The volumetric capacitance of microporous carbons in organic electrolyte

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Abstract

The study of 26 microporous carbons with average pore widths L_o between 0.7 and 1.8 nm shows that the volume-related capacitance C_{mi}(F cm^{-3}) in the organic electrolyte $(C_2H_5)_4NBF_4$/acetonitrile is an inverse function of the average micropore width L_o. This means that for a given micropore volume W_o, the gravimetric capacitance C(F g^{-1}) is larger for carbons with smaller pores due to the higher surface to volume ratio. Furthermore, the increase of C_{mi}(F cm^{-3}) in smaller pores suggests that the surface-related capacitance C(F m^{-2}) should be relatively constant in slit-shaped micropores. This has important technological consequences for the design of carbon-based supercapacitors.

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1. Introduction

Carbon-based capacitors are promising energy storage devices and their optimization is of great technological importance [1]. It is therefore essential to identify the parameters which may improve their performances.

The primary experimental information is the gravimetric capacitance C (F g^{-1}), of the supercapacitor, which can be determined unambiguously by standard methods [2]. It is also the parameter which one tries to improve and, for a given electrolyte, it depends on a number of structural parameters of the carbon. These are the micropore volume W_o, the pore size distribution with its average L_o, as well as the surface area S accessible to the largest ion, in the present case $(C_2H_5)_4N^+$ (0.68 nm) [1, 3]. Furthermore, treatments such as graphitization, which increases the electrical conductivity, can also improve C [1, 4]. On the other hand, in the case of organic electrolytes, as opposed to aqueous electrolytes, the chemistry of the surface has practically no influence on the capacitance at low current density (d ~1 mA cm^{-2}) [5]. However, at higher densities surface groups may reduce the mobility of the ions and consequently C [3,5].

Here we examine, as a model case, the organic electrolyte $(C_2H_5)_4NBF_4$ in acetonitrile (TEABF$_4$/AN) and we show that the volumetric capacitance in the micropores accessible to the largest ion is an inverse function of their average width L_o. This means that small pores contribute more to the gravimetric capacitance.

2. Experimental

The study is based on 26 microporous carbons (activated carbons (AC) and carbide-derived carbons (CDC)) of different origin and with a large variety of textural characteristics. However, with the exception of sample N-125-08, these carbons are predominantly microporous. The relevant data is given in Table 1.

Carbon tetrachloride (CCl$_4$) and 2,5-norbornadiene (NBD) isotherms were determined at 293 K in a gravimetric apparatus of the MacBaine type. In order to confirm the reduction in the accessible volume with respect to that obtained by

the classical small probes, earlier results for N_2 (77 K) isotherms were also used. The external (non-microprous) surface area S_e of the carbons was determined routinely from the nitrogen comparison plots, but other comparison plots (C_6H_6, CH_2Cl_2 and CCl_4) were also used for many samples. The different plots are usually in good agreement and provide a reliable assessment of S_e.

The use of probes such as CCl_4 (0.63 nm) and NBD (0.65 nm) is an important feature of the present study, because they allow the determination of the part of the microporous structure specifically available to the $(C_2H_5)_4N^+$ ion with a diameter of 0.68 nm and the largest component of the electrolyte. Small probes such as N_2, Ar or CO_2 are commonly used for the characterization of microporous carbons, but they include the part of porosity below 0.68 nm found in many carbons, but not accessible to the ion. Therefore, using the parameters provided by the classical analysis based on the small probes may provide a wrong picture.

CCl_4 , which follows Dubinin's equation, like N_2, Ar and CO_2, can be used with other non-specific molecules to characterize the porosity corresponding to pore sizes above their critical sizes L_c [6].

Immersion calorimetry was also applied as a complementary technique to determine the enthalpies of immersion of the carbons into benzene, carbon tetrachloride and norbornadiene at 293 K. The Tian-Calvet calorimeter and the experimental procedures have been described in detail elsewhere [6,7].

The electrochemical measurements were carried out in a sandwich-type capacitor set up with 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) [3,5]. 1M $(C_2H_5)_4NBF_4$ in acetonitrile was used as electrolyte.

The capacitance was determined by galvanostatic charge-discharge cycles from 0 to 2 V at 1 mA cm^{-2}. The data was further cross-checked by cyclic voltammetry (CV) experiments at a scan rate of 1 mV s^{-1}.

The capacitance values refer to the carbon in a single electrode.

3. Results and discussion

The fact that $C(F\ g^{-1})$ is a function $C(W_o, L_o; S; \ldots)$ of different variables, requires a careful analysis, in particular as W_o, L_o and the area of the micropores S_{mi} are related through the pore size distribution (PSD) of the carbon. As discussed elsewhere [8], current models used for the characterization of microporous carbons are based on Dubinin's theory [6,7] or on modeling (DFT/NLDFT, QSDFT, Monte Carlo). They all assume that the micropores are locally slit-shaped, which is a reasonable first approximation below 1.2 to 1.5 nm. These approaches provide self-coherent sets of structural parameters, which should be used as such. However, their surface area is often substituted by the area derived from the BET approach, S_{BET}, which is not suitable for micropores [8 and ref. therein]. This leads to inconsistencies when an increase in surface-related capacitance $C(F\ g^{-1})/S(m^2\ g^{-1})$ in pores below 1 nm (due to ions desolvation) is used as criteria for the improvement of the gravimetric capacitance [9-17].

An alternative and possibly less debatable approach may be provided by the analysis of the volumetric capacitance in the micropores,

$$C_{mi}(F\ cm^{-3}) =\ C(F\ g^{-1})_{mi}/W_o\ (cm^3\ g^{-1}) \tag{1}$$

It has received little attention so far, since most authors have analysed the volumetric capacitance calculated on the basis of the geometrical dimensions of the entire electrode ($C/V_{electrode}$). This parameter is highly relevant in order to establish a coherent picture of the industrial potentiality of the different carbon materials.

The primary information is the gravimetric capacitance in the micropores, $C_{mi}(F\ g^{-1})$, which is related to the experimental capacitance $C(F\ g^{-1})$ by

$$C_{mi}(F\ g^{-1}) = C(F\ g^{-1}) - 0.094\ (F\ m^{-2})\ S_e\ (m^2\ g^{-1}) \tag{2}$$

The last term represents the contribution of the external (non-microporous) surface area S_e to C. This area can be determined accurately by different techniques, in particular Sing's α_S-plot or a direct comparison plot [6]. In the present case, we choose the capacitance of 0.094 F m^{-2}, which has been reported recently [16,17]. It also corresponds to values around 0.08 to 0.10 F m^{-2} obtained for mesoporous carbons [18,19]. Moreover, for the 26 carbons listed in Table 1, the contribution of S_e represents less than 5 per cent of C, with the exception of samples Bourd-59 (8%), UO3-ox (9%), HK-650-8 (15%), N-125-08 (18%). This means that a highly accurate value of the surface-related capacitance is not essential in Eqn (2). It follows that in the micropores the volumetric capacitance is

$$C_{mi}(F\ cm^{-3}) = [C(F\ g^{-1}) - 0.094\ (F\ m^{-2})\ S_e\ (m^2\ g^{-1})]/W_o(cm^3\ g^{-1}) \qquad (3)$$

The advantage of this expression over the surface-related capacitance C/S is the fact that all its parameters can be determined unambiguously, with the proviso that W_o represents the volume of the micropores accessible to the largest ion, in the present case $(C_2H_5)_4N^+$ with a diameter of 0.68 nm. For carbons having either pores below this critical value, or constrictions at the entrance of wider pores (gate effect), the accessible volume may be reduced with respect to the micropore volume W_o(SM) obtained by using small molecules (SM), such as nitrogen, argon or CO_2 [6,7].

As described in detail elsewhere [16, 20], the volume accessible to the $(C_2H_5)_4N^+$ ion can be assessed by using spherical molecules such as CCl_4 (0.63 nm) and 2,5-norbornadiene (NBD) (0.65 nm) in both the vapour and the liquid states. The analysis of the adsorption isotherms by Dubinin's theory (or even the simple Langmuir model) leads to the volumes $W_o(CCl_4)$ and W_o(NBD) which correspond practically to the volume accessible to the $(C_2H_5)_4N^+$ ion. As described in detail elsewhere [16], Dubinin's theory also leads to $L_o(CCl_4)$, the average width of the pores accessible to this molecule. It reflects a PSD specific to this molecule, and

consequently to the ion, and it may be different from the classical PSD based on nitrogen, argon or CO_2.

The volumes $W_o(CCl_4)$ and $W_o(NBD)$ can also be cross-checked by comparing the calculated and the experimental enthalpies of immersion into the corresponding liquids, $\Delta_iH(CCl_4)$ and $\Delta_iH(NBD)$ [6], where the latter are corrected for the contribution from the external surface area S_e [6]. Moreover, if the ratios of these enthalpies to $\Delta_iH(C_6H_6)$ are close to 0.97, the micropore volume $W_o(CCl_4)$ and $W_o(SM)$ are equal and $L_o(CCl_4) = L_o(SM)$ [16]. This is usually the case for microporous carbons with average pore widths above approximately 1.2 nm.

It follows that the volumetric capacitance $C_{mi}(F\ cm^{-3})$ given by Eqn (3) and based on $W_o(CCl_4)$ or $W_o(SM)$ is a reliable quantity and it may be compared with the average micropore accessible to the ion, either $L_o(CCl_4)$ or $L_o(SM)$, depending on the accessibility. As illustrated by Fig. 1, the data for 26 carbons (Table 1) with accessible pore widths between 0.71 and 1.80 nm suggest that

$$C_{mi}/W_o[CCl_4]\ (F\ cm^{-3}) = (188 \pm 5)/L_o[CCl_4] \qquad (4)$$

or an average of $190 \pm 20\ F\ cm^{-3}$ nm for the individual values of C/W_o.

There is some dispersion, which reflects the influence of other parameters, but the present correlation reveals a general pattern for a variety of carbons, namely that the volumetric capacitance increases as the pore width decreases. This means that for a given micropore volume W_o a carbon with smaller pores will provide a higher gravimetric capacitance $C(F\ g^{-1})$. Obviously, this has important consequences in the design of supercapacitors.

It should be pointed out that the linearization of the $C(F\ cm^{-3})$ vs L_o plot reported by Raymundo-Piñero et al. [21] for five carbons and the 1M TEABF$_4$/AN electrolyte shows a trend similar to that of Fig. 1. However, no correction has been applied for the contribution of the unknown external surface area S_e and L_o is based on the nitrogen isotherm.

Eqn (4) also leads to another interesting consequence if one accepts that typical micropores are locally slit-shaped, as assumed by most researchers. In this case, the surface area corresponding to the volume $W_o(CCl_4)$ is given by the simple geometric relation between the volume and the average pore width,

$$S_{mi}(m^2\,g^{-1}) = 2000\, W_o[CCl_4]/L_o[CCl_4] \tag{5}$$

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From a general point of view, modeling based on Gaussian or skewed Gaussian distributions with pores between 0.7 and 1.8-2 nm shows that the surface areas calculated with the help of Eqn (5) are close to the cumulative surface area of the pores. Moreover, in the case of CCl_4 this has been verified for a few carbons by comparing S_{mi} with the areas obtained from the comparison plots of the CCl_4 isotherms obtained at 293 K, the reference being the graphitized carbon black *Vulcan-3*.

Inserting Eqn (5) into (4) leads to

$$C_{mi}(F\,g^{-1})/S_{mi}(m^2\,g^{-1}) = 188/2000 = 0.094\; F\; m^{-2} \tag{6}$$

It is an average value corresponding to the surface-related capacitance of the micropore walls for the range of porosity considered here (0.7-1.80 nm). It is equal to the value of 0.094 ± 0.011 F m^{-2} obtained earlier by considering the average total surface area S_{av} of microporous and mesoporous carbons [16].

On the other hand, the use of S_{BET} suggests an increase in C/S as the average pore width decreases [9,10,11,16,17]. However, if this was the case, one should observe a change in the slope of Fig. 1 at values of $1/L_o(CCl_4)$ above 1 nm^{-1} (pores below 1 nm). This is not the case, in spite of some dispersion, and the trend shown in Fig. 1 applies to the entire range of porosity considered here.

The present approach is based on the gravimetric capacitance, the volume accessible to the $(C_2H_5)_4N^+$ ion and the corresponding average pore width, and it does not involve the specific surface areas S_{av} or S_{BET}. Therefore, it may be regarded as an independent approach and Eqn (6) confirms that a systematic

increase in C/S is unlikely for the $TEABF_4$/AN electrolyte in slit-shaped micropores below 1-1.2 nm (It should also be pointed out that our samples contain five carbide-based carbons).

It is interesting to point out that a similar pattern is obtained for the volumetric capacitance C_{mi}(F cm^{-3}) of the 1-2M H_2SO_4 electrolyte, after correction for the relatively important corrections pseudocapacitance effects and the contribution of S_e to C. However, the scatter is somewhat larger than for the $TEABF_4$/AN electrolyte, due to the uncertainties in the correction for pseudocapacitance effects which greatly depend on the chemical groups found on the different carbons. The data suggests a slope of approximately 210 F cm^{-3} nm, which corresponds to 0.105 F m^{-2}.

In conclusion, it is shown that in the micropores the volumetric capacitance C_{mi}/W_o in $TEABF_4$/AN increases with decreasing pore width, as expected from the increase in the surface to volume ratio, but it also appears that the surface-related capacitance C_{mi}/S remains relatively constant in slit-shaped micropores of 0.7 to 1.8 nm. The increase in C_{mi}/W_o of carbons presents technological advantages, due to a gain in the volume of the device, but on the other hand, the reduction in the ions' mobility may limit the performances at higher current densities.

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Fig. 1 Volumetric capacitance of the microporous carbons in the TEABF$_4$/AN electrolyte, as a function of the average width of the pores accessible to CCl$_4$.
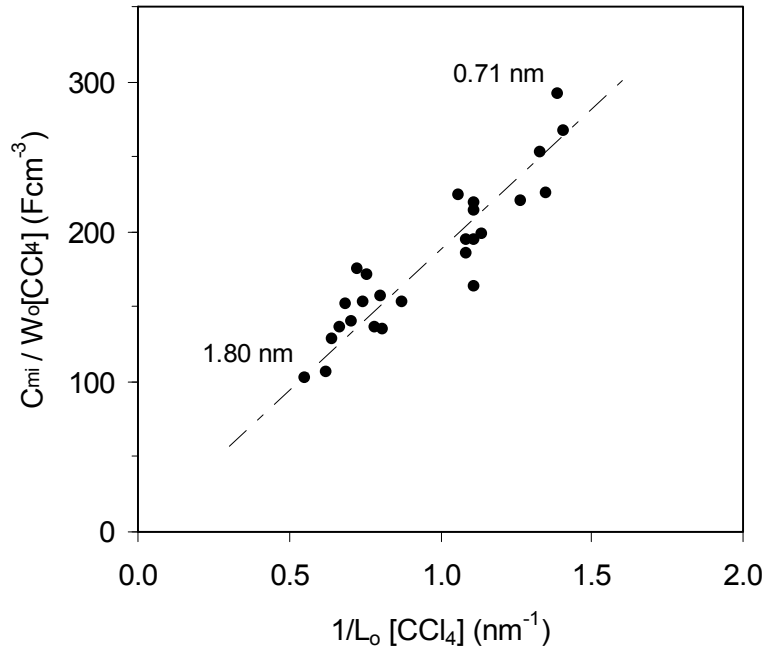
Table 1. Textural characteristics of microporous carbons derived from CCl_4 adsorption and specific capacitance in $TEABF_4/AN$

Carbon	Type	$W_o[CCl_4]$ $(cm^3\ g^{-1})$	$L_o[CCl_4]$ (nm)	S_e $(m^2\ g^{-1})$	C $(F\ g^{-1})$	C_{mi} $(F\ g^{-1})$
PAU-1-950	AC	0.347	0.71	4	93	93
HK-650-8	AC	0.116	0.72	65	40	34
PAU-1	AC	0.33	0.74	4	75	75
AC-507-11	AC	0.197	0.75	2	50	50
Bourdaine-59	AC	0.213	0.79	44	51	47
TIC-600	CDC	0.600	0.88	2	119	119
TiC/SiC	CDC	0.587	0.90	18	130	128
SiC-800	CDC	0.560	0.90	17	93	91
SiC-1000	CDC	0.580	0.90	50	129	124
AC-507-17	AC	0.487	0.90	1	95	95
CEP-2008	AC	0.483	0.92	7	90	89
SiC-900	CDC	0.600	0.92	35	120	117
CMS-H2	AC	0.235	0.94	25	55	53
BCK-A	AC	0.600	1.14	6	92	91
M1R	AC	0.670	1.23	7	91	90
Super-30	AC	0.600	1.24	9	95	94
MEKC	AC	0.580	1.27	11	80	79
A056	AC	0.294	1.32	20	52	50
DCG-5	AC	0.529	1.34	25	83	81
KF-1500/08	AC	0.600	1.38	21	107	105
M1R-950	AC	0.640	1.41	5	90	90
M30	AC	0.790	1.45	10	121	120
F-02	AC	0.625	1.50	45	89	85
U03	AC	0.500	1.56	25	66.5	64
N-125-08	AC	0.640	1.60	157	83	68
U03-ox	AC	0.574	1.80	60	64.5	59