EFFECT OF MESOPOROSITY ON SPECIFIC CAPACITANCE OF CARBONS

J.A. Fernández ^a, S. Tennison ^b, O.Kozynchenko ^b, F. Rubiera ^a, F. Stoeckli ^c, T.A.

Centeno ^{*a},

^a *Instituto Nacional del Carbón-CSIC. Apartado 73, E-33080 Oviedo, Spain*

^b *MAST Carbon International Ltd., Henley Park, Guildford, Surrey, GU3 2AF, United Kingdom*

^c *Physics Department, University of Neuchâtel. Rue Emile Argand 11, CH-2009 Neuchâtel, Switzerland*

Abstract

The study compares the structural and electrochemical properties of 12 porous carbons based on phenolic resins, using both aqueous (H₂SO₄) and aprotic ((C₂H₅)₄NBF₄ in acetonitrile) electrolytes. It appears that they fit into the general pattern observed for other carbons. The present carbons have micropore volumes varying between 0.29 and 0.66 cm³ g⁻¹ and average pore widths L_o between 0.62 and 1.23 nm. Five samples are exclusively microporous, whereas seven also display a relatively important mesoporosity. This allows a direct comparison between pairs of carbons with similar micropore systems, with and without mesopores, in order to assess the role of mesoporosity in the electrochemical properties. It appears that mesopores have only a limited influence on the decrease in capacitance at high current density as opposed to earlier assumptions.

* Corresponding author. Tel.: + 34.985119090

E-mail address: teresa@incar.csic.es

1. Introduction

Although the level of performance of current-generation supercapacitors (SCs) is sufficient for certain applications, the full potential of these systems has yet to be realized [1]. The improvement of such devices will benefit from recent insights into the relationships between the porous and chemical characteristics of carbons and their performance as electrodes in electric double layer capacitors (EDLCs) [2].

Systematic studies at low current density have already shown that the specific capacitance in aqueous electrolytes such as H_2SO_4 and KOH depends on a contribution from the total surface area and from redox processes involving surface functionalities [2-7]. Moreover, it has been shown [6] that the contributions from the microporous and the external (meso- and macropores) surface areas are identical, as opposed to an earlier hypothesis [8].

In the case of aprotic electrolytes with bulkier ions (e.g. $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile) and ionic liquids such as EMI-TFSI, the accessibility of the micropores may be considerably reduced for carbons with narrow pores (width < 0.7 nm) or showing 'gate' effects at the pores entrance [2, 7, 9, 10]. On the other hand, the contribution from pseudocapacitance effects in the $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ /acetonitrile electrolyte appears to be negligible compared to the aqueous media and the supercapacitor performance is essentially based on a double-layer mechanism through the extent of the accessible (effective) surface area of the carbon [2, 9, 10].

As the charge rate and/or the frequency increase, electrolyte penetration becomes poorer and less surface area is accessed. The hindering of ion transfer in the randomly connected micropores also leads to higher resistance. As a consequence, the formation of an effective double-layer fails notably at high current density and the energy and power density of super capacitor drop [1, 2].

The present work is based on the systematic analysis of the performance of phenolic resin-derived carbons, using vapour adsorption, immersion calorimetry and electrochemical techniques. It confirms the general trends reported earlier for other types of carbons examined by using exactly the same experimental protocols [6, 9, 10].

The study also challenges the long-held presumption that pores larger than 2 nm significantly enhance the capacitor performance by providing wider transport paths for ions diffusion into smaller pores [2, 11-16]. This observation is made possible by the fact that the present series of carbons, based on the same precursor, contains samples of similar microporous structures (average widths L_0 between 0.6 and 1.2 nm) and variable mesoporous volumes. This approach provides more detailed understanding of processes at the electrode/electrolyte interface of carbons.

2. Experimental

2.1. Carbons

Twelve porous carbons were developed and produced by MAST Carbon using a phenolic resin as raw material.

Phenolic resin is widely used as a carbon precursor for both porous and structural materials due to the high carbon yields (~50% weight) and the porous structures that can be achieved [17]. The micropore structure (<2nm) derives initially from phase separation that occurs during the resin curing process when the thermoplastic novolak is converted to the cross linked resin, usually using hexamethylene tetramine (hex). This gives rise to small uniform sized domains of around 6 nm diameter of high molecular weight cross linked resin in a matrix of lower molecular weight, less cross linked resin.

During the carbonisation process at 800°C the high molecular weight domains convert to interlinked spherical domains of high density, low porosity, glassy carbon

whilst the lower molecular weight matrix is largely decomposed creating the primary microporosity. This structure can be further modified by activation in carbon dioxide at temperatures in excess of 900°C. The initial effect is to remove more reactive pyrocarbon deposits from the low reactivity glassy carbon nanoparticles. More severe activation ultimately removes some of the nanoparticles and also probably creates some surface porosity in the nanoparticles [18].

Controlled meso (2-5 nm) and macroporosity is introduced into these carbons by the addition of a solvent pore former (ethylene glycol) prior to the resin curing step [19]. As the resin cures, it becomes insoluble in the solvent pore former leading to phase separation and the generation of large, interconnected voids. The meso/macro pore size and pore volume is controlled by increasing the solvent:resin ratio used in the preparation. These larger pores are generated without any significant modification to the micropore structure.

2.2. Characterization of the textural and chemical properties of the carbons

The porous structure of the carbons was evaluated by the classical analysis of the N₂ adsorption isotherms (77 K, Micromeritics ASAP 2010) following Dubinin's theory for the volume filling of micropores [20]. Dubinin-Radushkevich equation led to the volume W_0 of the micropores, their average width L_0 and the surface area of their walls, S_{mi} . Moreover, the comparison of the isotherm on the given sample with the adsorption data for a non-porous reference carbon black Vulcan-3G, provided information on the total pore volume and the external (non microporous) area S_e of the carbon [20, 21] (Table 1).

Beside vapour adsorption, immersion calorimetry was also used as a complementary tool for the characterization of the samples (Table 2). This technique, related to Dubinin's theory, is described in detail elsewhere [20]. The enthalpies of immersion into benzene, $\Delta_i H(C_6H_6)$, and into carbon tetrachloride, $\Delta_i H(CCl_4)$,

determined for most samples, provide information on the accessibility of the porous system to the various electrolytes. CCl_4 has a size (0.63-0.65 nm) similar to that of the $(\text{C}_2\text{H}_5)_4\text{N}^+$ ion (0.68 nm [22, 23]). Moreover, $\Delta_i\text{H}(\text{CCl}_4)$ is also related to the gravimetric capacitance in the $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{acetonitrile}$ electrolyte [9].

The chemical characteristics of resin derived-carbons are determined by the chemical composition of the resin precursors, the nature of the activation process and any post treatment [24]. The present carbons are high purity with a relatively low level of surface functionalities. The values of the enthalpy of immersion into water, $\Delta_i\text{H}(\text{H}_2\text{O})$, reported in Table 2 reflect quantitatively the presence of oxygen-containing surface complexes [21], part of which are responsible for pseudo-capacitance effects [4, 6, 8]. In the case of samples M6 and M10 further oxygen was introduced by treating the carbon dioxide activated carbonised resin with air at 300°C for 12 hours. This leads to higher enthalpies of immersion into water (Table 2).

2.3. Electrochemical measurements

The properties for charge storage were tested in two-electrode cells by galvanostatic charge-discharge voltage cycles (potentiostat-galvanostat Autolab-Ecochimie PGSTAT 30) at current densities of 50 and 6000 mA g^{-1} from 0 to 0.8 V in 2M H_2SO_4 aqueous electrolyte and from 0 to 2 V in 1M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile (Table 3). (The current density of 6000 mA g^{-1} corresponds approximately to 70 mA cm^{-2} and C_{50} is close to the limiting capacitance C_o at 1 mA cm^{-2} used elsewhere [6, 9]. The electrodes consist of carbon pellets (8-9 mg in weight, 8 mm in diameter) obtained by pressing a mixture of carbon (75 wt%), polyvinylidene fluoride (20 wt%) binder and carbon black (Super P, 5 wt%).

All capacitance values refer to the capacitance and mass of carbon in a single electrode. They were obtained by using the expression $C_{\text{electrode}} (\text{Fg}^{-1}) = 4C_{\text{cell}}$. Although the effect of the cations and anions is mixed in the overall capacitance of the cell, the electrode with the lower capacitance dominates the cell performance.

This is especially important in the case of the aprotic electrolyte with bulky cation.

3. Results and Discussion

3.1. Specific surface capacitances

A careful selection of the carbon precursor and the activation conditions led to high specific surface areas and to different pore size distributions in both the micropore and the mesopore ranges (Table 1). The micropore volumes, W_o , and the corresponding surface areas, S_{mi} , are obtained from the analysis of the nitrogen adsorption isotherm at 77 K by applying Dubinin's theory, as described in detail elsewhere [20]. On the other hand, the technique based on the comparison of the adsorption isotherm with a reference isotherm [20, 21] leads to the total surface area S_{comp} , the external (non-microporous) surface area S_e and the total pore volume V_{tot} . The latter is the sum of the microporous and mesoporous volumes $W_o + V_{meso}$. As seen in Table 1, there is a good agreement between S_{total} and S_{comp} , whereas S_{BET} diverges from these values outside the range of micropore widths L_o 0.8-1.1 nm. This feature has been discussed elsewhere [6, 20, 21]. Surface related quantities were calculated by using $S_{av} = (S_{comp} + S_{total})/2$. It also appears that the enthalpies of immersion $\Delta_i H(C_6H_6)$ calculated from the parameters of Dubinin's equation are in good agreement with the experimental values given in Table 2, which may be regarded as a test for self-consistency between the different techniques.

The average micropore sizes are calculated from the characteristic energy E_o of the nitrogen isotherm [20] and the mesopore size distributions (diameters D_{KJS}) are obtained by applying the Kruk-Jaroniec-Sayari (KJS) method to the adsorption isotherm branch [25]. Typical examples of mesoporosities are shown in Fig. 1.

The carbons, which are all microporous, have been divided into four different series (I-IV) on the basis of the porosity above 2nm, the upper limit of microporosity.

Series I (carbons M1 to M5) has practically no mesoporosity and S_e does not exceed

10 to 15 m² g⁻¹. Therefore, these carbons may be regarded as exclusively microporous with L_0 between 0.66 and 1.25 nm. Series II contains sample M6, which displays the only bimodal mesoporosity observed in this study. Series III (M7 to M10) is characterized by relatively narrow mesoporosities with maxima between 24.4 and 31.5 nm. Finally, series IV (M11, M12) corresponds to carbons with a broad porosity above 10 nm. The surface areas S_e associated with the carbons of series II-IV are in the range of 81 to 299 m² g⁻¹.

Figure 1. Mesopore size distributions obtained by applying the Kruk-Jaroniec-Sayari (KJS) method to MAST-carbons M5 (○), M6 (■), M8 (●), M12 (+).

The classification allows interesting comparisons between pairs of carbons of series I and series II-IV with similar micropore sizes, but higher porosities for the latter. For example, M1 and M11 have average micropore widths L_0 around 0.7 nm, but widely different surface areas S_e (respectively 10 and 81 m² g⁻¹) due to the macroporosity of M11. The same is true for the pairs [M2+M8], [M4+M12] and the group [M5+M9/M10]. It follows that the present MAST-carbons, derived from the

same precursor, provide a suitable basis for the study of the effect of pore size distributions on the electrochemical behaviour of carbons in supercapacitors.

As shown in Table 3, the specific double layer capacitance relative to the carbon mass in a single electrode at low current density (50 mA g^{-1}), C_{50} , ranges from 119 to 199 F g^{-1} in aqueous H_2SO_4 , in good agreement with data reported in the literature for typical activated carbons [2, 4, 6, 7, 9]. This leads to the corresponding specific capacitances C_{50}/S_{av} given in Table 3. They vary between 0.111 and 0.163 F m^{-2} , which reflects the contribution of pseudo-capacitance effects. This is confirmed by its correlation with the specific enthalpy of immersion into water, $h_i(\text{H}_2\text{O}) = \Delta_i H(\text{H}_2\text{O})/S_{av}$ (Table 2). The latter varies between -0.020 and -0.075 J m^{-2} , where the lower bound corresponds practically to the wetting of a carbon without surface oxygen [21]. This means that in the case of the acidic electrolyte the minimum surface capacitance of the present carbons is around 0.111 F m^{-2} . It increases with the amount of the oxygen-containing surface complexes leading to the evolution of CO in TPD (thermally programmed desorption) [6].

As shown in Fig. 2, the gravimetric capacitances of the MAST carbons $C_{50}(\text{acidic})$ and the enthalpies of immersion into benzene and water follow the correlation suggested earlier [9] for more than 80 different activated carbons, namely

$$C_o(\text{acidic}) [\text{F g}^{-1}] = -(0.56 \pm 0.02) \Delta_i H(\text{C}_6\text{H}_6) - (0.047 \pm 0.056) \Delta_i H(\text{H}_2\text{O}) \quad (1)$$

C_{50} being close to C_o determined at 1 mA cm^{-2} , this observation confirms the general pattern.

Figure 2. Calculated and experimental gravimetric capacitances $C_{50}(\text{acidic})$ using Eqn (1). Earlier study ($\square$) [9] and MAST-carbons ($\blacksquare$)

In the case of the aprotic electrolyte $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{acetonitrile}$, the situation is different, due to the fact that at low current densities $C(\text{aprotic})$ is practically independent of the oxygen-containing surface complexes (At higher densities, they may act as obstacles and reduce ionic mobility, which leads to a decrease in C) [9]. On the other hand, in the case of carbons with a substantial porosity below 0.7 nm or presenting 'gate' effects at the entrance of wider pores, the accessibility of the aprotic $(\text{C}_2\text{H}_5)_4\text{N}^+$ cation is reduced with respect to the acidic cation [9]. It follows that the available surface area is smaller than determined with the help of small probes such as N_2 or C_6H_6 . This means that the specific capacitance $C_{50}(\text{aprotic})/S_{\text{av}}$ is too low. Theoretically, in the case of equal accessibility to CCl_4 and C_6H_6 , the ratio $\Delta_i H(\text{CCl}_4)/\Delta_i H(\text{C}_6\text{H}_6) = 0.96$. In view of the similar sizes of CCl_4 and $(\text{C}_2\text{H}_5)_4\text{N}^+$, this ratio is an indicator for the accessibility of the microporous structure to the ion. For example, the value of 0.45 found for sample M1 confirms that the capacitance of 0.033 F m^{-2} is not

realistic, but due to a reduced accessibility. The true value for the present carbons is probably close to $0.09\text{--}0.10 \text{ F m}^{-2}$, in agreement with typical porous carbons [9] which have not been subjected to specific chemical or thermal treatments following their preparation. This regular behaviour is also confirmed by the good correlation between $C_{50}(\text{aprotic})$ and $\Delta_i H(\text{CCl}_4)$ for most of the samples. As suggested by the data of Table 2, their average ratio ($0.66 \pm 0.09 \text{ F J}^{-1}$) is close to the average value of 0.63 F J^{-1} reported for 31 untreated carbons with pore sizes L_0 between 0.5 and 10 nm [9].

The present study confirms the detrimental effect of mesopores on the specific capacitance related to the electrode volume [26]. For our carbons, $C_{50}(\text{acidic})/V_{\text{electrode}}$ is approximately 60 F cm^{-3} for series I (only micropores) and only $43\text{--}47 \text{ F cm}^{-3}$ for series III (micropores + mesopores). In the case of the aprotic medium, the ratio $C_{50}(\text{aprotic})/V_{\text{electrode}}$ drops to 46 and 26 F cm^{-3} for series I and III, respectively. From a technological point of view, this decrease is important since it does not contribute to the development of small supercapacitors.

3.2. Contribution of the pores above 2 nm to the performance of supercapacitors

The present series of carbons also allows an assessment of the role of pores wider than 2 nm in the performances of supercapacitors. It is assumed that pores larger than 2 nm significantly enhance the capacitor performance by providing wider transport paths for ions diffusion into smaller pores [2, 11-16]. However, this view can be challenged by the following analysis based on the comparison of series I and II-IV (Table 1), where similar micropore systems can be found with and without a wider porosity, all samples being derived from the same precursor.

First of all, it confirms that the approach based on different contributions from micropores and mesopores to the overall capacitance [8, 13] is too limited [26, 27]. The contribution of the wider pores to the gravimetric capacitance appears to be

small, as it results from their surface area and not from the volume. It has been already shown that the specific capacitance in mesoporous carbons is the same as in microporous carbons [6, 21, 28]. The contribution is therefore equal to S_e multiplied by the specific capacitance of the given carbon or simply to $C_{50}(S_e/S_{av})$. On the other hand, a possible contribution of mesopores to the dynamic performances should be revealed by the comparison of the decrease in C with the current density under standard conditions, for example the ratio C_{6000}/C_{50} . Figures 3 and 4 compare these relative capacitances for the twelve carbons in the H_2SO_4 and $(C_2H_5)_4NBF_4$ /acetonitrile electrolytes, both as functions of L_o .

Fig. 3 shows that C_{6000}/C_{50} is practically independent of the average micropore width between 0.6 and 1.2 nm. No systematic increase is observed within pairs/groups of carbons with similar micropore systems with and without larger pores namely (M1+M11), (M2+M8), (M4+M12) and (M5+M9/M10). The small increase observed for some cases would not justify the claim of an improvement due to the wider pores in the same type of carbon. This probably reflects the total accessibility of the micropore systems to the relatively small ions of the aqueous electrolyte.

Figure 3. Evolution of normalised specific capacitance (C_{6000}/C_{50}) in 2M H_2SO_4 with the average micropore width for MAST-carbons

In the case of the aprotic electrolyte, the increase of C_{6000}/C_{50} (Fig. 4) clearly reflects the ratio of the dimension of the larger $(C_2H_5)_4N^+$ ion (0.68 nm) and the average micropore width L_o (0.6 to 1.2 nm). Acetonitrile being smaller than the $(C_2H_5)_4N^+$ cation, it fills all pores (like C_6H_6 or CH_2Cl_2) and at least a planar solvation is likely in slit-shaped micropores of 0.65 to 0.70 nm [29, 30].

Figure 4. Evolution of normalised specific capacitance (C_{6000}/C_{50}) in 1M $(C_2H_5)_4NBF_4$ /acetonitrile with the average micropore width for MAST-carbons.

The profile displayed here indicates that the diffusion of aprotic cations is strongly hindered by the smaller micropores. The mobility is dictated by the largest ion, here the $(C_2H_5)_4N^+$ cation, with a size close to that of CCl_4 .

An average width around 1.2 nm appears to optimize the rate capability of carbons at high current density and it is important to point out that it is similar to that observed for essentially mesoporous carbons [28]. This experimental observation contrasts with the optimum size of 0.7 to 0.8 nm reported for carbide-derived carbons [22]. The difference may reflect both the precursor materials and the carbonization treatment.

On the other hand, it appears that for the same pairs of carbons, the difference is still small, with the exceptions of M1 and M11. This could be explained by the reduction in the micropore lengths rather than their width during the formation of the wider pores. However, in view of the similarities between L_o (around 0.7 nm) and the size of the ion (0.68 nm), M1 and M11 are exceptions anyway and it would appear

that for carbons with wider micropores the contribution of the mesopores to the ionic mobility is smaller than assumed.

Further evidence is provided by the fact that the enhancement of the power capability suggested for microporous carbons with a significant mesoporosity, is not confirmed by the Ragone-type plots (Fig. 5). The comparison of the pairs [M2+M8] and [M5+M10], groups of carbons with a micropore size around 0.95 nm and 1.23 nm, respectively, confirms similar performance within materials with and without mesoporosity fraction.

Figure 5. Power density vs. Energy density for carbons with a micropore size around 0.95 nm (M2+M8) and 1.24 nm (M5+M10) and different mesoporosity fraction.

4. Conclusions

The present study shows that the electrochemical properties of MAST-based carbons fit well into the general pattern established earlier, for both the acidic and the aprotic electrolytes. It also confirms the similar accessibility in pores wider than 0.8 nm, provided that no 'gate' effects are present. Moreover, the comparison of carbons

obtained from the same precursor, with and without a significant mesoporosity, suggests that the latter does not contribute significantly to the enhancement of capacitor performance.

The good rate capability of the microporous carbons may be due to a reduction in the micropore length.

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Table 1. Main textural characteristics of the phenolic resin-derived activated carbons

Series	Carbon	V_{total} (cm^3g^{-1})	W_o (cm^3g^{-1})	E_o (kJ mol^{-1})	L_o (nm)	D_{KJS} (nm)	S_{BET} (m^2g^{-1})	S_{comp} (m^2g^{-1})	S_{mi} (m^2g^{-1})	S_e (m^2g^{-1})	$S_{\text{total}} = S_{\text{mi}} + S_e$ (m^2g^{-1})	$S_{\text{av}} = (S_{\text{comp}} + S_{\text{total}})/2$ (m^2g^{-1})
I	M1	0.35	0.33	27.7	0.66	-	710	875	1000	10	1010	943
	M2	0.55	0.51	22.9	0.94	-	1105	1047	1085	11	1096	1072
	M3	0.60	0.54	22.0	1.02	-	1200	1046	1059	8	1067	1057
	M4	0.58	0.50	21.5	1.07	-	1190	1061	935	13	948	1005
	M5	0.85	0.71	20.1	1.25	-	1773	1256	1136	6	1142	1199
II	M6	1.50	0.36	21.0	1.12	5.2-54.0	909	947	643	269	912	930
III	M7	0.55	0.29	24.2	0.84	24.4	648	880	690	187	877	879
	M8	0.71	0.45	22.8	0.95	26.5	961	967	947	140	1087	1027
	M9	0.85	0.64	20.2	1.23	29.7	1472	1079	1041	116	1157	1118
	M10	1.36	0.63	20.4	1.20	31.5	1488	1288	1050	299	1349	1319
IV	M11	0.27	0.25	26.5	0.71	Broad PSD >10	550	794	704	81	785	790
	M12	0.59	0.51	22.1	1.01	Broad PSD >10	1140	1140	1010	110	1120	1130

Table 2. Enthalpies of immersion of the phenolic resin-based activated carbons

Series	Carbon	$-\Delta_i H(C_6H_6)$ (J g ⁻¹)	$-\Delta_i H(CCl_4)$ (J g ⁻¹)	$\Delta_i H(CCl_4)/\Delta_i H(C_6H_6)$	$-\Delta_i H(H_2O)$ (J g ⁻¹)	$-h_i(H_2O)$ (J m ⁻²)	$C_{50}(\text{aprotic})/\Delta_i H(CCl_4)$ (F J ⁻¹)
I	M1	125.9	56.2	0.45	22.3	0.024	0.55
	M2	151.7	166.7	1.10	21.9	0.020	0.58
	M3	190.5	167.1	0.86	47.6	0.075	0.57
	M4	152.4	91.0	0.58	27.8	0.028	0.83
	M5	209.9	196.3	0.94	59.7	0.050	0.63
II	M6	118.5	101.9	0.86	70.1	0.075	0.75
III	M8	133.3	124.4	0.93	38.5	0.037	0.68
	M10	197.8	175.6	0.89	85.2	0.065	0.64
IV	M12	191.6	146.8	0.77	31.7	0.028	0.71

Table 3. Electrochemical properties of the phenolic resin-based activated carbons

	Carbon	C ₅₀		C ₅₀	
		[H ₂ SO ₄]		[(C ₂ H ₅) ₄ NBF ₄ /acetonitrile]	
		(F g ⁻¹)	(F m ⁻²)	(F g ⁻¹)	(F m ⁻²)
I	M1	119	0.126	31	0.033
	M2	121	0.113	97	0.090
	M3	155	0.147	95	0.090
	M4	128	0.127	76	0.076
	M5	166	0.138	124	0.103
II	M6	152	0.163	76	0.082
III	M7	112	0.127	47	0.053
	M8	124	0.121	85	0.083
	M9	159	0.142	105	0.094
	M10	199	0.151	113	0.086
IV	M11	125	0.158	19	0.024
	M12	125	0.111	105	0.093