of C with d should depend significantly on $[CO_2]$, the amount of CO_2 released by TPD by acidic groups.

The analysis carried out with the data for the 12 carbons of Table 2 and d up to 100-150 mA cm^{-2} suggests that

$$C \, [F \, g^{-1}] = C_o \, \exp[\, -d \, (0.00180/L_o + \ 0.00602 \, [CO_2 \,]) \,] \qquad (6)$$

The correlation coefficient is 0.990 (130 experimental points and deviations mostly below 10 per cent). Deviations larger than 10 to 15 per cent, gradually observed for many carbons beyond 100 to 150 mA cm^{-2}, may reflect yet other factors not considered in Eqn (6). For example, the connectivity of the micropores, which plays a role in adsorption kinetics. The correlation between the calculated and the experimental values of C is shown in Fig. 4.

The inclusion of the corresponding amounts of CO in Eqn (6) leads to a supplementary term -0.001[CO], which suggests that the variation of C with d, does not depend significantly on the CO-generating groups. On the other hand, the influence of $1/L_o$ on C is clearly suggested by carbons CMS, BV46, U03, Supra DLC-50 and XC-72 with relatively low $[CO_2]$ contents (see Table 2) and average micropore widths L_o between

0.75 and 1.8 nm (Table 1). For these five carbons, the leading term in the exponent of Eqn (6) is $0.0019/L_o$, which appears to be 1.5 to 3 times larger than the contribution from the second term, $0.0069[CO_2]$.

The CO_2-generating surface species are mainly acidic groups and $[CO_2]$ is often close to [meq NaOH], the amount of NaOH required to neutralize these groups. Therefore, it is not too surprising to obtain a relatively good correlation if one uses [meq NaOH]. The same is true if one uses $2[CO_2] + [CO]$, which is close to the total amount of surface oxygen [O] and one obtains (correlation coefficient 0.983)

$$C\,[F\,g^{-1}] = C_o \exp[\, -d\,(\, 0.00176/L_o + \; 0.00125(\, 2[CO_2\,] + [CO])) \,] \tag{7}$$

With respect to Eqn (6), the reduced prefactor 0.00125 compensates for counting twice $[CO_2]$ and reflects the fact that [CO] has practically no influence. This means that for a large number of carbons C can be calculated on the basis of [O] and L_o, using Eqn (7). This expression is, like Eqn (5), a useful working expression.

4. Conclusions

This paper shows that the assessment of carbons to be used as supercapacitors requires a thorough a reliable structural and chemical characterization. In the present case, the use of this information is limited to the study of the electrochemical capacitance determined with the 2 M H_2SO_4 electrolyte, but it appears that this approach provides a better overall picture. The relevant features examined here are:

(a) The BET-surface area is often unreliable for carbons with high surface areas, which are precisely the most interesting candidates as supercapacitors. This may lead to contradictory results for specific capacitances given in $F\,m^{-2}$.

(b) The capacitance at low current density, C_o, depends on the total surface area (0.080 F m^{-2}) and on the surface groups which generate CO in TPD. The contribution from the latter corresponds to a pseudo-capacitance of approximately 62 F per mmol of CO. Eqn (3) replaces the earlier correlation suggested by Shi [5], which considers different contributions from S_{mi} and S_e, but does not lead to an overall agreement between different classes of carbons.

(c) It appears that in the case of the 2M H_2SO_4 aqueous electrolyte the two- and three electrode techniques are in agreement (Detailed results will be published in due course)

(d) Oxygen-containing groups are distributed over the entire micropore system and not limited to the external surface area, as shown by immersion calorimetry and confirmed by the modelling of water adsorption isotherms in various pore size distributions. This means that the entire micropore system and the oxygen contained in it contribute to the electrochemical properties. Moreover, in the case of the variation of C with the current density d, given by Eqn (6), it appears that both the CO_2-generating surface groups and the average micropore width L_o play a role. The influence of $1/L_o$ is perceptible for activated carbons with low oxygen contents, but for oxidized carbons the CO_2-generating groups (mostly acidic) have a predominant effect on C at high current densities, d.

(d) It is likely that the present approach can be extended to the description of the influence of other chemical species or groups on the capacitance of carbons (*e.g.* the case of nitrogen atoms included in the surface structure [16,36]).

Obviously, the elements presented here are only the first stage of an attempt to provide a better understanding of the relation between the structural and the chemical characteristics of activated carbons, on the one hand, and some of their properties when used as supercapacitors. Further steps should also consider in more detail the correlation with dynamic aspects such as the release of stored electric energy and electrochemical properties at high frequencies.

Similar studies carried out with non-aqueous electrolytes will certainly provide complementary information and results will be published in due course.

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Fig. 1. The decrease of the enthalpy of immersion of carbons U03 (□) and U03-ox (○) into water, following the preadsorption of n-undecane in the microporous structure (degree of micropore filling θ)
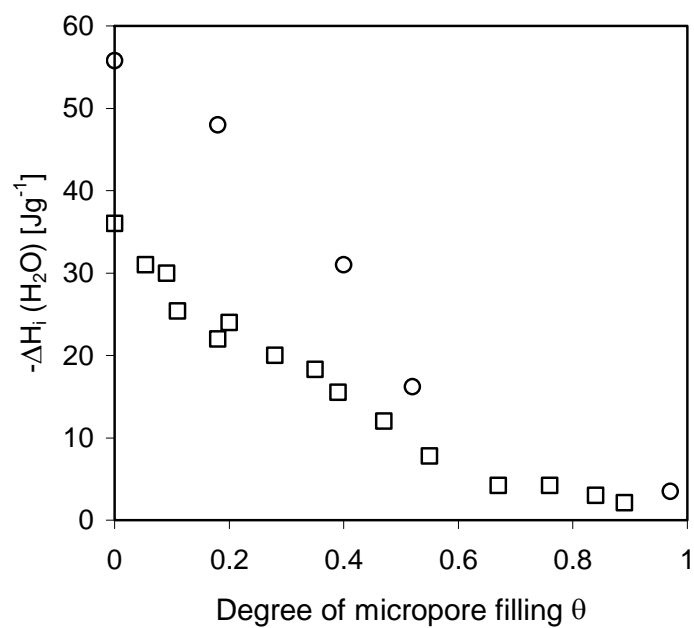
Fig. 2. Correlation between C_o/S_{tot} and $[CO]/S_{tot}$ for the carbons of Table 2 (♦) and from refs. [13,14] (●) and [19] (■).
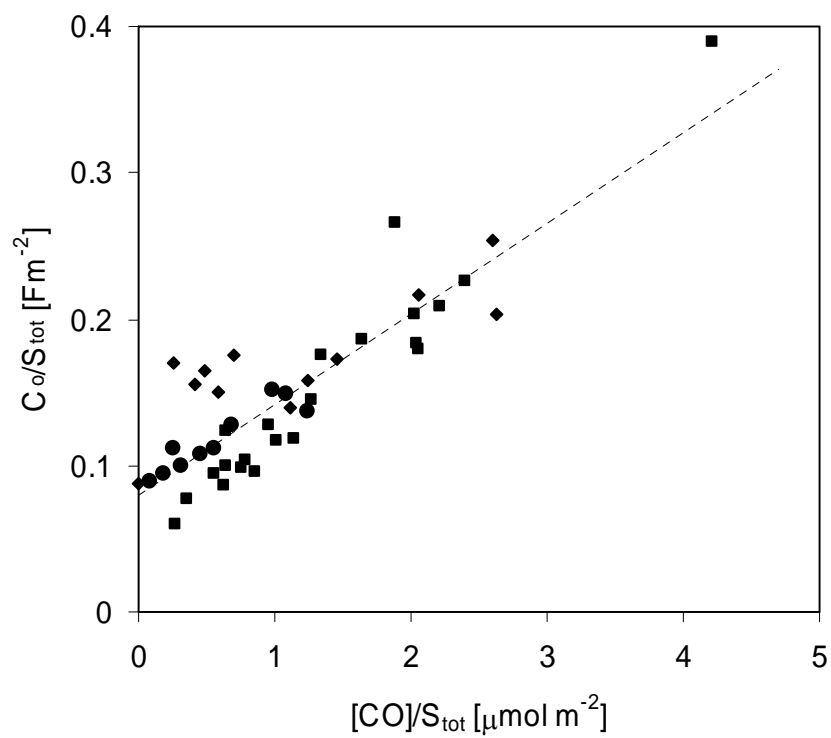
Fig.3. Decrease of C/C_o with increasing current density d. Carbons U03 (♦), U03-ox (■), Maxsorb (▲) and HSAG300 (□).
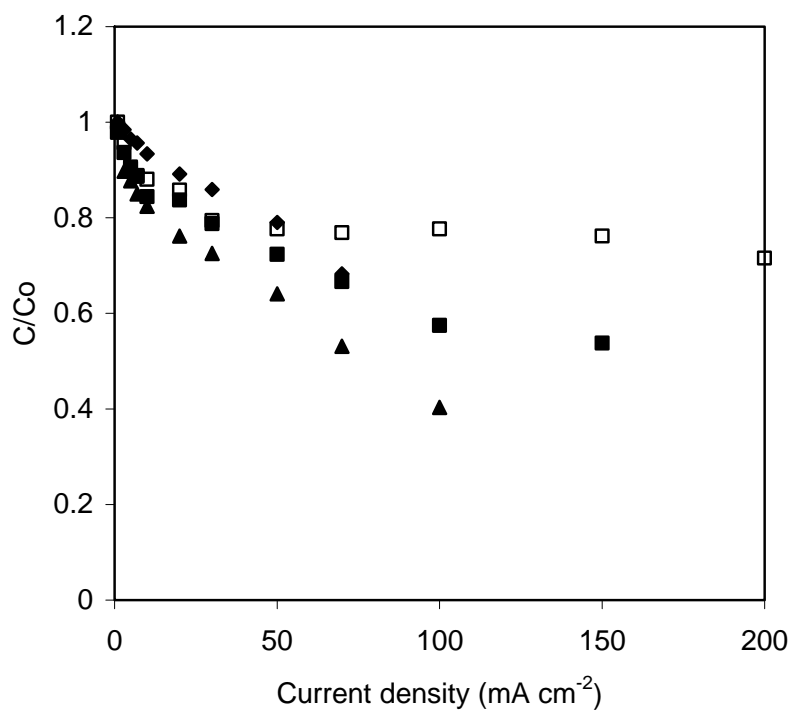
Fig. 4. Correlation between calculated and experimental values of C for the carbons of Table 2, using Eqn. (6) and current density d up to 150 mA cm^{-2} (130 experimental points).
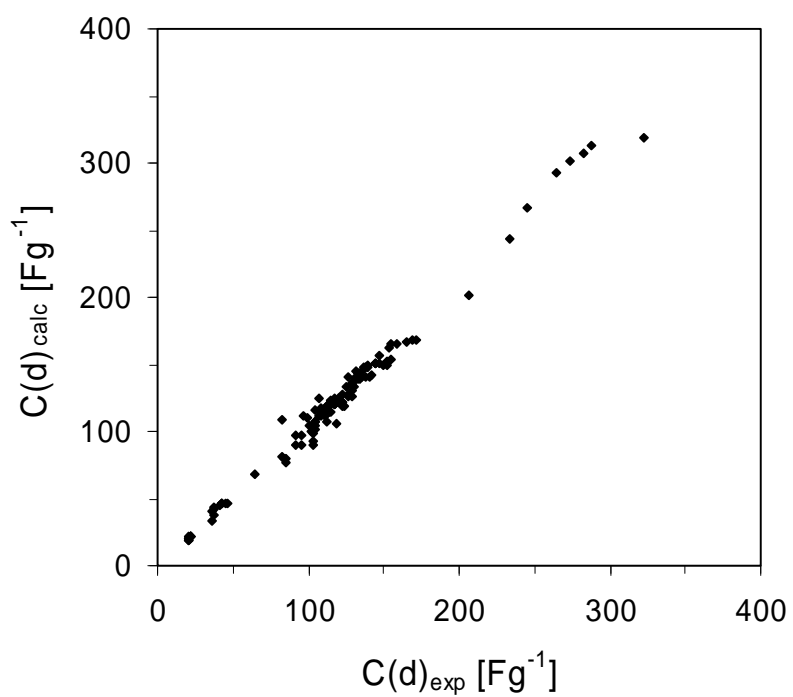
Table 1. Structural characteristics and electrochemical capacitances of the carbons in order of increasing average micropore width L_o

Carbon	S_{mi} $(m^2\,g^{-1})$	S_e $(m^2\,g^{-1})$	S_{total} $(m^2\,g^{-1})$	L_o (nm)	C_o $(F\,g^{-1})$	C_o/S_{tot} $(F\,m^{-2})$
MSC-5	500	5	505	0.68	65	0.129
S-3	788	6	794	0.70	125	0.157
CMSH2	685	28	713	0.73	104	0.146
CMS	645	20	665	0.75	115	0.173
MH6	976	17	993	0.86	168	0.169
MH2	851	28	879	0.87	140	0.159
AZ46-3	719	131	850	0.89	150	0.176
MH2-HCl	1078	25	1103	0.90	185	0.168
AZ46-0	668	140	808	0.96	136	0.168
XC-72	145	105	250	0.96	22	0.088
MH8	710	25	735	1.02	132	0.180
MH3	717	32	749	1.06	132	0.176
DCG-5	982	40	1022	1.10	169	0.165
BV46	727	110	837	1.10	142	0.170
MH7	709	25	734	1.10	136	0.185
MH4	549	36	585	1.13	109	0.186
MH8HCl	804	45	849	1.17	183	0.216
UO2	714	105	819	1.26	128	0.156
BV46-Ox	651	112	763	1.29	155	0.203
M-30	1050	50	1100	1.33	204	0.185
Supra DLC-50	1038	11	1049	1.33	152	0.145
AC-35	554	250	804	1.36	121	0.150
KF-1500	910	28	938	1.38	135	0.144
MH4cz	841	107	948	1.39	174	0.184
Super DLC-50	829	22	851	1.52	149	0.175
Oigines-70	1182	6	1188	1.54	198	0.167
UO3	570	60	630	1.80	122	0.194
UO3-ox	630	60	690	1.80	150	0.217
Maxsorb (PX-21)	1166	104	1270	2.00	322	0.254
N-125	610	157	767	2.10	122	0.159

Table 2. Amounts of CO and CO_2 determined by TPD. The carbons are listed in order of increasing average micrpore width L_o, as in Table 1.

Carbon	[CO] (mmol g^{-1})	[CO$_2$] (mmol g^{-1})
CMS	0.97	0.17
AZ46-0	0.33	0.24
XC-72	2.10^{-4}	9.10^{-3}
DCG-5	0.50	0.34
BV46	0.22	0.10
BV46-ox	2.01	0.63
Supra DLC-50	0.62	0.18
UO3	0.44	0.12
UO3-ox	1.42	0.88
Maxsorb(PX-21)	3.30	1.40
N-125	0.96	0.27
HSAG-300	0.65	0.38