

# Correlation between capacitances of porous carbons in acidic and aprotic EDLC electrolytes

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## Abstract

A study based on a total of 41 nanoporous carbons shows that there exists a good correlation between the limiting gravimetric capacitances  $C_o$  at low current densities  $j$  ( $1 \text{ mA cm}^{-2}$ ) measured in aprotic ( $1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NBF}_4$  in acetonitrile) and in acidic ( $2 \text{ M}$  aqueous  $\text{H}_2\text{SO}_4$ ) electrolytes. The comparison of the surface-related capacitances ( $\text{F m}^{-2}$ ) of well characterized samples with the amount of thermodesorbed CO suggests a strong contribution of CO generating surface groups to charge storage in the acidic electrolyte, but a negligible contribution in the aprotic medium. It also appears that the decrease of the capacitance with current density is similar in both electrolytes. This confirms that the average micropore width and the  $\text{CO}_2$  generating surface groups are the main factors which limit the ionic mobility in both electrolytes.

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

## 1. Introduction

In view of their technological applications, supercapacitors based on porous carbons have been investigated extensively [1], using either aqueous (*e.g.*  $\text{H}_2\text{SO}_4$ ,  $\text{KOH}$ ) or aprotic (*e.g.*  $(\text{C}_2\text{H}_5)_4\text{NBF}_4$  in acetonitrile or propylene carbonate) media. A number of useful correlations have been established so far, relating their electrical double layer capacitance (EDLC) to structural and chemical properties of the carbons [1–4]. For example, it has been shown recently that in the  $2 \text{ M}$  aqueous  $\text{H}_2\text{SO}_4$  electrolyte the specific capacitance depends on a contribution from the total surface area  $S_{\text{tot}}$  (the sum of the micropore and external areas) and from oxygen-containing surface groups [3]. These can be divided into species generating either CO or  $\text{CO}_2$  in thermally programmed desorption (TPD). The limiting gravimetric capacitance  $C_{o,\text{acidic}}$  measured at low cur-

rent densities  $j$  (typically  $1 \text{ mA cm}^{-2}$ ) was shown to depend essentially on the groups generating CO. An analysis based on a large number of well performing carbons leads to [3]

$$C_{o,\text{acidic}} (\text{F g}^{-1}) = (0.081 \pm 0.007) (\text{F m}^{-2}) S_{\text{tot}} (\text{m}^2 \text{g}^{-1}) + (63 \pm 5) (\text{F mmol}^{-1}) [\text{CO}] (\text{mmol g}^{-1}) \quad (1)$$

(This correlation did not consider carbons subjected to oxidation by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , as well as fibers, for which the CO contribution is well below  $60 \text{ F mmol}^{-1}$ ).

At higher current densities  $j$ , the capacitance  $C[j]_{\text{acidic}}$ , a function of  $j$ , depends also on the  $\text{CO}_2$ -generating surface groups and on the average width  $L_0$  of the slit-shaped nanopores ( $0.4 < L_0 < 2 \text{ nm}$ ). It was shown [3] that

$$C[j]_{\text{acidic}} (\text{F g}^{-1}) = C_{o,\text{acidic}} \exp(-j(0.00180/L_0 + 0.00602[\text{CO}_2])) \quad (2)$$

This leads to a coherent description of the EDLC properties of carbons in the  $\text{H}_2\text{SO}_4$  electrolyte.

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The present study examines, how far this approach can be extended to the case of an aprotic electrolyte such as  $(C_2H_5)_4NBF_4$  in acetonitrile. The latter is also very popular in view of the higher working voltage and in view of the fact that almost all of today's commercially available carbon based EDLCs utilize organic electrolytes. However, a systematic comparison between the EDLC performances of the two electrolytes for the same carbons and under similar experimental conditions is still lacking.

## 2. Experimental

### 2.1. Carbons

The comparative EDLC study is based on a total of 30 microporous carbons [3] and 5 templated mesoporous carbons [2,4,5], as well as a high surface area graphite (HSAG-300) [2]. As discussed in detail [6], a reliable determination of the surface areas of the carbons is essential for the study of EDLC properties in carbons. It appears that the relevant quantity is the total surface area  $S_{tot}$ , which is the sum of the micropore surface area and the external surface area.

All the samples have been characterized within the framework of Dubinin's theory [6] by standard techniques based on vapour adsorption, typically with nitrogen at 77 K and/or benzene near 293–298 K, and by immersion calorimetry (293 K) into liquids with various molecular dimensions. In some cases, the characterization also included the analysis of the  $CO_2$  isotherm by Monte Carlo simulations, which leads to the pore size distribution. Moreover, the analysis of the nitrogen isotherms by different methods such as the comparison plot based on the reference nitrogen isotherm for *Vulcan 3G* and the DFT method leads to an independent assessment of the microporous and exter-

nal surface areas of the carbons. This data was further cross-checked with the corresponding enthalpy of immersion of the carbons into dilute aqueous solution of phenol (0.4 M), which gives directly  $S_{tot}$ . The foregoing techniques lead therefore to reliable values of the total surface area [2,3]. The corresponding values are given in Table 1.

Twenty carbons, presented in Table 1, have also been characterized by TPD, which provides further information on the role of surface groups in the EDLC properties. Some of the carbons (nos. 2, 14, 19 and 20) show deviations from Eq. (1), but they nevertheless allow useful comparisons between aprotic and acidic electrolytes.

For comparison purposes, we added the data for another 5 porous carbons reported in the literature by Frackowiak et al. [7,8], determined for both electrolytes and under similar experimental conditions. Carbon T-0 [9], a molecular sieve with a marked 'gate' effect around 0.60 nm was also investigated. This 'gate' effect limits the internal surface area accessible to larger ions such as  $(C_2H_5)_4N^+$  (0.69 nm), as opposed to the solvated  $SO_4^{2-}$  ion (0.53 nm).

### 2.2. Electrochemical measurements

The electrochemical measurements were carried out in sandwich-type capacitors made of two carbon pellets (8 mm in diameter, ca. 0.3 mm thick) separated by glassy fibrous paper (0.3 mm thick). 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). 1 M  $(C_2H_5)_4NBF_4$  in acetonitrile and 2 M aqueous  $H_2SO_4$  were used as electrolytes.

The full cell capacitance was determined by galvanostatic charge-discharge cycles at constant current density  $j$

Table 1  
Main characteristics and electrochemical properties of carbons characterized by TPD

Carbon	$C_{o, aprotic}$ ( $F g^{-1}$ )	$C_{o, acidic}$ ( $F g^{-1}$ )	$S_{tot}$ ( $m^2 g^{-1}$ )	$C_{o, aprotic}/S_{tot}$ ( $F m^{-2}$ )	$C_{o, acidic}/S_{tot}$ ( $F m^{-2}$ )	[CO] ( $\mu mol m^{-2}$ )	[CO <sub>2</sub> ] ( $\mu mol m^{-2}$ )	$L_0$ (nm)
1 CMS	48.6	115	665	0.073	0.173	1.46	0.26	0.75
2 AZ46-3	73.0	150	850	0.086	0.176	2.66	0.96	0.89
3 AZ46-0	75.0	126	808	0.093	0.156	1.12	0.43	0.96
4 XC-72	15.8	22	250	0.063	0.088	$4 \times 10^{-3}$	0.04	1.02
5 BV-46	78.0	142	837	0.093	0.170	0.26	0.12	1.10
6 DCG-5	82.5	169	1022	0.081	0.165	0.85	0.38	1.10
7 PC94-11	80.0	136	909	0.088	0.150	1.00	0.57	1.12
8 PC94-11-ox	78.0	156	830	0.094	0.188	1.44	1.04	1.18
9 M-1R	91.0	156	1057	0.086	0.147	0.75	0.10	1.23
10 M-1R(PM)	103.0	156	1089	0.095	0.143	0.48	0.02	1.25
11 U02-ox	58.2	102	587	0.099	0.174	0.99	0.94	1.26
12 BV46-Ox	86.0	155	763	0.113	0.203	2.63	0.82	1.29
13 SUPRA DLC-50	95.6	152	1031	0.093	0.147	0.60	0.18	1.33
14 KF-1500	74.5	135	938	0.079	0.144	1.60	0.33	1.38
15 U03	66.5	122	630	0.106	0.194	1.78	0.46	1.80
16 U03-ox.	64.5	150	690	0.093	0.217	2.06	1.27	1.80
17 PX-21	144.6	322	1270	0.114	0.253	2.60	1.10	2.0
18 N-125	83.0	122	772	0.108	0.158	1.24	0.35	2.1
19 Picactif SC	75.3	157	1230	0.061	0.128	1.20	0.18	2.3
20 HSAG 300	21.5	47	330	0.065	0.142	1.97	1.15	Graphite

up to  $150 \text{ mA cm}^{-2}$ . The cell voltage ranged from 0 to 0.8 V for aqueous medium and between 0 and 2 V for the aprotic electrolyte. All capacitance values refer to the capacitance and mass of a single electrode. The data was further cross-checked by cyclic voltammetry (CV) experiments at scan rates of 1, 2, 5, 10, 20 and  $50 \text{ mV s}^{-1}$ .

For selected samples, CV experiments were also carried out by controlling the single electrode potential with respect to a reference electrode using a standard 3-electrode set-up. The average single electrode (half cell) capacitance was then evaluated for a potential range of  $\pm 0.4 \text{ V}$  around the immersion potential (ip) for the acidic electrolyte and  $\pm 1.0 \text{ V}$  around the ip for the aprotic electrolyte, and a sweep rate of  $5 \text{ mV s}^{-1}$ .

### 3. Results and discussion

Fig. 1 shows, for selected samples, the observed good agreement of the specific capacitances measured with the 2-electrodes (full cell) and the 3-electrodes (half cell) set-up in the acidic and in the aprotic electrolyte. In the following, all correlations are therefore based on the galvanostatic charge-discharge cycles on two-electrode system.

As shown in Fig. 2, there exists an overall correlation between the limiting gravimetric capacitances at low current densities  $j$  ( $1 \text{ mA cm}^{-2}$ ),  $C_o$  ( $\text{F g}^{-1}$ ), of the 41 carbons in the aprotic and the acidic electrolytes,

$$C_{o,\text{aprotic}} = (0.54 \pm 0.09) C_{o,\text{acidic}} \quad (3)$$

A similar correlation is seen (Fig. 3) when comparing the surface related capacitances  $C_o/S_{\text{tot}}$  ( $\text{F m}^{-2}$ ), which are more relevant quantities in EDLC studies. (differences between the two graphs are due to the fact that the surfaces

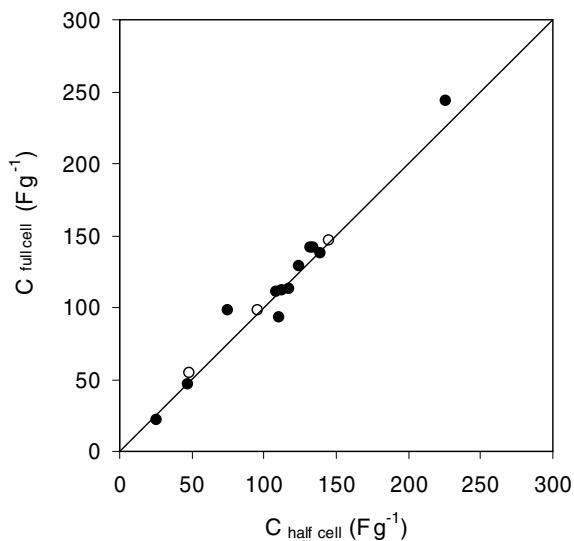


Fig. 1. Correlation between the gravimetric capacitances estimated by cyclic voltammetry in 3-electrodes (half cell) and 2-electrodes (full cell) configuration: (●) at  $5 \text{ mV s}^{-1}$  in  $\text{H}_2\text{SO}_4$  and (○) at  $2 \text{ mV s}^{-1}$  in  $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ . All values refer to the capacitance and mass of a single electrode.

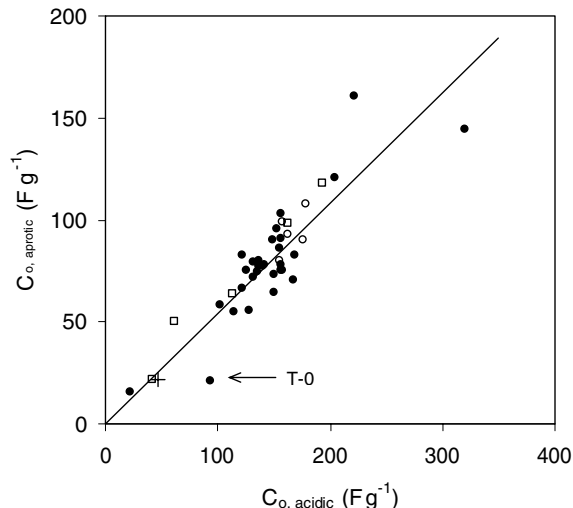


Fig. 2. Comparison of the gravimetric capacitances  $C_{o,\text{aprotic}}$  and  $C_{o,\text{acidic}}$  in  $\text{F g}^{-1}$ , obtained for 30 different microporous carbons (●), a high surface area graphite (+) and 10 templated mesoporous carbons (data from Ref. [2,4,5] (○) and from Ref. [7,8] (□)). The deviation for T-0 reflects exclusion effects in the aprotic electrolyte.

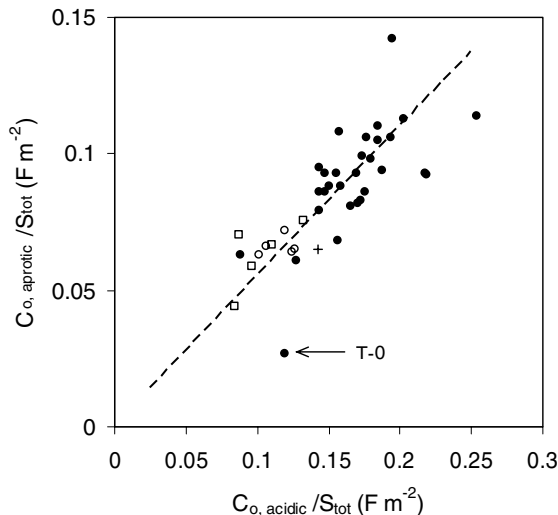


Fig. 3. Comparison of the specific capacitances  $C_{o,\text{aprotic}}/S_{\text{tot}}$  and  $C_{o,\text{acidic}}/S_{\text{tot}}$  in  $\text{F m}^{-2}$ , obtained for 30 different microporous carbons (●), a high surface area graphite (+) and 10 templated mesoporous carbons (data from Ref. [2,4,5] (○) and from Ref. [7,8] (□)). The deviation for T-0 reflects exclusion effects in the aprotic electrolyte.

areas  $S_{\text{tot}}$  vary from carbon to carbon). The obvious deviation observed for carbon T-0 may be attributed to the fact that this material displays a gate effect around  $0.6 \text{ nm}$  [9]. Accordingly, this reduces the accessibility of the micropore system to the large  $(\text{C}_2\text{H}_5)_4\text{N}^+$  ions.

By analogy with our previous studies on the effect of the CO-generating surface groups on the EDLC properties in the acidic electrolyte [3], Fig. 4 shows the correlations between both surface-related capacitances  $C_{o,\text{aprotic}}/S_{\text{tot}}$  and  $C_{o,\text{acidic}}/S_{\text{tot}}$  and the surface density of CO-generating groups,  $[\text{CO}]/S_{\text{tot}}$ , for the 20 carbons of Table 1. The

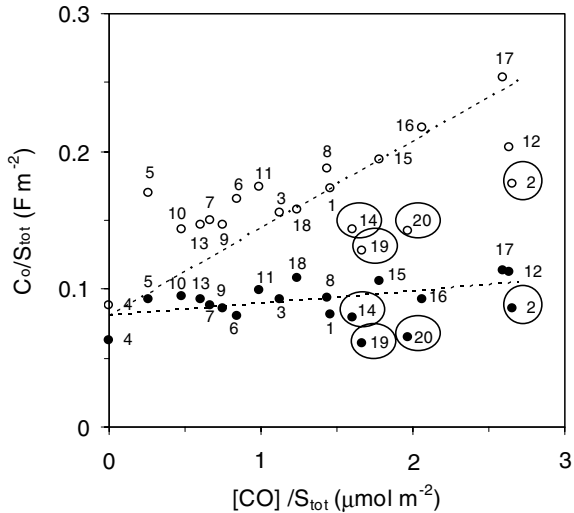


Fig. 4. Variation of the specific capacitances  $C_{o,aprotic}/S_{tot}$  (●) and  $C_{o,acidic}/S_{tot}$  (○) with the surface density of CO-generating groups,  $[CO]/S_{tot}$  (see Table 1). The dotted lines correspond to Eqs. (1) (top) and (4) (bottom).

comparison between the two sets indicates similar trends, the ‘good’ and the ‘bad’ performers being mostly the same in both electrolytes. In particular, carbons nos. 2, 14, 19 and 20, which do not follow Eq. (1) show smaller pseudocapacitance contributions in both media. However, the ratios of their capacitances are close to the average given by Eq. (3). This suggests a scaling between the two electrolytes.

In the case of the aprotic electrolyte, one obtains the following approximate correlation for the carbons which follow closely Eq. (1) in the acidic electrolyte,

$$C_{o,aprotic} \text{ (F g}^{-1}\text{)} = 0.08 \text{ (F m}^2\text{)}^{-1} S_{tot} \text{ (m}^2 \text{ g}^{-1}\text{)} + 9 \text{ (F mmol}^{-1}\text{)} [CO] \text{ (mmol g}^{-1}\text{)} \quad (4)$$

This means that, if surface oxide related pseudocapacitance effects exist in the aprotic electrolyte, they are much weaker than in the acidic electrolyte ( $63 \text{ F mmol}^{-1}$  of CO). The possibility of pseudocapacitance effects in the aprotic electrolyte is supported by our analysis of data provided by Frackowiak et al. [8] for a series of activated carbons derived from polyacrylonitrile. These carbons contain nitrogen and oxygen on their surface and it appears that both  $C_{o,acidic}/S_{tot}$  and  $C_{o,aprotic}/S_{tot}$  increase linearly with the total amount of nitrogen and oxygen of these samples, relative to carbon. Although the amounts derived from elemental analysis are often different from their density on the surface, the data of Frackowiak et al. suggests pseudocapacitance effects in the aprotic electrolyte.

It appears that the lower bounds for the specific surface capacitances in the  $(C_2H_5)_4NBF_4$  and in the  $H_2SO_4$  electrolytes are respectively  $0.063\text{--}0.065 \text{ F m}^{-2}$  and  $0.080 \text{ F m}^{-2}$  (no oxygen containing complexes). Similar values are derived from the analysis of Frackowiak’s data [8].

It is also interesting to point out that the values of  $C_{o,aprotic}$  confirm an earlier correlation observed between  $C_{o,acidic}$  and  $-\Delta_i H(C_6H_6)$  ( $\text{J g}^{-1}$ ), the enthalpy of immersion into benzene at 298 K [2]. This is not too surprising in view of the fact that both properties are related to surface effects. It appears that

$$C_{o,aprotic} \text{ (F g}^{-1}\text{)} = -(0.544 \pm 0.013)\Delta_i H[C_6H_6] \text{ (J g}^{-1}\text{)} \quad (5)$$

This correlation shows less scatter than observed in the case of the acidic electrolyte,  $-(1.1 \pm 0.04)$ . It is not surprising, in view of the smaller influence of the CO-generating surface groups on  $C_{o,acidic}$  and the fact that  $-\Delta_i H[C_6H_6]$  does not depend on the presence of oxygen at all. These correlations provide an alternative means to assess, with a relatively good accuracy, the suitability of a carbon to be used in supercapacitor with both aprotic and acidic electrolytes.

Finally, we compare the variation of the capacitance in the  $(C_2H_5)_4NBF_4$  and the  $H_2SO_4$  electrolytes with increasing current density  $j$ . As summed up by Eq. (2) in the case of the acidic electrolyte, the decrease of the gravimetric capacitance with  $j$  depends mainly on the number of  $CO_2$ -desorbing surface groups and, to some extent, on the average micropore width  $L_0$  below  $0.8\text{--}1 \text{ nm}$  [3]. Data for  $C[j]$  obtained for carbons with both electrolytes in the range  $1 \text{ mA cm}^{-2} < j < 70 \text{ mA cm}^{-2}$  suggests that Eq. (2) also provides a reasonable working basis for the aprotic electrolyte. This is best shown by the ratios of  $C[j]_{aprotic}/C[j]_{acidic}$ , for carbons of different origins and containing surface groups which generate between  $0.10$  and  $1.4 \text{ mmol}$  of  $CO_2$  in TPD. As seen in Table 2, the ratios are similar in the range of  $1$  to  $50\text{--}70 \text{ mA cm}^{-2}$ . This pattern includes carbons with low pseudocapacitances (e.g. AZ46-3), which suggests that the underlying mechanism is the same in both electrolytes (hindered ionic mobility due mainly to the  $CO_2$ -desorbing groups and to the width  $L$  of the smaller micropores). Consequently, Eq. (2) can be used in a straightforward manner for carbons of different origins, with the help of a scaling factor equal to  $C_{o,aprotic}/C_{o,acidic}$ .

Table 2

Ratios of the gravimetric capacitances  $C[j]_{aprotic}/C[j]_{acidic}$  as function of the current density  $j$  (Typical examples for carbons with different amounts of  $CO_2$ -desorbing groups)

Carbon	$CO_2$ (mmol $g^{-1}$ )	Current density, $j$ ( $\text{mA cm}^{-2}$ )							
		1	3	7	10	20	30	50	70
BV46	0.10	0.55	0.56	0.58	0.57	0.57	0.54	0.52	0.46
M-1R	0.13	0.58	0.60	0.62	0.61	0.62	0.59	0.56	0.43
N125	0.27	0.68	0.70	0.71	0.72	0.73	0.73	0.73	0.72
PC94-11	0.52	0.61	0.64	0.66	0.65	0.66	0.62	0.59	0.49
AZ46-3	0.81	0.49	0.48	0.50	0.52	0.56	0.60	0.55	0.61
PC-94-	0.86	0.50	0.51	0.52	0.51	0.49	0.47	0.44	0.45
11-Ox									
PX-21	1.4	0.46	0.43	0.42	0.44	0.43	0.43	0.44	0.37

#### 4. Conclusions

The comparison between the electrochemical properties of a number of activated carbons and mesoporous templated carbons in the aprotic (1 M  $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ /acetonitrile) and in the acidic (2 M aqueous  $\text{H}_2\text{SO}_4$ ) electrolytes suggests that:

- (a) To a first approximation the ratio of the gravimetric capacitances  $C_{o,\text{aprotic}}/C_{o,\text{acidic}}$  for carbons displaying no distinct ion sieving is  $0.54 \pm 0.09$ .
- (b) There may be pseudocapacitance effects in the  $(\text{C}_2\text{H}_5)_4\text{NBF}_4$  electrolyte, but they are much smaller than in the  $\text{H}_2\text{SO}_4$  electrolyte (respectively 9 and  $63 \text{ F mmol}^{-1}$  of CO generated in TPD for the best performing carbons).
- (c) In both electrolytes, the decrease of the capacitance with increasing current density (up to  $50\text{--}70 \text{ mA cm}^{-2}$ ) is controlled in a similar way by the micropore width and the amount of  $\text{CO}_2$  generating surface groups.
- (d) There exists a useful correlation between the limiting specific capacitance  $C_o$  in both electrolytes and the

enthalpy of immersion of carbons into benzene  $-\Delta_f\text{H}(\text{C}_6\text{H}_6)$ , which allows an alternative assessment of the suitability of a given carbon to be used as a supercapacitor electrode material.

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