

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

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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 to 1270 m² g⁻¹ and specific capacitances C up to 320 Fg⁻¹ have been investigated, using H₂SO₄ 2M as electrolyte. Some of the carbons have also been oxidized with (NH₄)₂S₂O₈, which leads to specific oxygen contents between 0.4 and 7.1 μmol per m² of carbon surface area. It appears that C_o , the limiting capacitance at a current density of 1 mA per cm² 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 to 70 mA per cm² 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 250 to 270 F m⁻² for supermicropores. It is suggested, that the volume W_o^* of the electrolyte found between the surface layers in pores wider than 0.7 to 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.

Keywords: A. Electrochemical capacitor; Activated carbon; Microporosity; Surface area; Surface oxygen; Calorimetry

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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 ref. [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 consist of interconnected cavities between twisted graphitic (or aromatic) sheets. Classical techniques based on the adsorption of molecules of variable dimensions (0.4 to 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 to 1 $\text{cm}^3 \text{g}^{-1}$. For commercial activated carbons, the surface area of the micropore walls, S_{mi} , is in the range of 700 to 1000 $\text{m}^2 \text{g}^{-1}$, but in special cases it can reach 1200 to 1400 $\text{m}^2 \text{g}^{-1}$. (This limit seems realistic for activated carbons, if one keeps in 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_{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 to six layers, the upper limit corresponding to supermicropores ($L \sim 2.5$ nm). The layers which are not in direct contact with the surface (up to 4 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 on 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 to 300 F per gram of carbon. Attempts have been made to correlate this property with the microporous and external surface areas S_{mi} and S_e , as well as S_{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_{BET} corresponds to the total surface area $S_{mi} + S_e$ 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 m^2 of BET surface area can be misleading for carbons with a large proportion of supermicropores. Since C depend on the actual surface area of a carbon, it is necessary to use the correct values of S_{mi} and S_e . On the basis of 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 emphasis 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 ($d \sim 1mA$ per cm^2 of electrode). It appears that the volume W_o^* also plays an important role, beside S_{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 mA per 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°C of ligno-cellulosic precursors (series BV, AZ46), of anthracites (CMS, DCG-5, and of 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 F per gram 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 CO₂ isotherm with the help of model isotherms obtained by Monte Carlo simulations (CMS, DCG-5, 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 $2000W_o$ (cm³g⁻¹)/ S_{mi} (m²g⁻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 N₂ [22, 23], C₆H₆ [24] or CH₂Cl₂ [25] on the given carbon and on a non-porous reference (usually a carbon black). The foregoing techniques leads therefore to reliable values of the micropore surface area S_{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 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^{-1}) 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 twelve carbons cover a wide range of pore sizes (0.7 to 2 nm) and of oxygen contents (0.2 to 6.6 mmol g^{-1} or 0.4 to 7.1 $\mu\text{mol m}^{-2}$). This includes most commercial activated carbons (oxygen contents below 1 $\mu\text{mol m}^{-2}$), 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). 2M H_2SO_4 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 per cm^2

of electrode surface. The specific capacitance C (Fg^{-1}) of a single electrode has been calculated by using the expression

$$C = 2 I (\Delta t_d) / (m_c \Delta V_d) \quad (1)$$

where I is the current, Δt_d is the time spent during the discharge, ΔV_d is the voltage decrease in the discharge and m_c the weight of carbon loaded in the composite electrode [9]. From this data, it is possible to calculate the capacitances either in F per gram or F per cm^3 for the actual capacitor (carbon + carbon black + binder, etc.). Voltammetry experiments at scan rates of 5, 20 and 50 mV s^{-1} were also used for estimating the specific capacitance of each electrode according to

$$C = (q_a + |q_c|) / m_c \Delta V \quad (2)$$

where q_a and q_c are the anodic and cathodic voltammetric charges on positive and negative sweeps and ΔV 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^{-2} and structural properties of the carbons

As shown by Shi [9,10], who investigated the double layer capacitance at low current density for more than 30 carbons (activated microbeads and fibers), S_{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_o , in F per m^2 of carbon surface area and given by the ratio

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

varies between 0.06 and 0.22 F m^{-2} for a 5M KOH electrolyte, On the other hand, for highly activated carbon fibers with BET surface areas between 2700 and 3200 $m^2 \text{ g}^{-1}$ and a 1 M H_2SO_4 electrolyte [5], one obtains values as low as 0.07 to 0.11 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_o if one use $S_{\text{tot}} = S_{\text{mi}} + S_e$. This leads to an average capacitance of (0.138 ± 0.038) F m^{-2} (standard deviation for 30 values). For our carbons and 2M H_2SO_4 (Table 1), S_{tot} leads to (0.172 ± 0.038) 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 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} . 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_o , the capacitance at low current density results from separate contribution from S_{mi} and S_e ,

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

For the aqueous KOH electrolyte used by Shi, parameters c_{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. (It should be noted that the value of 0.74 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 H_2SO_4 , leads to $c_{mi} = 0.20 \text{ F m}^{-2}$ and $c_{ext} = 0.043 \text{ F m}^{-2}$ ($R = 0.893$).

These results show that Shi's Eq. (4) provides a better description for C_o , but parameters c_{mi} and c_{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 (lignocellulosic) 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_o and C .

First of all, one may assume that the contribution from the external surface area, c_{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_e . This means also, that the S_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 F m^{-2} obtained with 6M KOH for mesoporous carbon nanotubes and a carbon template without microporosity. This is a plausible range for c_{ext} and using, for example 0.14 F m^{-2} , it appears that for the carbons of

Table 1 c_{mi} varies from 0.15 F m^{-2} (CMS-H2) to 0.26 F m^{-2} (PX-21). The data of Shi [9] shows a similar trend, which suggests that c_{mi} may be a function of the average micropore width L_o . Fitting the data of Table 1 to a simple three parameter equation leads to the correlation ($R = 0.980$, see Fig. 1)

$$C_o (\text{F g}^{-1}) = (0.096 + 0.081L_o)S_{mi} + 0.124 S_e \quad (5)$$

It covers the range $0.7\text{-}0.8 \text{ nm} < L_o < 2 \text{ nm}$, where the lower bound corresponds typically to two layers in the micropores, one on each wall. For $L_o = 0.75 \text{ nm}$, $c_{mi} = 0.156 \text{ F m}^{-2}$, against 0.258 F m^{-2} for cage-like supermicropores with $L_o = 2 \text{ nm}$. 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 $2\text{-}2.5 \text{ nm}$.

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 to 4 and their contribution is a specific property, limited to micropores (As pointed out above, in meso- and macropores c_{mi} probably reduces rapidly to c_{ext}).

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

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

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

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

Parameter $c_4 = 3.5 \cdot 10^{-4} \text{ cm}^3 \text{ nm}^{-1}$ corresponds to an average monolayer thickness of 0.35 nm for the electrolyte (in the present case H_2SO_4 2M), which is reasonable. However, it is likely that other electrolytes may lead to different values for parameters c_1 to c_4 .

The value of W_o^* (see Table 1), is practically zero for the carbons with average micropore width $L_o < 0.7$ to 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 F cm^{-3} to the capacitance C_o seems plausible, as long as it is limited to the 1-4 intermediate layers found inside micropores. This is suggested, for example, by the value of 460 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 ($L_o = 0.75 \text{ nm}$) 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 $W_o (\text{cm}^3 \text{ g}^{-1}) = S_{\text{mi}}(\text{m}^2 \text{ g}^{-1})L_o (\text{nm})/2000$ [19], Eq. (8) becomes

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

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

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

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

Equations (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 to c_4 depend on the experimental conditions and on the electrolyte (in the present case 2M H_2SO_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 $[\text{O}]$ varies respectively from 0.38 to 4.27 $\mu\text{mol m}^{-2}$ 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 to 70 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-b), showing the variation of the relative capacitance C/C_0 for carbons AZ-46-0, AZ46-3 and AZ-46-10, where the oxygen content increases from 0.81 to 6.56 mmol g⁻¹, or 1 to 7.13 μmol per m² of total surface $S_{mi} + S_e$. The same pattern is observed for carbons BV46 and BV46-ox (respectively 0.38 and 4.27 μmol $[O]$ m⁻²). 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.

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 suggests the following overall, but provisional and empirical expression, with a correlation coefficient of 0.975 (see Fig. 3)

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

C_0 is the value for a current density d of 1 mA per cm² of electrode and $[O]$ is given in 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 (meq. NaOH g^{-1}) and the total oxygen content $[\text{O}]$ [27]. It appears that three types of oxygen atoms (acidic, basic and inert) are evenly distributed in these carbons. Obviously, the 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 Equations (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_o 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_o 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 twelve carbons of Table 1 and another eight carbons currently under investigation,

$$C_o[\text{F g}^{-1}] = -k \Delta_i H(C_6H_6) [\text{J g}^{-1}] \quad (k = 1.15 \pm 0.10 \text{ F J}^{-1}) \quad (12)$$

A similar correlation ($k = 1.2 \text{ F J}^{-1}$) is found for immersion into the electrolyte solution itself, (2 M H_2SO_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_{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 mA cm^{-2} of electrode), depends essentially on the structural characteristics S_{mi} , S_e , and W_o^* , as expressed by Eqs. (7)-(10). The contribution of the ‘core’ volume W_o^* to C_o (158 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_{tot} should be close to c_{ext} (approximately 0.13 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, Daguerre and Guillot [33], relating the evolution of the micropore volume W_o , the average micropore width L_o and S_{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 Eq. is empirical and obviously, a sound theoretical basis is still needed. However, equations (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_0 and $\Delta_i H$ into benzene or any non-specific liquid.

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Captions to the figures

Fig. 1. Correlation between the calculated and experimental capacitances C_0 ($F g^{-1}$) at 1 mA per cm^2 of electrode, using Equations (5) (\blacktriangle) and (8) (\blacksquare).

Fig. 2 (a-b). Variation of the relative capacitance C/C_0 with the current density d for carbons AZ46-0 (\blacksquare), AZ46-3 (\blacktriangle), AZ46-10 (\bullet) (a), and BV46 (\blacksquare), BV46-ox (\blacktriangle) (b). The data was obtained by the galvanostatic charge-discharge technique.

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

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

Fig. 1

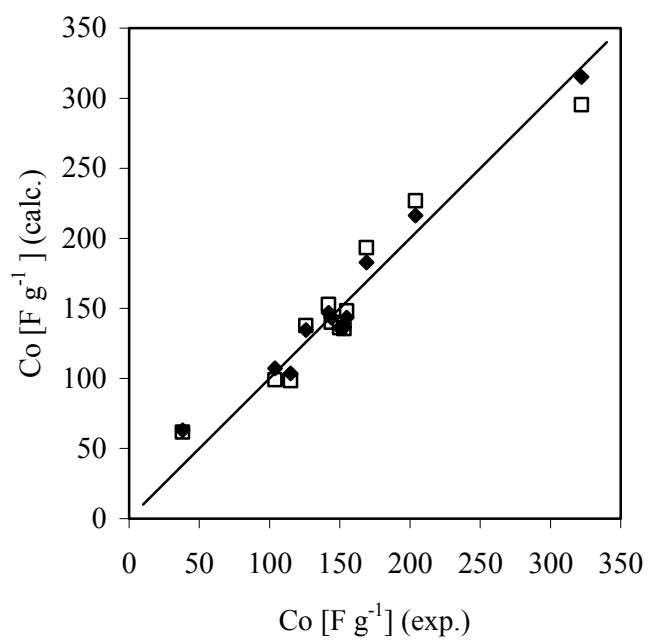


Fig. 2 (a-b)

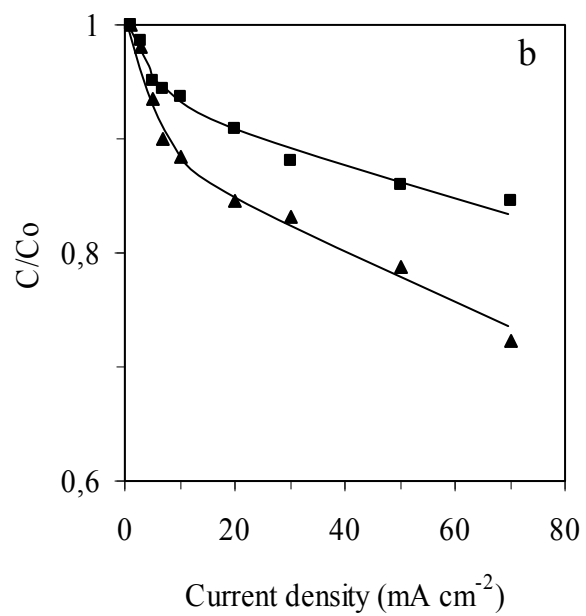
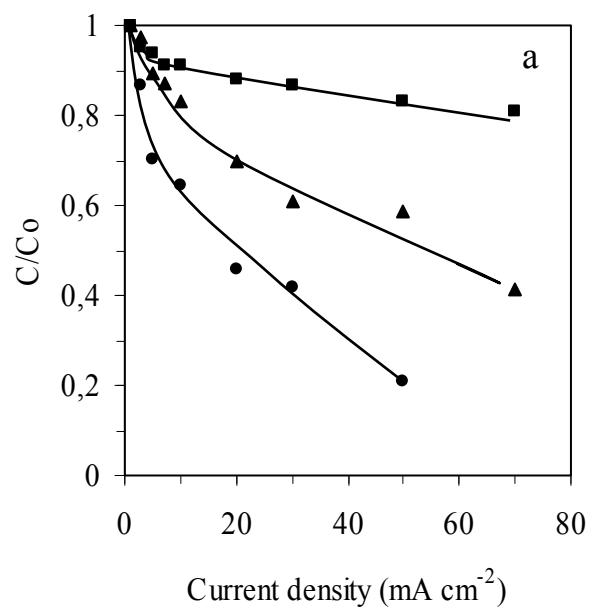


Fig. 3.

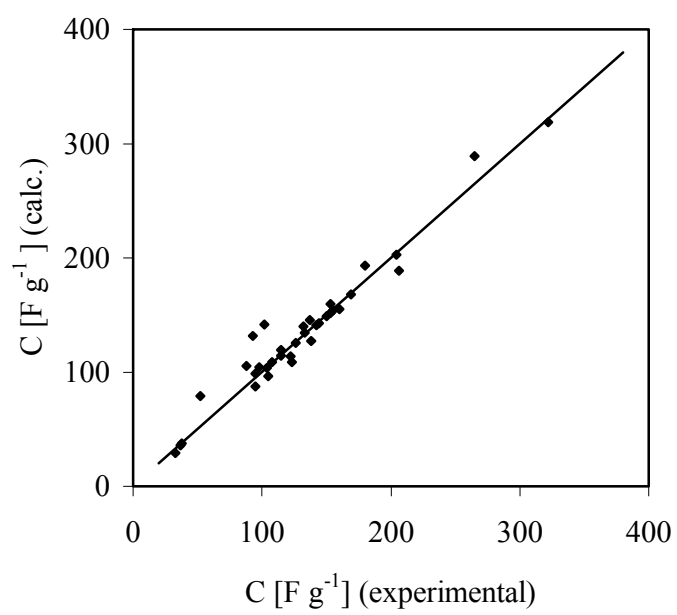


Fig. 4.

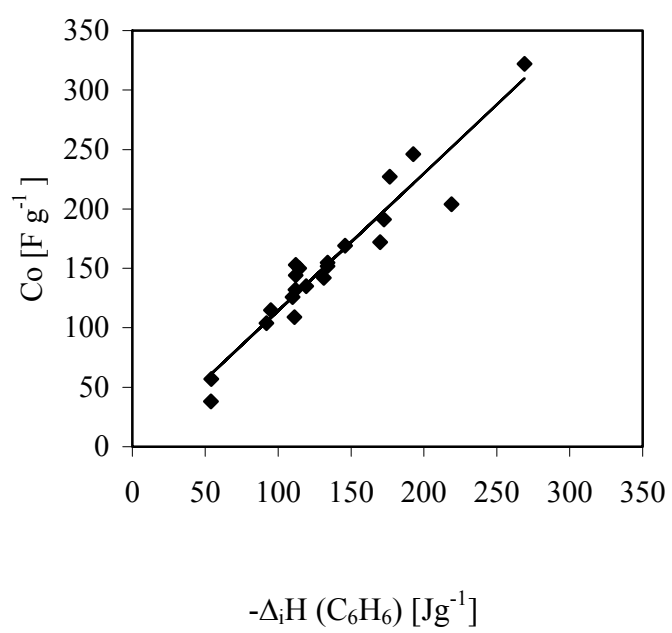


Table 1. Structural, chemical and electrochemical characteristics of the activated carbons. $W_o^* = W_o - 3.5 \times 10^{-4} S_{mi}$

Carbon		CMS	CMSH2	DCG-5	XC-72-17%	BV46	BV46-Ox	PX-21	M-30	AZ46-0	AZ46-3	AZ46-5	AZ46-10
W_o ($\text{cm}^3 \text{g}^{-1}$)		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^* ($\text{cm}^3 \text{g}^{-1}$)		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 (kJmol^{-1})		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} ($\text{m}^2 \text{g}^{-1}$)		625	685	982	259	727	651	1166	1050	668	719	744	805
S_e ($\text{m}^2 \text{g}^{-1}$)		~20	28	40	119	110	112	104	50	140	131	117	115
$-\Delta_i H[\text{C}_6\text{H}_6]$ (Jg^{-1})		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^{-1})		1.31	1.2	2.2	0.2	0.32	3.26	8	1.3	0.81	4.50	5.31	6.56
[O] ($\mu\text{mol m}^{-2}$)		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	[1 mAcm^{-2}]	115	104	169	38	142	155	322	204	126	150	153	144
	[10 mAcm^{-2}]	108	95	153	37	133	137	265	180	115	132	102	93
	[50 mAcm^{-2}]	95	52	138	33	123	122	206	160	105	88	98	30
	[70 mAcm^{-2}]	91	-	129	-	120	112	171	146	102	62	69	-
C (Fg^{-1})													
	[5 mVs^{-1}]	115	104	160	43	147	148	263	193	124	147	141	121
	[20 mVs^{-1}]	105	77	130	41	129	134	165	152	113	94	106	97
Voltammetry	[50 mVs^{-1}]	84	47	85	35	107	106	84	-	90	49	71	39