Capacitance in carbon pores of 0.7 to 15 nm: a regular pattern

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The study of 28 porous carbons shows that the specific capacitance in the electrolyte $(C_2H_5)_4NBF_4$/acetonitrile is relatively constant between 0.7 and 15 nm (0.094±0.011 Fm^{-2}). The increase in pores below 1 nm and the lower values between 1 and 2 nm reported earlier, are not observed in the present work.

Carbon-based supercapacitors are promising energy storage devices and their optimization is of great technological importance. It has been reported that the surface-related capacitance of TiC-based carbons increases considerably in pores of less than 1 nm for the $(C_2H_5)_4NBF_4$ in acetonitrile ($TEABF_4$/ACN) electrolyte.[1,2] Values as high as 0.14 F m^{-2} were obtained near 0.7 nm. On the other hand, as suggested by additional data taken from the literature, the rise in capacitance is preceded by a decrease from approximately 0.07-0.08 F m^{-2} near 5 nm, to 0.05 Fm^{-2} between 1 and 2 nm. A model has also been proposed to describe this behaviour.[3,4] However, this contrasts with the relatively constant value around 0.08 F m^{-2} already reported for $TEABF_4$/ACN and a variety of carbons with pore sizes between 0.9 and 2.3 nm.[5-8] Recent modelling[9] of the $TEABF_4$/ACN electrolyte in a slit-shaped micropore of 3.9 nm also suggests a capacitance of 0.09 F m^{-2}.

The apparent contradiction seems to be due to the fact that the assessment of the TiC-derived carbons[1,2], like that of many carbons reported in the literature, was based on the BET surface area S_{BET}, known to be unreliable in the case of microporous carbons with pore widths between 1 and 2 nm.[10-13] Modelling [13] has also shown that this is the case for S_{BET} of the TiC-based carbons.

A recent study[12] based on Kaneko's comparison plot for nitrogen,[14] the selective adsorption of phenol from aqueous solutions,[15] Dubinin's theory and its extensions[16-18] (see Supplementary Information) and the non local density functional theory (NLDFT)[19] has shown that these techniques lead to relatively similar total surface areas S_{tot} for carbons with slit-shaped micropores. The comparison of their averages S_{av} with S_{BET} leads to

$$S_{av}\ (m^2 g^{-1}) = \frac{S_{BET}\ (m^2 g^{-1})}{(1.19 \pm 0.03\ nm^{-1}) L_o (nm)} \qquad (1)$$

where L_o covers the range of 0.5 to 1.7 nm. This implies a fundamental difference between these areas and it is surprising that the existence of two sets of values for the surface area has not received more attention. In spite of the IUPAC recommendation,[10] S_{BET} is still used by many authors, although S_{av} appears to be more reliable, due to the convergence of values obtained from three to four independent and equally valid techniques.

Below 0.9 nm S_{BET} underrates the more realistic surface area S_{av} and gradually overrates it between 0.9 and 3-4 nm or even beyond, before becoming similar. Moreover, in view of the size of the $(C_2H_5)_4N^+$ ion (0.68 nm[1]) and the presence of constrictions in carbons of medium or low activation, the surface area accessible to the electrolyte may be much smaller than assessed by classical, but smaller probes such as nitrogen, argon or CO_2. This must also be taken into account in the assessment of the surface-related capacitance.

It is therefore justified to re-examine the problem of the accessible surface by considering different techniques applied to a relatively large sampling of various types of carbons. Basically, this should provide a more reliable assessment of the specific capacitance C/S at low current density (~1 mA cm^{-2}). The present study is limited to 1M $TEABF_4$/ACN, which does not depend on the surface chemistry of untreated carbons,[5] but it may be repeated with other electrolytes.

Here we show that the surface-related capacitance is practically constant in the range of 0.7 to 1.6 nm for this electrolyte (0.094 ± 0.011 F m^{-2}). This pattern agrees with the recent study of Zh. Feng *et al.*[20] on activated carbon beads with $TEABF_4$/polypropylene carbonate (PC). It was based on the DFT approach and considered the surface areas of the different types of pores (micro- and mesopores) present simultaneously in these solids. Their study also illustrates the discrepancy between S_{DFT} and S_{BET}.

As described in the experimental section (see also Supplementary Information), we considered 22 microporous carbons with average pore sizes L_o between 0.7 and 1.6 nm, including carbide-based carbons similar to those of refs. (1-2). For comparison purposes, 6 mesoporous carbons with pore diameters D_p between 3.4 and 15.7 nm were also included. The average surface areas were determined as described recently,[12] but using now simultaneously up to eight different techniques. This includes the systematic use of CCl_4 (0.63 nm [21]) and 2,5-norbornadiene (NBD) (0.65 nm from modelling) in the liquid and the vapour states. It either confirms the accessibility of the total surface area determined with small probes to the $(C_2H_5)_4N^+$ ion, or leads to a smaller effective area. (This was the case for five carbons with average pore-widths below 0.8 nm).

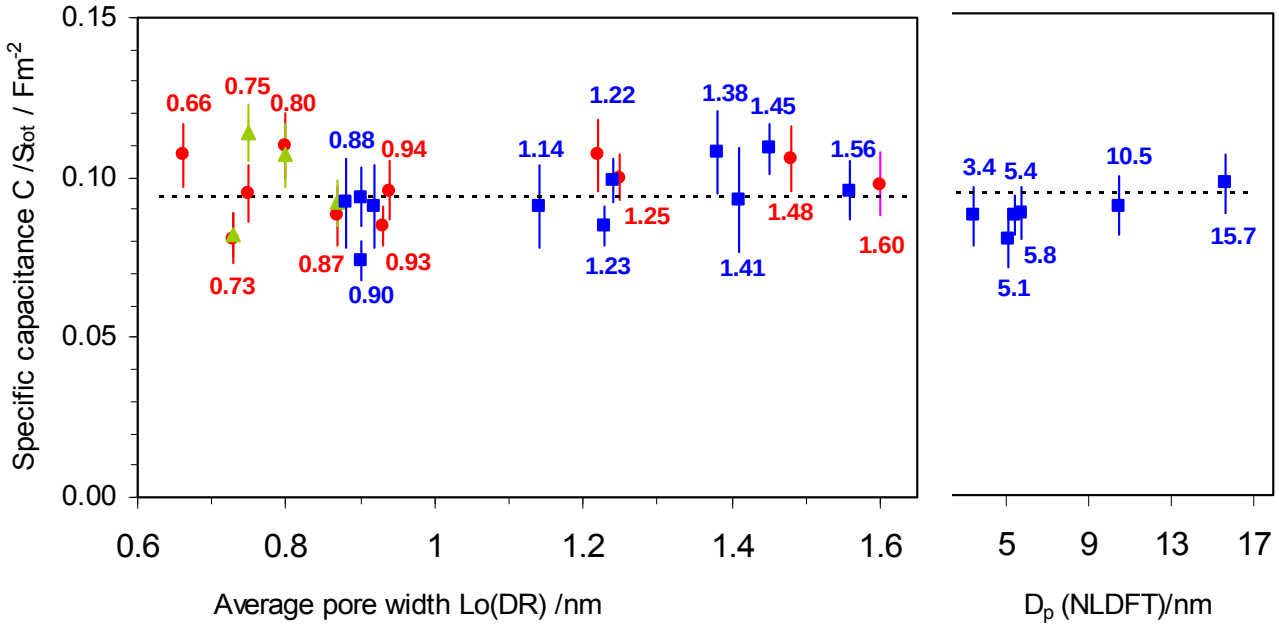

Fig. 1. Specific capacitances of porous carbons in the $TEABF_4$/ACN electrolyte. Left:C/S_{tot} versus the average pore width L_o(DR) for microporous carbons (Table S3). The data shows no anomalous behaviour below 1 nm and in the range of 0.66 to 1.50 nm the average capacitance is 0.094 ± 0.011 Fm^{-2}. Right: mesoporous carbons (Table S4) with pore diameters D_p between 3.4 and 15.7 nm, confirming the absence of a trend. S_{tot} and L_o(DR) are obtained from CCl_4 isotherms (●) supplemented by norbornadiene (▲), or by small molecules only (■) (mainly nitrogen and phenol), where the enthalpies of immersion indicate full accessibility of the pore system to the $(C_2H_5)_4N^+$ ion (Tables S1 and S2).

Table S1 (Supplementary information) gives the average total surface areas S_{tot}(SM) derived from different techniques and based on small molecules (e.g. N_2, CO_2, C_6H_6). For carbons without pores below 0.7 nm and in the absence of constrictions at the entrance of larger pores, S_{tot}(SM) also represents the area accessible to the $(C_2H_5)_4N^+$ ion. On the other hand, five samples (7-11) with average pore sizes between 0.66 and 0.90 nm showed a much reduced accessibility, as indicated by the limited adsorption of CCl_4 and NBD from the vapour phase. The analysis of these isotherms based on Dubinin's theory leads to smaller areas $S_{tot}(CCl_4)$ and S_{tot}(NBD) and larger average micropore widths L_o(DR) than obtained with the small probes. Furthermore, the validity of the data derived from the isotherm is confirmed by the agreement between the calculated and the experimental enthalpies of immersion into the corresponding liquids, the latter being a thermodynamic consequence of Dubinin's theory.[15,16] The enthalpy of immersion into benzene, $\Delta_iH(C_6H_6)$, can also be calculated from the nitrogen isotherm and the good agreement confirms the same accessibility. This is due to the similar critical dimensions of the two molecules with respect to the locally slit-shaped micropores (benzene is flat).

For all carbons the accessibility of the porous system to the $(C_2H_5)_4N^+$ ion was therefore assessed with the help of the enthalpies of immersion into C_6H_6, CCl_4 and NBD (Table S3-S4). In the case of equal accessibility, the ratios $\Delta_iH(CCl_4)/\Delta_iH(C_6H_6)$ and $\Delta_iH(NBD)/\Delta_iH(C_6H_6)$

should be close to 0.97 (see Table S3). This is confirmed for carbons 1 to 6, with average pore sizes between 0.9 and 1.6 nm, whereas smaller ratios are obtained for carbons 7 to 11, with average pore sizes below 0.9 nm.

Consequently, the lengthy determination of CCl_4 and NBD isotherms can be limited to carbons with average pore sizes L_o(DR) or L_o(NLDFT) below 0.8 to 0.9 with reduced accessibility, revealed by the enthalpies of immersion. For these carbons, the surface areas relevant to EDLC properties are $S_{tot}(CCl_4)$ and S_{tot}(NBD).

As illustrated by Figure 1, the specific capacitances of the 22 microporous carbons show no definite trend with respect to the average pore width in the range of 0.7 to 1.6 nm. C/S_{tot} is based on $S_{tot}(CCl_4)$ and S_{tot}(NBD) for samples 1 to 11, and on S_{tot}(SM) for samples 12 to 22 (Table S1). It should be noted that the use of L_o(NLDFT) instead of L_o(DR) does not modify the overall pattern, the two being close. Obviously, variations within series of carbons cannot be excluded, but the overall pattern shows that one can find in the range of 1.1 to 1.6 nm values of C/S_{tot} as high as those in the subnanometer range. Also, as seen in Table S3 the use of S_{BET} for the carbons with L_o above 1.2 nm leads to smaller values of C/S, which suggests a general increase of this parameter in small pores.This is no longer the case for the average total surface areas used here.

The mesoporous carbons of Table S4, characterized by at least three different techniques and covering the range of pore diameters D_p from 3.4 to 15 nm,[22] provide further information on C/S in wider pores. The data, also shown in Figure 1, suggests no trend in C/S_{tot} with decreasing pore diameter D_p.

The uncertainty of our combined protocols can be as high as 10 to 15%, which illustrates the difficulty in the assessment of surface areas determined by equally valid techniques. However, the present results show that the specific capacitance in $TEABF_4$/ACN is relatively constant in pores of size between 0.7 and 1.6 nm, with an overall average of (0.094 ± 0.011) F m^{-2}. This value may be compared with the earlier estimate of approximately 0.08 to 0.09 F m^{-2}.[9] It would appear that the lower values C/S for typical micropores (1 to 2 nm) reported by a number of authors[1-4] reflect mainly the use of S_{BET}.

These results agree very well with the observation of Zh. Feng *et al.*[20] for the specific capacitances in the different pores of eight activated carbon beads in $TEABF_4$/PC. These carbons are predominantly mesoporous, with some microporosity.

From a best fit of the DFT-based areas of the different types of pores to the gravimetric capacitance, these authors obtained respectively 0.087, 0.099 and 0.097 F m^{-2} at pore widths below 1 nm, between 1 and 2 nm, and above 2 nm. Although the solvent (PC) is different, these values are similar to those shown in Fig. 1 and the refined analysis indicates that C/S is independent of the pore size distribution and of the average pore width. Moreover, as pointed out earlier[12], S_{NLDFT} is close to S_{av} and it may differ significantly from S_{BET}, as shown by Zh.

Feng's data. Using the higher S_{BET} areas, one obtains specific capacitances between 0.05 and 0.07 F m^{-2}, for the domain of 2 to 4 nm, which correspond to the apparent dip reported earlier [1,2].

Our results, and indirectly those of Zh. Feng *et al.*,[20] are in contradiction with the increase in C/S_{BET} reported for the $TEABF_4$/ACN electrolyte in pores of less than 1 nm and the relatively low values between 1 and 2 nm. The general pattern suggested previously[1,2] has been analyzed by modelling[3,4], but such models assume implicitly that the dielectric constant (or better the relative permittivity) ε_r of the electrolyte in the pores is constant. Mathematically, a constant value of C/S, as suggested here and reported by Zh. Feng *et al.*, implies a decrease in ε_r as the pore width decreases. This possibility cannot be rejected, in particular following recent modelling of the $TEABF_4$/ACN electrolyte in slit-shaped nanopores of 3.9 nm between graphene sheets.[9] This approach suggests that for ACN $\varepsilon_r = 26.3 \pm 0.3$, as opposed to 35.8 for the free solvent.

Furthermore, there exists experimental evidence showing that the relative permittivity of an ionic solution in micropores decreases with the solvent to ion ratio. For example, it has been reported that in the case of water filling the micropores of expanding clays[23,24] such as bentonites[25], ε_r decreases as the interlayer spacing decreases. These micropores consist of negatively charged layers with a constant amount of Na^+ or Ca^{+2} ions surrounded by a variable amount of water. The latter depends on the pore width which can reach 1 to 1.2 nm [26]. This situation corresponds to the negative electrode of a carbon-based supercapacitor, except that the bentonite layers are not conducting.

One may assume that the $TEABF_4$/ACN electrolyte follows a similar pattern in porous carbons, with smaller values of ε_r in narrow pores, due to desolvation.

The models of Huang *et al.* themselves indicate variable dielectric constants of the electrolyte, depending on the range of porosity considered. The values of approximately 9 between 5 and 2 nm and of 2.2 below 1 nm suggest a decrease of ε_r as the pore width decreases and one may assume that there is a gradual change, as observed for the water-bentonite system.

In conclusion, it appears that the surface-related capacitance of different carbons in 1M $TEABF_4$/ACN is relatively constant between 0.7 and 15 nm, as suggested previously.[5-8] The anomalous increase in C/S_{BET} reported earlier for pore sizes below 1 nm, as well as the low values between 1 and 2 nm, probably reflect the shortcoming of the BET approach. It is often overlooked, but of fundamental importance. With respect to current models,[3,4] the constant values of C/S reported here and by Zh. Feng would imply a gradual decrease of the relative permittivity of the organic electrolyte as the pore size decreases from mesopores to subnanometer pores. This aspect is being further investigated and results will be published in due course.

Experimental

The study is based on 28 porous carbons of different origins. They are listed in Tables S1-S4 (Supplementary Information) with their main structural, calorimetric and electrochemical properties. The textural characterization was performed by gas adsorption and immersion calorimetry.

The electrochemical performances were tested in a sandwich-type capacitor, set up with two carbon pellets (8 mm diameter, around 350 μm thick) separated by glassy fibrous paper (300 μm thick) and placed in a Swagelock cell. The electrodes were obtained by pressing a mixture of the carbon (75 %wt), PVDF (20 %wt) as binder and carbon black (Super P, 5 %wt). The electrolyte was 1M $(C_2H_5)_4NBF_4$ in acetonitrile. The capacitance was determined by galvanostatic charge-discharge cycles Autolab-Ecochimie PGSTAT 30) from 0 to 2 V at a constant current density of 1 mA cm_{-2}. The gravimetric capacitance (Fg^{-1}) given in the present study is relative to the carbon mass in a single electrode.

The accuracy with our laboratory-scale device has been estimated to be around ± 5 %.

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References

1 J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon and P.L.Taberna, *Science*, 2006, **313**, 1760.

2 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845.

3 J. Huang, B.G. Sumpter and V. Meunier, *Angew. Chem.*, 2008, **47**, 520.

4 J. Huang, B.G. Sumpter and V. Meunier, *Chem. Eur. J.*, 2008, **14**, 6614.

5 T. A. Centeno, M. Hahn, J.A. Fernández, R. Kötz and F. Stoeckli, *Electrochem. Commun.*, 2007, **9**, 1242.

6 G. Lota, T.A. Centeno, E. Frackowiak and F. Stoeckli, *Electrochim. Acta,* 2008, **53**, 2210.

7 J.A. Fernández, M. Arulepp, J. Leis, F. Stoeckli and T. Centeno, *Electrochim. Acta*, 2008, **53**, 7111.

8 O. Barbieri, M. Hahn, A. Herzog and R. Kötz , *Carbon*, 2005, **43**, 1303.

9 G. Feng, J. Huang, B.G. Sumpter and V. Meunier, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5468.

10 J. Rouquérol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing and K. K. Unger, *Pure Appl. Chem.*,1994, **66**, 1739.

11 J. Rouquérol, P. Llewellyn and F. Rouquérol, in Studies in Surface Science and Catalysis, Vol. 160, (Eds: P.L. Llewellyn, F. Rodríguez-Reinoso, J. Rouquerol, N. Seaton), Elsevier, Amsterdam, 2007 pp. 49-56.

12 T. A. Centeno and F. Stoeckli, *Carbon*, 2010, **48**, 2478.

13 J.C. Palmer , A. Llobet, S.-H. Yeon, J.E. Fischer, Y. Shi, Y. Gogotsi and K.E. Gubbins, *Carbon,* 2010, **48**, 1116.

14 N. Setoyama, T. Suzuki and K. Kaneko, *Carbon*, 1998, **36**, 1459.

15 E. Fernández, D. Hugi-Cleary, V. López-Ramón and F. Stoeckli, *Langmuir*, 2003, **19**, 9719.

16 M.M. Dubinin, *Carbon*, 1989, **27**, 457.

17 F. Stoeckli, in Porosity in carbons. Characterization and applications, (Ed: J. Patrick), Arnold, London, 1995, pp. 67-92.

18 F. Stoeckli, *Russ. Chem. Bull. Int. Ed.*, 2001, *50*, 2265.

19 P.I. Ravikovich, A. Vishniakov, R.A.Russo and V. Neimark, *Langmuir*, 2000, **16**, 2311.

20 Zh. Feng, R. Xue and X. Shao, *Electrochim. Acta,* 2010, **55**, 7334.

21 T. Suzuki, T. Iiyama, K.E. Gubbins and K. Kaneko, *Langmuir*, 1999, **15**, 5870.

22 J.A. Fernández, T. Morishita, M. Toyoda, M. Inagaki, F. Stoeckli and T.A. Centeno, *J. Power Sources*, 2008, **175**, 675.

23 P. Cosenza and A. Tabbagh, *Appl. Clay Sci.*, 2004, **26**, 21.

24 V. Saltas, F. Vallianatos and D. Triantis, *J. Non-Cryst. Solids*, 2008, **354**, 5533.

25 H. Bidadi, P.A. Schroederer and T. Pinnavaia, *J. Phys. Chem. Solids*, 1988, **49**, 1435.

26 F. Kraehenbuehl, F. Stoeckli, F. Brunner, G. Kahr and A. Müller-Vonmoos, *Clay Minerals*, 1987, **22**, 1.