

# On the specific double-layer capacitance of activated carbons, in relation to their structural and chemical properties

T.A. Centeno<sup>a</sup>, F. Stoeckli<sup>b,\*</sup>

<sup>a</sup> Instituto Nacional del Carbon-CSIC, Apartado 73, E-33080 Oviedo, Spain

<sup>b</sup> Institut de Chimie de l'Université, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

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## Abstract

Twelve well-characterized activated carbons with average micropore widths between 0.7 and 2 nm, total surface areas of 378–1270 m<sup>2</sup> g<sup>-1</sup> and specific capacitances  $C$  up to 320 F g<sup>-1</sup> have been investigated, using H<sub>2</sub>SO<sub>4</sub> 2 M as electrolyte. Some of the carbons have also been oxidized with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, which leads to specific oxygen contents between 0.4 and 7.1 μmol m<sup>-2</sup> of carbon surface area. It appears that  $C_o$ , the limiting capacitance at a current density of 1 mA cm<sup>-2</sup> of electrode surface, does not depend significantly on the oxygen content. An empirical equation is proposed to describe the decrease of  $C$  with increasing current density  $d$  (1–70 mA cm<sup>-2</sup> of electrode surface), as a function of the oxygen content.

As suggested by different authors,  $C_o$  can be expressed as a sum of contributions from the external surface area  $S_e$  and the surface of the micropores  $S_{mi}$ . A closer investigation shows that  $C_o/S_{mi}$  increases with the pore size and reaches values as high as 0.250–0.270 F m<sup>-2</sup> for supermicropores. It is suggested that the volume  $W_o^*$  of the electrolyte found between the surface layers in pores wider than 0.7–0.8 nm contributes to  $C_o$ . However, this property is limited to microporosity, like the enthalpy of immersion of the carbons into benzene. The latter is also correlated to  $C_o$ , which provides a useful means to identify potential supercapacitors.

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## 1. Introduction

Activated carbons [1] are used mainly in filtration technology, but in recent years they have also found applications in electrical energy storage, as double-layer capacitors (see, for example, reviews [2,3] and Refs. [4–10]). This type of carbon is characterized by a developed microporous structure and a correspondingly large surface area. A number of studies based on direct and indirect observations [1,11–15] show that the material consists of interconnected cavities between twisted graphitic (or aromatic) sheets. Classical techniques based on the adsorption of molecules of variable dimensions (0.4–1.5 nm), either from the vapour phase or monitored by

immersion calorimetry [16], suggest that the pore widths correspond to these dimensions.

Observations in high resolution electron microscopy [10–12] (bright- and dark-field techniques) show that micropores are locally slit-shaped, at least for widths  $L$  and extensions up to 1–1.2 nm. Larger micropores, often called ‘supermicropores’ have more complicated and cage-like structures. The upper limit for microporosity is around 2–2.5 nm, where capillary condensation begins and a number of specific properties disappear (for example, the energy of adsorption of the vapour and the liquid phases). Depending on the precursor material and the activation process [1], the micropore volume  $W_o$  can be as high as 0.8–1 cm<sup>3</sup> g<sup>-1</sup>. For commercial activated carbons, the surface area of the micropore walls,  $S_{mi}$ , is in the range of 700–1000 m<sup>2</sup> g<sup>-1</sup>, but in special cases it can reach 1200–1400 m<sup>2</sup> g<sup>-1</sup> (this limit seems realistic for activated carbons, if one keeps in

\* Corresponding author. Tel.: +41 32 718 2400; fax: +41 32 718 2511.  
E-mail address: [fritz.stoeckli@unine.ch](mailto:fritz.stoeckli@unine.ch) (F. Stoeckli).

mind the fact that graphene sheets have a maximum surface area of  $2600 \text{ m}^2 \text{ g}^{-1}$  and that they usually come in pairs or larger stacks). The total surface area can be assessed directly by the selective adsorption of sparingly soluble molecules, such as phenol and caffeine from aqueous solutions [17–19]. In this case, adsorption is limited to a monolayer, as opposed to vapour adsorption, where the entire micropore volume is filled. The latter process is described by Dubinin's classical theory [1,13,19]. The value of  $S_{\text{mi}}$  is also confirmed by the cumulative surface area of the micropore walls calculated from the pore size distribution obtained by various techniques [19–21] including modelling of adsorption.

Depending on their accessible width  $L$ , micropores can accommodate a variable number of layers of adsorbate between their walls. For a typical molecule, such as water, nitrogen or benzene, micropores wider than 0.7–0.8 nm will accommodate between two and five–six layers, the upper limit corresponding to supermicropores ( $L \sim 2.5 \text{ nm}$ ). The layers which are not in direct contact with the surface (up to four layers) define a 'core' with a volume  $W_o^*$  with properties strictly limited to microporosity. For example, as discussed elsewhere [21], immersion calorimetry suggests that adsorption by microporous carbons can be formally divided into three distinct contributions, namely from the first layers in the micropore walls and on the external surface  $S_e$  found in pores larger than 2 nm (meso- and macropores [22]), as well as from the volume  $W_o^*$ . As shown below, a similar approach can probably be applied to the description of the capacitance  $C_o$  of microporous carbons.

Depending on the development of the microporous texture, one may obtain with aqueous electrolytes specific capacitances  $C$  for carbon electrodes in aqueous media in the range of approximately  $50\text{--}300 \text{ F g}^{-1}$  of carbon. Attempts have been made to correlate this property with the microporous and external surface areas  $S_{\text{mi}}$  and  $S_e$ , as well as  $S_{\text{BET}}$  [2,4,5,7–10]. The latter is derived from the BET theory [22], but it is often unrealistic, as it is the monolayer equivalent of the adsorbate filling the micropores.

As shown elsewhere [13,21],  $S_{\text{BET}}$  corresponds to the total surface area  $S_{\text{mi}} + S_e$  only for microporous carbons with average pore widths  $L_o$  around 1 nm. It follows that specific properties, such as enthalpies of immersion, oxygen contents or capacitances  $C$  expressed in units per square metre of BET surface area, can be misleading for carbons with a large proportion of supermicropores. Since  $C$  depends on the actual surface area of a carbon, it is necessary to use the correct values of  $S_{\text{mi}}$  and  $S_e$ . On the basis of Qu and Shi's work [9,10], it appears that using these parameters separately improves the situation. However, they are still not sufficient to allow reliable predictions of the capacitances of a range of typical activated carbons at low density currents.

The aim of this paper is to suggest further correlations between structural and chemical characteristics of activated carbons and their capacitance  $C$ , in view of practical applications, such as the optimization of capacitors. The empha-

sis is on the role of microporosity and therefore a selection of well-characterized carbons [19–21] has been considered, with average pore widths  $L_o$  between 0.75 and 2 nm.

As a first step (Section 3.1), we outline an approach, which offers the possibility to predict with reasonable accuracy  $C_o$ , the limiting capacitance of carbon electrodes at low density currents ( $d \sim 1 \text{ mA cm}^{-2}$  of electrode). It appears that the volume  $W_o^*$  also plays an important role, beside  $S_{\text{mi}}$  and  $S_e$ , and it follows that reasonable predictions can be made for  $C_o$  with the help of these three structural characteristics. Secondly (Section 3.2), an equation is proposed to describe the variation of  $C$  with increasing current density (up to  $70 \text{ mA cm}^{-2}$  of electrode) and the oxygen content of the carbon [O]. Finally (Section 3.3), it will be shown that that an empirical, but interesting correlation exists between  $C_o$  and the enthalpy of immersion of the carbons into inert liquids, such as benzene. This observation can be used to assess the suitability of an unknown carbon to be used as a capacitor.

## 2. Experimental

### 2.1. Materials

The study is based on a broad spectrum of microporous carbons obtained by steam activation around  $800 \text{ }^\circ\text{C}$  of lignocellulosic precursors (series BV, AZ46), of anthracites (CMS and DCG-5) and a carbon black (XC-72-17). A KOH activated petroleum pitch (PX-21) was also included in the study, in view of its high capacitance under the given experimental conditions ( $322 \text{ F g}^{-1}$  of carbon at low current density). The solids have been well characterized by a variety of techniques, such as vapour adsorption [1,13,19], immersion calorimetry into liquids with different molecular sizes [16,21], the selective adsorption of phenol from aqueous solutions [17,18] and, in some cases, by the analysis of the  $\text{CO}_2$  isotherm with the help of model isotherms obtained by Monte Carlo simulations (CMS, DCG-5 and XC-72-17) [20]. The latter technique assumes slit-shaped micropores, which is a reasonable model for pore widths up to approximately 1.2–1.5 nm. Beyond, for the cage-like supermicropores, one must use an equivalent width equal to  $2000W_o \text{ (cm}^3 \text{ g}^{-1})/S_{\text{mi}} \text{ (m}^2 \text{ g}^{-1})$  [19].

The external (non-porous) surface area  $S_e$  can be determined accurately from a classical comparison plot based on the adsorption of a vapour, such as  $\text{N}_2$  [22,23],  $\text{C}_6\text{H}_6$  [24] or  $\text{CH}_2\text{Cl}_2$  [25] on the given carbon and on a non-porous reference (usually a carbon black). The foregoing techniques lead therefore to reliable values of the micropore surface area  $S_{\text{mi}}$  and the external surface  $S_e$  (the corresponding values are given in Table 1).

The amount and the type of oxygen found on the surface was determined by TPD [26,27] and/or a technique based on  $\Delta_i H(\text{H}_2\text{O})$ , the enthalpy of immersion of the carbons into water [28]. As discussed elsewhere [26], for the oxidized

Table 1  
Structural, chemical and electrochemical characteristics of the activated carbons

Carbon	CMS	CMS-H2	DCG-5	XC-72-17%	BV46	BV46-ox	PX-21	M-30	AZ46-0	AZ46-3	AZ46-5	AZ46-10
$W_o$ (cm <sup>3</sup> g <sup>-1</sup> )	0.25	0.25	0.54	0.13	0.40	0.42	1.20	0.7	0.33	0.32	0.32	0.33
$W_o^*$ (cm <sup>3</sup> g <sup>-1</sup> )	0.01	0.01	0.20	0.04	0.15	0.19	0.79	0.33	0.10	0.07	0.06	0.05
$E_o$ (kJ mol <sup>-1</sup> )	26.1	26.2	21.2	21.3	21.4	19.8	17.5	19.6	22.6	23.5	23.9	24.5
$L_o$ (nm)	0.75	0.73	1.1	1.1	1.1	1.29	~2	1.33	0.96	0.89	0.86	0.82
$S_{mi}$ (m <sup>2</sup> g <sup>-1</sup> )	625	685	982	259	727	651	1166	1050	668	719	744	805
$S_e$ (m <sup>2</sup> g <sup>-1</sup> )	~20	28	40	119	110	112	104	50	140	131	117	115
$-\Delta_f H[C_6H_6]$ (J g <sup>-1</sup> )	95.1	92.0	146.0	54.0	131.4	134.0	268.9	219.0	110.0	114.4	112	112
[O] (mmol g <sup>-1</sup> )	1.31	1.2	2.2	0.2	0.32	3.26	8	1.3	0.81	4.50	5.31	6.56
[O] (μmol m <sup>-2</sup> )	1.96	1.68	2.15	0.53	0.38	4.27	6.30	1.20	1.00	5.30	6.17	7.13
Charge–discharge, $C$ (F g <sup>-1</sup> )												
1 mA cm <sup>-2</sup>	115	104	169	38	142	155	322	204	126	150	153	144
10 mA cm <sup>-2</sup>	108	95	153	37	133	137	265	180	115	132	102	93
50 mA cm <sup>-2</sup>	95	52	138	33	123	122	206	160	105	88	98	30
70 mA cm <sup>-2</sup>	91	–	129	–	120	112	171	146	102	62	69	–
Voltammetry												
5 mVs <sup>-1</sup>	115	104	160	43	147	148	263	193	124	147	141	121
20 mVs <sup>-1</sup>	105	77	130	41	129	134	165	152	113	94	106	97
50 mVs <sup>-1</sup>	84	47	85	35	107	106	84	–	90	49	71	39

$$W_o^* = W_o - 3.5 \times 10^{-4} S_{mi}$$

carbons of the present series, the surface oxygen is evenly distributed between the main chemical functions, namely acidic, phenolic and inert groups (e.g. carbonyl). For example, in the case of carbons of series AZ46, there exists a linear relationship between the surface acidity (meq. NaOH g<sup>-1</sup>) and the total oxygen content. As shown by immersion calorimetry into water, following the preadsorption of *n*-nonane, the oxygen-containing complexes are distributed relatively evenly over the microporous structure [19,29]. This hypothesis is also confirmed by the modelling of water adsorption in typical PSDs [30] and it follows that the chemistry of the external surface is not distinct from that found in the micropores.

These techniques provide a reliable structural characterization of the material and, in particular, a reliable assessment of the microporous and external surface areas,  $S_{mi}$  and  $S_e$ . Moreover, as seen in Table 1, the 12 carbons cover a wide range of pore sizes (0.7–2 nm) and of oxygen contents (0.2–6.6 mmol g<sup>-1</sup> or 0.4–7.1 μmol m<sup>-2</sup>). This includes most commercial activated carbons (oxygen contents below 1 μmol m<sup>-2</sup>), as well as their oxidized forms, which justifies an analysis leading to the correlations presented below.

## 2.2. Electrochemical characteristics

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). Two molar H<sub>2</sub>SO<sub>4</sub> aqueous solution

was used as electrolyte. The capacitance  $C$  was determined by galvanostatic charge–discharge voltage cycles from 0 to 0.8 V at current density  $d$  of 1, 10, 50 and 70 mA cm<sup>-2</sup> of electrode surface. The specific capacitance  $C$  (F g<sup>-1</sup>) of a single electrode has been calculated by using the expression

$$C = 2I \frac{\Delta t_d}{m_c \Delta V_d} \quad (1)$$

where  $I$  is the current,  $\Delta t_d$  the time spent during the discharge,  $\Delta V_d$  the voltage decrease in the discharge and  $m_c$  is the weight of carbon loaded in the composite electrode [9]. From these data, it is possible to calculate the capacitances either in F g<sup>-1</sup> or F cm<sup>-3</sup> for the actual capacitor (carbon + carbon black + binder, etc.). Voltammetry experiments at scan rates of 5, 20 and 50 mV s<sup>-1</sup> were also used for estimating the specific capacitance of each electrode according to

$$C = \frac{q_a + |q_c|}{m_c \Delta V} \quad (2)$$

where  $q_a$  and  $q_c$  are the anodic and cathodic voltammetric charges on positive and negative sweeps and  $\Delta V$  is the potential range of CV (0.8 V) [31]. As shown in Table 1, a satisfactory agreement was found between the data obtained by both techniques, but our correlations are based exclusively on the first technique, which appears to be more accurate.

## 3. Results and discussion

### 3.1. Limiting capacitance $C_o$ at 1 mA cm<sup>-2</sup> and structural properties of the carbons

As shown by Qu and Shi [9,10], who investigated the double-layer capacitance at low current density for more than

30 carbons (activated microbeads and fibers),  $S_{\text{BET}}$  is often larger than  $S_{\text{mi}} + S_{\text{e}}$ , which is not surprising [21]. These different areas were obtained, respectively, from the analysis of the nitrogen isotherm with the BET model, the DFT technique and comparison plots. The specific capacitance at low current densities,  $C_0$ , in  $\text{F m}^{-2}$  of carbon surface area and given by the ratio

$$C_0 (\text{F m}^{-2}) = \frac{C_0 (\text{F g}^{-1})}{S_{\text{BET}} (\text{m}^2 \text{g}^{-1})} \quad (3)$$

varies between 0.06 and  $0.22 \text{ F m}^{-2}$  for a 5 M KOH electrolyte. On the other hand, for highly activated carbon fibers with BET surface areas between  $2700$  and  $3200 \text{ m}^2 \text{g}^{-1}$  and a 1 M  $\text{H}_2\text{SO}_4$  electrolyte [5], one obtains values as low as  $0.07$ – $0.11 \text{ F m}^{-2}$ . However, the average micropore sizes and volumes suggest much smaller real surfaces.

A closer examination of Shi's data shows that a better correlation is obtained for  $C_0$  if one use  $S_{\text{tot}} = S_{\text{mi}} + S_{\text{e}}$ . This leads to an average capacitance of  $0.138 \pm 0.038 \text{ F m}^{-2}$  (standard deviation for 30 values). For our carbons and 2 M  $\text{H}_2\text{SO}_4$  (Table 1),  $S_{\text{tot}}$  leads to  $0.172 \pm 0.038 \text{ F m}^{-2}$ . These values are similar, but in view of their scatter, they are only indicative for the whole spectrum of activated carbons. The recent data of Gryglewicz et al. [4] for 1 M  $\text{H}_2\text{SO}_4$  and 6 M KOH electrolytes lead, respectively, to  $0.127 \pm 0.028$  and  $0.095 \pm 0.024 \text{ F m}^{-2}$ . Although no estimate is given by these authors, the simple relation  $L$  (nm) =  $2000V_{\text{mi}} (\text{cm}^3 \text{g}^{-1})/S_{\text{mi}} (\text{m}^2 \text{g}^{-1})$  [19] suggests average micropore widths of 0.72 nm for all carbons, which is surprising.

It was first suggested by Shi that  $C_0$ , the capacitance at low current density, results from separate contribution from  $S_{\text{mi}}$  and  $S_{\text{e}}$ ,

$$C_0 (\text{F g}^{-1}) = c_{\text{mi}} S_{\text{mi}} + c_{\text{ext}} S_{\text{ext}} \quad (4)$$

For the aqueous KOH electrolyte used by Shi, parameters  $c_{\text{mi}}$  and  $c_{\text{ext}}$  are, respectively, 0.195 and  $0.74 \text{ F m}^{-2}$  for activated microbeads and 0.145 and  $0.075 \text{ F m}^{-2}$  for activated fibers (it should be noted that the value of  $0.74 \text{ F m}^{-2}$  is unusually high, since the external surface area of the two types of carbons are similar). Our own data (Table 1), based on 2 M  $\text{H}_2\text{SO}_4$ , leads to  $c_{\text{mi}} = 0.20 \text{ F m}^{-2}$  and  $c_{\text{ext}} = 0.022 \text{ F m}^{-2}$  ( $R = 0.916$ ).

These results show that Shi's Eq. (4) provides a better description for  $C_0$ , but parameters  $c_{\text{mi}}$  and  $c_{\text{ext}}$  depend both on the electrolyte, which is not too surprising, and other factors. The latter may include experimental conditions, as well as structural and chemical properties of the carbons, as suggested by different authors. For example, Gryglewicz et al. [4] suggest that for activated carbons with highly developed surface areas and a low mesopore fraction, the double-layer capacitance also depends on the pore size distribution. It follows that a closer examination of the parameters leading to a further improvement of Eq. (4) should be based on clearly defined experimental conditions, using sets of well-characterized carbons, ideally of the same type (activated carbons), of the same origin (ligno-

cellulosic) and known chemical treatments. Consequently, we shall use only the data of Table 1, in order to examine the role of structural and chemical properties on  $C_0$  and  $C$ .

First of all, one may assume that the contribution from the external surface area,  $c_{\text{ext}}$ , is relatively constant for classical activated carbons, often of similar origin. Moreover, as shown by immersion calorimetry [19] and confirmed by the modeling of water adsorption isotherms [29,30], the oxygen-containing complexes are distributed over the entire micropore system, and not limited to the external surface  $S_{\text{e}}$ . This means also that the  $S_{\text{e}}$  will not be the main cause for a decrease in  $C$  with increasing current density.

Frakowiak et al. [2] report values between 0.1 and  $0.16 \text{ F m}^{-2}$  obtained with 6 M KOH for mesoporous carbon nanotubes and a carbon template without microporosity. This is a plausible range for  $c_{\text{ext}}$  and using, for example,  $0.14 \text{ F m}^{-2}$ , it appears that for the carbons of Table 1  $c_{\text{mi}}$  varies from  $0.15 \text{ F m}^{-2}$  (CMS-H2) to  $0.26 \text{ F m}^{-2}$  (PX-21). The data of Qu and Shi [9] show a similar trend, which suggests that  $c_{\text{mi}}$  may be a function of the average micropore width  $L_0$ . Fitting the data of Table 1 to a simple three-parameter equation leads to the correlation ( $R = 0.980$ , see Fig. 1)

$$C_0 (\text{F g}^{-1}) = (0.096 + 0.081L_0)S_{\text{mi}} + 0.124S_{\text{e}} \quad (5)$$

It covers the range  $0.7$ – $0.8 \text{ nm} < L_0 < 2 \text{ nm}$ , where the lower bound corresponds typically to two layers in the micropores, one on each wall. For  $L_0 = 0.75 \text{ nm}$ ,  $c_{\text{mi}} = 0.156 \text{ F m}^{-2}$  against  $0.258 \text{ F m}^{-2}$  for cage-like supermicropores with  $L_0 = 2 \text{ nm}$ . Beyond, one may expect a rapid decrease and the surface acquires the properties of an external surface. One reason is the rapid decrease of the force field in pores beyond 2 nm. This is clearly the case for adsorption, where Dubinin's theory for the volume filling of micropores (TVFM) is no longer valid beyond 2–2.5 nm.

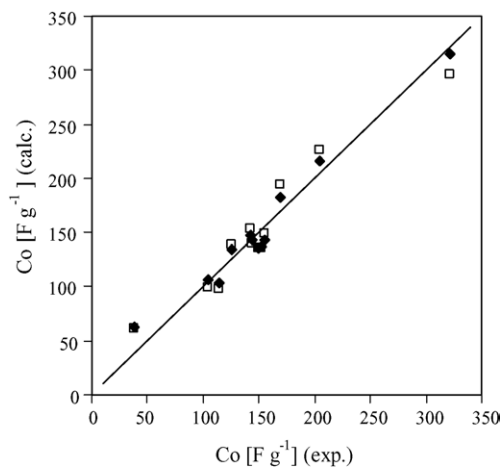


Fig. 1. Correlation between the calculated and experimental capacitances  $C_0$  ( $\text{F g}^{-1}$ ) at  $1 \text{ mA cm}^{-2}$  of electrode, using Eqs. (5) (◆) and (8) (□).



A possible explanation for the increase of  $C_o$  with  $L_o$  is a contribution to  $c_{mi}$  from the layers found between the surface layers. Their number varies between 0 and 3–4 and their contribution is a specific property, possibly limited to micropores. As discussed elsewhere [21], immersion calorimetry suggests that liquid adsorption in microporous carbons can be divided into three contributions, namely from the surface areas  $S_{mi}$  and  $S_e$ , and from the volume  $W_o^*$ . The latter is defined as the volume of liquid found between the layers in contact with the micropore walls, given by

$$W_o^* = W_o - cS_{mi} \quad (6)$$

In the case of benzene, it is found that  $c$  corresponds to a monolayer thickness of 0.41 nm, which is reasonable for this molecule lying flat on a graphitic surface [21,22]. As suggested by Eq. (5),  $C_o$  depends on  $L_o$  and therefore on  $W_o^*$ , which leads to

$$C_o (\text{F g}^{-1}) = c_1 S_{mi} + c_2 S_{ext} + c_3 (W_o - c_4 S_{mi}) \quad (7)$$

The data for the 12 carbons of Table 1 lead to the correlation ( $R=0.982$ , see Fig. 1)

$$C_o (\text{F g}^{-1}) = 0.150 S_{mi} + 0.134 S_{ext} + 158 (W_o - 3.5 \times 10^{-4} S_{mi}) \quad (8)$$

Parameter  $c_4 = 3.5 \times 10^{-4} \text{ cm}^3 \text{ nm}^{-1}$  corresponds to an average monolayer thickness of 0.35 nm for the electrolyte (in the present case,  $\text{H}_2\text{SO}_4$  2 M), which is reasonable. However, it is likely that other electrolytes may lead to different values for parameters  $c_1$ – $c_4$ .

The value of  $W_o^*$  (see Table 1) is practically zero for the carbons with average micropore width  $L_o < 0.7$ – $0.8$  nm (CMS) it increases with  $L_o$ , as more electrolyte can be accommodated between the layer directly in contact with the micropore walls. The contribution of  $W_o^*$  to  $C_o$  varies between 0 and 40% (carbon PX-21).

It should also be pointed out that a contribution of  $158 \text{ F cm}^{-3}$  to the capacitance  $C_o$  seems plausible, as long as it is limited to the one to four intermediate layers found inside micropores. This is suggested, for example, by the value of  $460 \text{ F cm}^{-3}$  for the layers which are in direct contact with the surface, as obtained for carbon CMS ( $C_o = 115 \text{ F g}^{-1}$  and  $W_o = 0.25 \text{ cm}^3 \text{ g}^{-1}$ ). The micropores of this solid ( $L_o = 0.75$  nm) can accommodate only two layers of 0.35 nm.

Eqs. (8) and (5) are obviously related, as shown by simple algebra. With the definition of  $W_o^*$  (Eq. (6)) and the fact that for slit-shaped micropores  $W_o (\text{cm}^3 \text{ g}^{-1}) = S_{mi} (\text{m}^2 \text{ g}^{-1}) L_o (\text{nm}) / 2000$  [19], Eq. (8) becomes

$$C_o (\text{F g}^{-1}) = [0.150 + 0.079(L_o - 0.70)] S_{mi} + 0.134 S_e \quad (9)$$

0.70 nm is the lower bound for  $L_o$ , as it represents the minimum average pore width in which the walls are covered by a

single layer. After regrouping one obtains

$$C_o (\text{F g}^{-1}) = (0.095 + 0.079 L_o) S_{mi} + 0.134 S_e \quad (10)$$

which is practically Eq. (5). However, the latter has been obtained with only three adjustable parameters.

Eqs. (8) and (10) may provide, formally at least, a good estimate of  $C_o$  for activated carbons with micropores and supermicropores, thus covering practically the whole range of commercially available carbons. However, more data will be needed for carbons with average pore sizes  $L_o$  between 1.5 and 2.5 nm, based preferably on activation series. It is also likely that parameters  $c_1$ – $c_4$  depend on the experimental conditions and on the electrolyte (in the present case, 2 M  $\text{H}_2\text{SO}_4$ ).

Inspection of the data of Table 1 shows that within the experimental uncertainty on  $C_o$  ( $\pm 10\%$ ), this quantity does not depend on the amount of oxygen present on the surface. For example, in the case of series BV and AZ46, where [O] varies, respectively, from 0.38 to 4.27 and 1 to  $7.13 \mu\text{mol m}^{-2}$ . This means that the limiting capacitance  $C_o$  can be assessed on the basis of the structural parameters  $S_{mi}$ ,  $S_e$  and  $W_o^*$  alone (at this stage, we cannot explain the relatively low value of  $C_o = 126 \text{ F g}^{-1}$  observed for carbon AZ46-0, whereas the structural parameters of the carbons in this series are similar).

### 3.2. Variation of $C$ with current density and oxygen content

As shown in the table and reported by different authors, for example [7,9],  $C$  decreases generally with increasing electrode current density  $d$  (1–70  $\text{mA cm}^{-2}$  in the present case). This pattern reflects a large resistance in pores due to the hindering of ion transfer in the randomly connected micropores. Ionic motion in such small pores may be so slow that the total microporous surface may not be utilized for charge storage at high current [2].

It has been reported [32] that the resistance is also an increasing function of the degree of oxidation of the carbon and suggests that the imparted polarity may hinder the motion of ionic species in the micropores. Our preliminary experiments suggest a somewhat faster decrease of  $C$  at higher electrode current densities, as the oxygen content [O] increases. This is clearly illustrated by Fig. 2(a and b), showing the variation of the relative capacitance  $C/C_o$  for carbons AZ46-0, AZ46-3 and AZ46-10, where the oxygen content increases from 0.81 to  $6.56 \text{ mmol g}^{-1}$  or from 1 to  $7.13 \mu\text{mol m}^{-2}$  of total surface  $S_{mi} + S_e$ . The same pattern is observed for carbons BV46 and BV46-ox (0.38 and  $4.27 \mu\text{mol [O] m}^{-2}$ , respectively). Since the carbons of these series have very similar structural characteristics, there is little doubt about the influence of oxygen on the capacitance, even at moderate current densities. However, it should be pointed out that the amounts of oxygen [O] are much higher than is found in standard activated carbons.

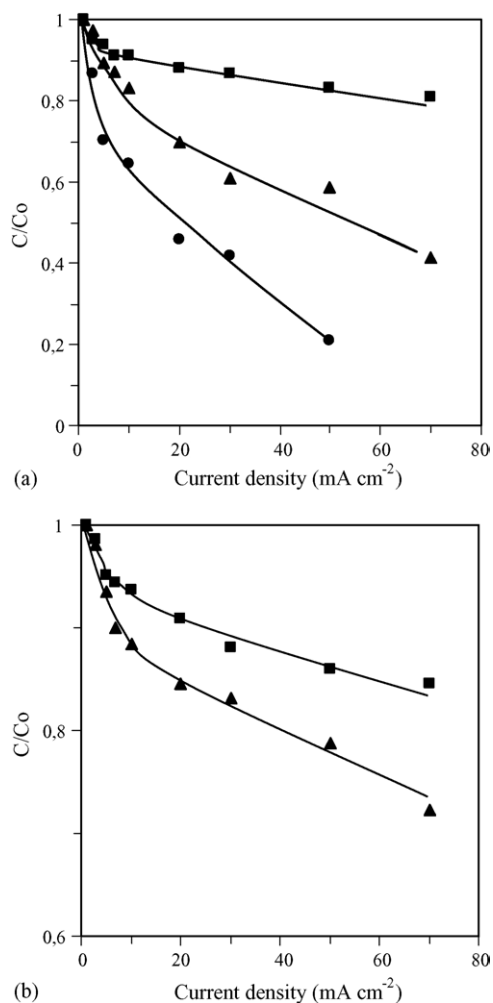


Fig. 2. (a and b) Variation of the relative capacitance  $C/C_0$  with the current density  $d$  for carbons AZ46-0 (■), AZ46-3 (▲), AZ46-10 (●) (a), and BV46 (■), BV46-ox (▲) (b). The data were obtained by the galvanostatic charge–discharge technique.

At this stage of our research, the data for the capacitance  $C$  determined by the galvanostatic charge–discharge technique, the current density  $d$  and the total oxygen content  $[O]$  of the carbons suggest the following overall, but provisional and empirical expression, with a correlation coefficient of 0.975 (see Fig. 3)

$$C \text{ (F g}^{-1}\text{)} = C_0 \exp[-5.32 \times 10^{-3} d(1 + 0.0158[O]^2)] \quad (11)$$

$C_0$  is the value for a current density  $d$  of  $1 \text{ mA cm}^{-2}$  of electrode and  $[O]$  is given in  $\text{mmol g}^{-1}$ . The use of the total oxygen content in Eq. (11) may be questioned, since the mobility may depend on the different types of surface groups (in particular acids). However, for most of the carbons used in this study, there exists a linear relation between the acidity ( $\text{meq. NaOH g}^{-1}$ ) and the total oxygen content  $[O]$  [27]. It appears that three types of oxygen atoms (acidic, basic and inert) are evenly distributed in these carbons. Obviously, the

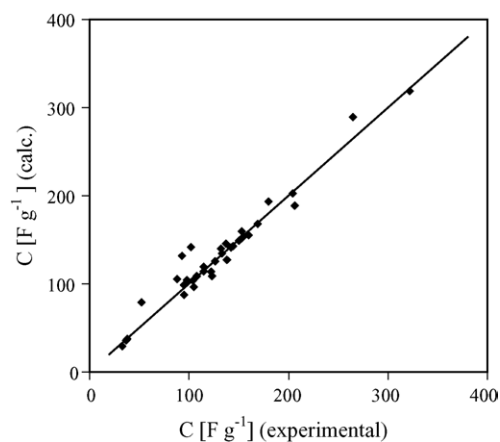


Fig. 3. Correlation between the calculated and experimental capacitances  $C$  ( $\text{F g}^{-1}$ ) for the carbons of Table 1 at electrode current densities  $d$  of 1, 10, 50 and  $70 \text{ mA cm}^{-2}$ , using Eq. (11).  $C_0$  is the capacitance for  $1 \text{ mA cm}^{-2}$ .

influence of the different oxygen-containing surface complexes requires a further study, but Eq. (11) suggests interesting trends. Moreover, this expression provides a useful correlation for the evaluation of the performance of a given carbon to be used for electrochemical applications (capacitors and energy storage devices). Like Eqs. (8) and (10), Eq. (11) also covers a wide range of active carbons and it provides a useful tool for the prediction of their performances as capacitors.

### 3.3. Correlation between $C_0$ and the enthalpy of immersion $\Delta_i H(C_6H_6)$

Finally, it is worthwhile, from a practical point of view, to mention that the limiting capacitance  $C_0$  is related to the enthalpy of immersion of the corresponding carbon into a non-specific liquid, such as benzene (see Table 1). As illustrated by Fig. 4, one obtains a relatively good correlation for the 12 carbons of Table 1 and another 8 carbons currently

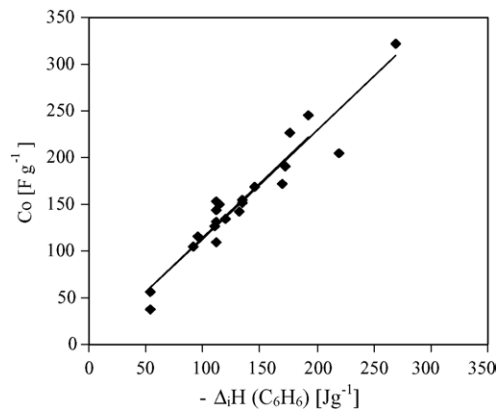


Fig. 4. Empirical correlation between  $C_0$ , the capacitance  $C$  ( $\text{F g}^{-1}$ ) at  $1 \text{ mA cm}^{-2}$  and the enthalpy of immersion  $\Delta_i H(C_6H_6)$  ( $\text{J g}^{-1}$ ) at 293 K for 20 microporous carbons.

under investigation,

$$C_o (\text{F g}^{-1}) = -k \Delta_i H (\text{C}_6\text{H}_6) (\text{J g}^{-1})$$

$$(k = 1.15 \pm 0.10 \text{ FJ}^{-1}) \quad (12)$$

A similar correlation ( $k = 1.2 \text{ FJ}^{-1}$ ) is found for immersion into the electrolyte solution itself (2 M  $\text{H}_2\text{SO}_4$  aq.), but individual deviations exist, due to specific chemical reactions of the acid with surface groups and to the relatively strong physical interaction between water and the surface oxygen atoms [19,26,28]. Although no explanation can be offered at this stage for the origin of Eq. (12), it should be pointed out that the enthalpy of immersion of a microporous carbon into a non-specific liquid, such as benzene, also depends on the structural parameters  $S_{\text{mi}}$ ,  $S_e$  and  $W_o^*$  [21]. At the present stage, Eq. (12) can be used to evaluate, on an empirical basis, the performance of a given carbon as a capacitor.

#### 4. Conclusions

The present study, based on well-characterized activated carbons and investigated under specified electrochemical conditions, is a preliminary report. It examines the structural and chemical parameters which appear to play a role in their capacitance. The limiting capacitance  $C_o$ , corresponding to low current densities  $d$  (e.g.  $1 \text{ mA cm}^{-2}$  of electrode), depends essentially on the structural characteristics  $S_{\text{mi}}$ ,  $S_e$  and  $W_o^*$ , as expressed by Eqs. (7)–(10). The contribution of the ‘core’ volume  $W_o^*$  to  $C_o$  ( $158 \text{ F cm}^{-3}$  on average) is limited to micropores, since the surface of meso and macropores is effectively an external surface area. However, this has to be confirmed by a further study of carbons with supermicropores, subjected to reactivation and of ‘template’ carbons which have virtually no microporosity. Under the present experimental conditions,  $C_o/S_{\text{tot}}$  should be close to  $c_{\text{ext}}$  (approximately,  $0.13 \text{ F m}^{-2}$ ).

From a practical point of view, it appears at this stage that estimates can be made to optimize typical microporous carbons with respect to their capacitance  $C_o$ . This approach can be based on earlier correlations established by Stoeckli et al. [33], relating the evolution of the micropore volume  $W_o$ , the average micropore width  $L_o$  and  $S_{\text{mi}}$ , following chemical and physical activation of various precursor. In this context, the ‘tailoring’ of micropores, described recently by Py et al. [15,34] is highly relevant for the design of carbon supercapacitors.

As expressed by Eq. (11), the present study also suggests a possible correlation between the current density  $d$  and the oxygen content [O] of the carbon and the capacitance. This equation is empirical and obviously a sound theoretical basis is still needed. However, Eqs. (8) and (11), or their analogues for other experimental conditions, provide a useful tool for the prediction of  $C$  for typical activated carbons. The same is true for Eq. (12), which relates empirically  $C_o$  and  $\Delta_i H$  into benzene or any non-specific liquid.

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