

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_0 at low current densities j (1 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 M aqueous H_2SO_4) electrolytes. The comparison of the surface-related capacitances (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 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

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1. Introduction

In view of their technological applications, supercapacitors based on porous carbons have been investigated extensively [1], using either aqueous (e.g. H₂SO₄, KOH) or aprotic (e.g. (C₂H₅)₄NBF₄ 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 2M aqueous H₂SO₄ electrolyte the specific capacitance depends on a contribution from the total surface area S_{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 CO₂ in thermally programmed desorption (TPD). The limiting gravimetric capacitance $C_{\text{o, acidic}}$ measured at low current densities j (typically 1 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]

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

(This correlation did not consider carbons subjected to oxidation by (NH₄)₂S₂O₈, as well as fibers, for which the CO contribution is well below 60 F mmol⁻¹).

At higher current densities j , the capacitance $C[j]_{\text{acidic}}$, a function of j , depends also on the CO₂-generating surface groups and on the average width L_0 of the slit-shaped nanopores ($0.4 < L_0 < 2$ nm). It was shown [3] that

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

This leads to a coherent description of the EDLC properties of carbons in the H₂SO₄ electrolyte.

The present study examines, how far this approach can be extended to the case of an aprotic electrolyte such as (C₂H₅)₄NBF₄ 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

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 (293K) into liquids with various molecular dimensions. In some cases, the characterization

also included the analysis of the CO₂ 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 led to an independent assessment of the microporous and external 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, 20) show deviations from Eqn. (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 (C₂H₅)₄N⁺ (0.69 nm), as opposed to the solvated SO₄⁻² ion (0.53 nm).

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). 1M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile and 2M aqueous H_2SO_4 were used as electrolytes.

The full cell capacitance was determined by galvanostatic charge-discharge cycles at constant current density j up to 150 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 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 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 mA cm^{-2}], C_o (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_{tot} (F m^{-2}), which are more relevant quantities in EDLC studies. (Differences between the two graphs are due to the fact that the surfaces areas S_{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 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 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 Eqn. (1) show smaller pseudocapacitance contributions in both media. However, the ratios of their capacitances are close to the average given by Eqn. (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 Eqn. (1) in the acidic electrolyte,

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

This means that, if surface oxide related pseudocapacitance effects exist in the aprotic electrolyte, they are much weaker than in the acidic electrolyte (63 F per mmol 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 $C_{o, \text{acidic}}/S_{\text{tot}}$ and $C_{o, \text{aprotic}}/S_{\text{tot}}$ 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 $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ and in the H_2SO_4 electrolytes are respectively 0.063-0.065 F m^{-2} and 0.080 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 $C_{o, \text{aprotic}}$ confirm an earlier correlation observed between $C_{o, \text{acidic}}$ and $-\Delta_i\text{H}(\text{C}_6\text{H}_6)$ (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

$$C_{o, \text{aprotic}} (\text{Fg}^{-1}) = -(0.544 \pm 0.013) \Delta_i\text{H}[\text{C}_6\text{H}_6] (\text{J g}^{-1}) \quad (5)$$

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 $C_{o, \text{acidic}}$ and the fact that $-\Delta_i\text{H}[\text{C}_6\text{H}_6]$ 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 $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ and the H_2SO_4 electrolytes with increasing current density j . As summed up by Eqn. (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 0.8-1 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 Eqn. (2) also provides a reasonable working basis for the aprotic electrolyte. This is best shown by the ratios of $C[j]_{\text{aprotic}}/C[j]_{\text{acidic}}$, for carbons of different origins and containing surface groups which generate between 0.10 and 1.4 mmol of CO_2 in TPD. As seen in Table 2, the ratios are similar in the range of 1 to 50-70 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, Eqn. (2) can be used in a straightforward manner for

carbons of different origins, with the help of a scaling factor equal to $C_{o, \text{aprotic}}/C_{o, \text{acidic}}$.

4. Conclusions

The comparison between the electrochemical properties of a number of activated carbons and mesoporous templated carbons in the aprotic (1 M $(C_2H_5)_4NBF_4$ /acetonitrile) and in the acidic (2 M aqueous H_2SO_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 ± 0.09 .
- (b) There may be pseudocapacitance effects in the $(C_2H_5)_4NBF_4$ electrolyte, but they are much smaller than in the H_2SO_4 electrolyte (respectively 9 and 63 F per mmol 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 $50 - 70 \text{ mA cm}^{-2}$) is controlled in a similar way by the micropore width and the amount of 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 $-\Delta_i H(C_6H_6)$, which allows an alternative assessment of the suitability of a given carbon to be used as a supercapacitor electrode material.

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Fig. 1. Correlation between the gravimetric capacitances estimated by cyclic voltammetry in 3-electrodes (half cell) and 2-electrodes (full cell) configuration: (●) at 5 mVs^{-1} in H_2SO_4 and (○) at 2 mVs^{-1} in $(\text{C}_2\text{H}_5)_4\text{NBF}_4$. All values refer to the capacitance and mass of a single electrode.

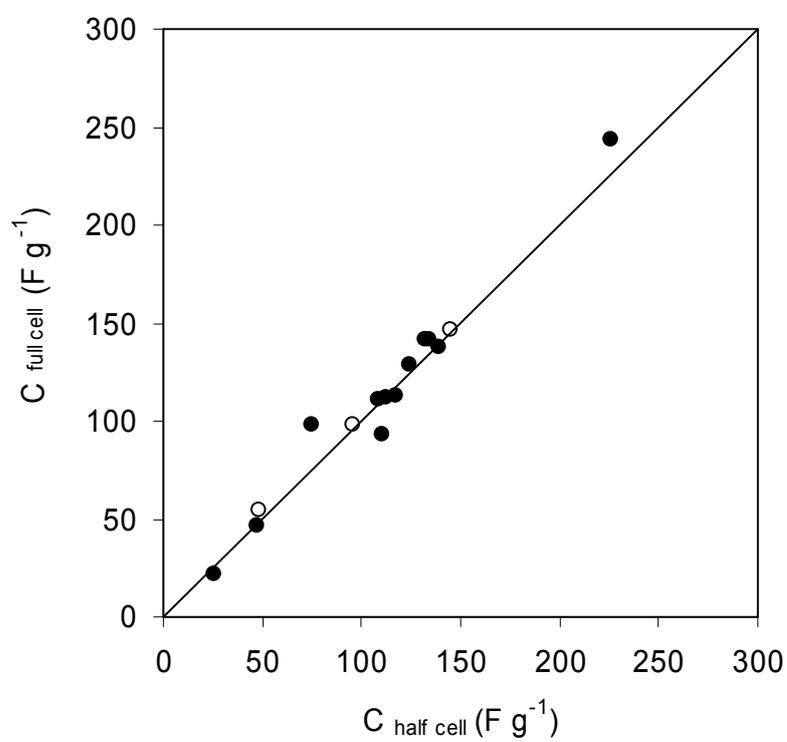


Fig. 2. Comparison of the gravimetric capacitances $C_{o, \text{aprotic}}$ and $C_{o, \text{acidic}}$ in F g^{-1} , obtained for 30 different microporous carbons (\bullet), a high surface area graphite (+) and 10 templated mesoporous carbons (data from ref. [2, 4, 5] (\circ) and from ref. [7,8] (\square)).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

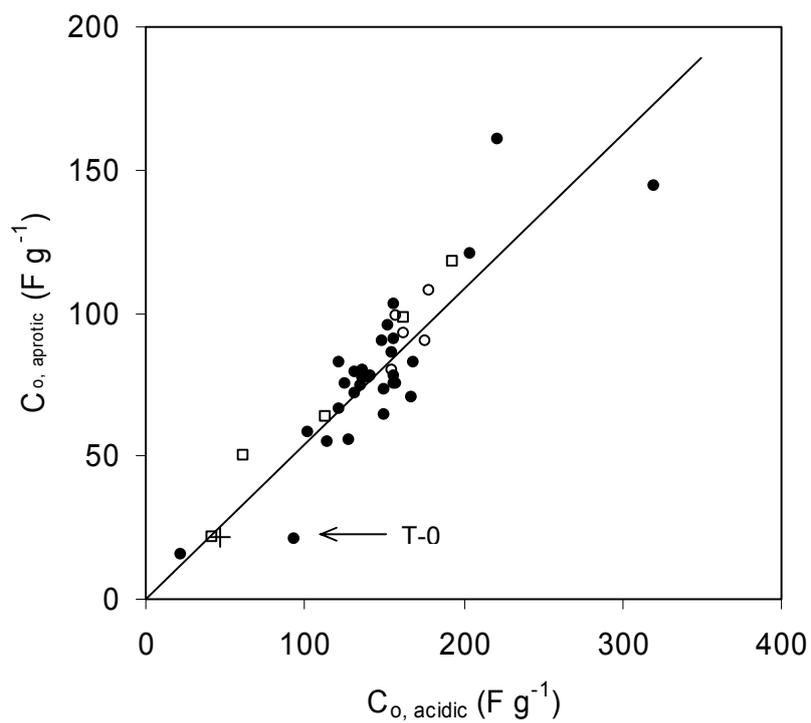


Fig. 3 Comparison of the specific capacitances $C_{o, \text{aprotic}}/S_{\text{tot}}$ and $C_{o, \text{acidic}}/S_{\text{tot}}$ in F m^{-2} , obtained for 30 different microporous carbons (\bullet), a high surface area graphite (+) and 10 templated mesoporous carbons (data from ref. [2, 4, 5] (\circ)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

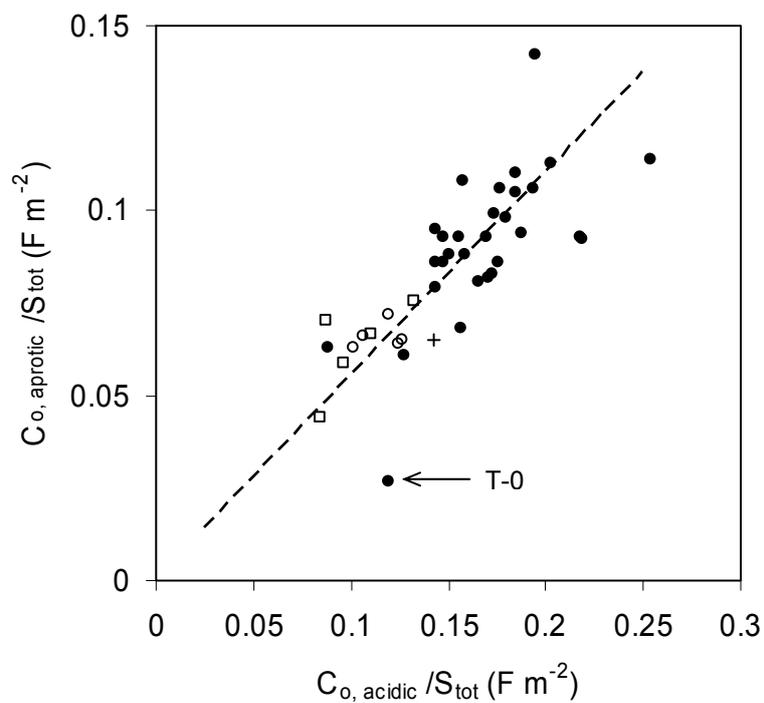


Fig. 4. Variation of the specific capacitances $C_{o, \text{aprotic}}/S_{\text{tot}}$ (●) and $C_{o, \text{acidic}}/S_{\text{tot}}$ (○) with the surface density of CO-generating groups, $[\text{CO}]/S_{\text{tot}}$ (see Table 1). The dotted lines correspond to Eqns. (1) (top) and (4) (bottom).

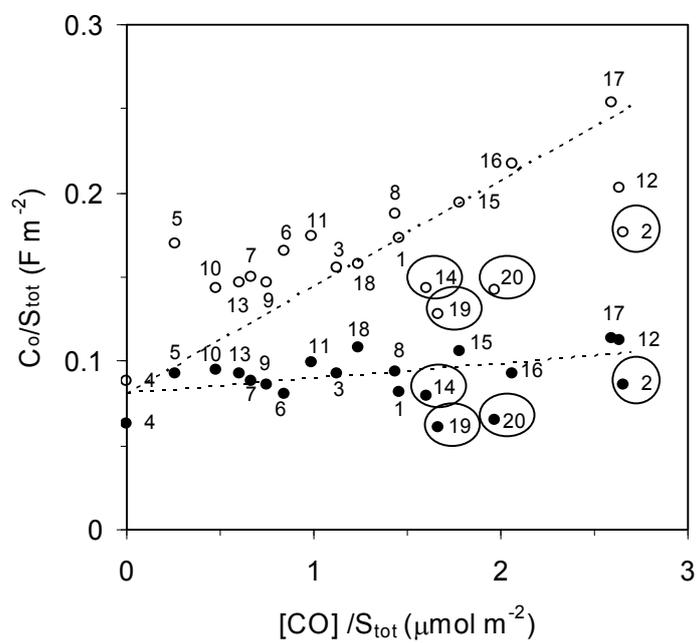


Table 1.

Main characteristics and electrochemical properties of carbons characterized by TPD.

Carbon	$C_{o, \text{aprotic}}$ (F g ⁻¹)	$C_{o, \text{acidic}}$ (F g ⁻¹)	S_{tot} (m ² g ⁻¹)	$C_{o, \text{aprotic}}/S_{\text{tot}}$ (F m ⁻²)	$C_{o, \text{acidic}}/S_{\text{tot}}$ (F m ⁻²)	[CO] (μmol m ⁻²)	[CO ₂] (μmol m ⁻²)	L_o (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 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 Picatif 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

Table 2. Ratios of the gravimetric capacitances $C[j]_{\text{aprotic}}/C[j]_{\text{acidic}}$ as function of the current density j
 (Typical examples for carbons with different amounts of CO₂-desorbing groups)

Carbon	CO ₂ (mmol g ⁻¹)	Current density, j (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
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-94-11-Ox	0.86	0.50	0.51	0.52	0.51	0.49	0.47	0.44	0.45
PX-21	1.4	0.46	0.43	0.42	0.44	0.43	0.43	0.44	0.37