The Importance of Electrode Characterization to Assess the Supercapacitor Performance of Ordered Mesoporous Carbons

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ABSTRACT

Carbon based-supercapacitors are widely used in numerous applications but the knowledge of the specific role of carbon features in their performance is still insufficient. The main aim of this work is to warn readers that the current interpretation of the device operation, mostly based on powdered carbon properties, may be misleading in certain cases and should be complemented with the physicochemical characterization of the corresponding electrodes. Ordered mesoporous carbons highly enriched in surface functionalities were prepared by carbonization of 3-aminobenzoic acid into SBA-15 template. These carbons achieved a specific capacitance as high as 220 F/g in 2M H₂SO₄ aqueous electrolyte. The pseudocapacitance contribution ranged between 35 and 70% of the overall capacitance. It was shown that the structural and textural changes underwent by these advanced carbons during their processing in form of electrodes prevented the full exploitation of their outstanding properties for high-power applications. This makes a difference regarding conventional, disordered activated carbons, which virtually preserve their structure during electrode preparation.

KEYWORDS: Ordered mesoporous carbon, Doped carbon, Supercapacitor, Electrode characterization.

1. INTRODUCTION

Supercapacitors (SCs) are energy storage systems which display high power capability, short charging time and good cyclability. They are widely used in numerous applications such as regenerative braking in hybrid vehicles, cold engine starting, ride-through backup power systems, digital electronic items, military and aerospace devices, etc [1-4]. Currently, SCs are being considered promising candidates for the storage of renewable energy but significant improvements in their performance are still highly required for their implementation at large scale. In view of their potentiality, intensive research efforts are presently being devoted to develop the optimal device in a short-medium-term.

Virtually all commercial supercapacitors use conventional activated carbons in their electrodes although advanced carbons such as nanotemplated carbons, carbon onions, carbon nanosheets, hierarchical porous carbons, carbon microspheres, graphene, etc. are being extensively investigated to improve their performance [2,4-14].

As the operation of carbon supercapacitors is based on the electrostatic accumulation of electrolyte ions on the charged surface of an electrode (electrochemical double-layer, EDL), the ability for energy storage and power release of SCs predominantly depends on the extent of the specific surface area of the electrode and its accessibility to the electrolyte ions [2,5-8]. In this context, most research has been focused in developing carbons with an appropriate porosity (i.e. specific surface area as well as a suitable pore size distribution). More recent approaches are dealing with doping the carbon surface with functional groups, to not only introduce pseudocapacitance but also enhance the surface wettability [2,4-14].

Various correlations between the physico-chemical properties of carbons and the operation of the corresponding SCs have been proposed so far [14-21] by the assessment of a large variety of

materials under the same experimental conditions [22]. They appear to be successful in most cases, but the behavior of certain carbons such as graphene-type materials cannot be explained within the general patterns found for a number of typical porous materials [23,24]. In this context, Wu et al. [25], have reported the difficulties for assessing adequately the combined roles of surface area and surface functionalities in the performance of nanoporous carbons in supercapacitors. They pointed out the need for an appropriate textural characterization of ultramicroporous carbons by the combination of N₂ and CO₂ adsorption.

As reported elsewhere [26], nanocasting of 3-aminobenzoic acid (MABA) inside the porosity of an SBA-15 template in the presence of H₃PO₄ gave rise to ordered mesoporous carbons (OMCs). Both the textural characteristics and surface chemical properties of the carbons were modified in a controlled way by varying the amount of H₃PO₄ and carbonization temperature [26-28]. H₃PO₄ influences the pyrolysis mechanism of the MABA precursor and a progressive degradation of the structural order and the mesopore arrangement was observed for high H₃PO₄ concentrations. In general, larger pore volumes and wider mesopore size distributions were obtained for samples prepared at 800 and 900 °C and concentrations of H₃PO₄ above 50 wt.%. On the contrary, low amounts of H₃PO₄ led to OMCs with very narrow pore size distributions and favored nitrogen retention at the carbon surface.

Such ordered mesoporous carbons having a doped surface with a wide variety of surface functionalities and a highly periodic and interconnected structure with specific surface areas above 1000 m²/g look a priori attractive as candidates for supercapacitors. The presence of surface groups would provide an extra capacitance by redox-type reactions (pseudocapacitance) to be added to the EDL-Capacitance, and the solvated ions would diffuse easily through the ordered mesoporous channels [10, 29-31]. Surprisingly, as we will see in this work, the

electrochemical measurements in 2M H₂SO₄ electrolyte reveal a rather limited performance in terms of energy storage and power release, which differs considerably from the optimal operation expected for OMCs.

This study goes one step further by illustrating significant changes that take place in the structure and textural properties of OMCs when processed in electrodes with features of commercial devices. These should not be neglected for understanding the supercapacitor performance and the specific role of carbon characteristics. It also suggests possible constraints of advanced carbons for application in SCs as their outstanding characteristics may not be preserved when they are processed in commercial electrodes.

2. EXPERIMENTAL

2.1. Synthesis of the Ordered Mesoporous Carbons.

OMCs were synthesized through polymerization of a polyamide precursor (3-aminobenzoic acid, MABA) inside the SBA-15 template porosity; the synthesis was accomplished in phosphoric acid medium in order to achieve an additional porosity development and/or to enrich the surface in functional groups. In a typical synthesis, 1 g of SBA-15 was infiltrated with 1.4 g of MABA dissolved in 50 ml of acetone, the solvent was evaporated under vacuum and the MABA was thermally polymerized at 160 °C. The MABA/SBA-15 composite was then impregnated with H₃PO₄ at different impregnation ratios and carbonized under inert atmosphere at 800 or 900 °C. The carbonized composites were washed with water to eliminate the phosphoric acid and the OMCs were isolated by etching the SBA-15 with HF. Samples were denoted here as PACXp/T, where Xp is the impregnation ratio (0, 5 or 50 wt.% H₃PO₄) and T is the temperature of carbonization. A detailed preparation process can be found elsewhere [26].

2.2. Characterization Techniques.

Porous texture of the OMCs samples, both in powder (as synthesized) or in electrodes, was characterized by N₂ adsorption/desorption isotherms at -196 °C using a volumetric adsorption apparatus, ASAP 2010 (Micromeritics). The specific surface areas and pore size distributions (PSDs) were obtained by applying the BET equation and the NLDFT-cylindrical model, respectively. Prior to the adsorption measurements, the OMCs in powder or in form of electrodes were degassed at 150 or 110 °C during 16 h, respectively.

Structural and morphological characterizations of the powdered OMCs and the electrodes prepared from them were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) using a Siemens D5000 diffractometer (Cu K α radiation; scanning range 2θ = 0.5-5 °; step width = 0.01 °; time per step = 1 second) and a Carl Zeiss DMS-942 microscope.

Chemical characterization was performed by XPS in a SPECS system using a monochromatic Al K α excitation source (1486.3 eV, 150 W) and working at a pressure of 10⁻⁹ mbar. The photo-excited electrons were analyzed in constant pass energy mode (pass energy of 30 eV for the survey spectra and 10 eV for the high-resolution core level spectra). A detailed study of the surface chemistry of the present OMCs has been reported elsewhere [27,28].

2.3. Electrochemical Performance Measurements.

The electrochemical performance of the studied mesoporous carbons was tested in a sandwich-type capacitor set up with two carbon pellets separated by glassy fibrous paper (Whatman) and placed in a Swagelok cell. The dried OMCs were mixed with polytetrafluoroethylene (5 wt.%) and carbon black Super P (MMM Carbon) (5 wt.%) to form electrodes weighing around 5 mg. The resulting film was rolled to a thickness of ~300 μ m, punched into a diameter of 8 mm and dried in an oven at 100 °C for 24 h. The electrolyte was 2 M H₂SO₄ aqueous solution. The

electrochemical tests involved cyclic voltammetry at scan rates between 1 and 50 mV/s and galvanostatic charge-discharge cycles at current densities from 1 to 70 mA/cm², the cell voltage ranging from 0 to 0.8 V. Electrochemical impedance spectroscopy (EIS) measurements were performed by using a sinusoidal signal of ± 15 mV from 10⁻³ to 60 kHz (PGSTAT 30 (Autolab B.V., Metrohm) potentiostat equipped with a FRA32M module).

A conventional microporous activated carbon with specific surface area of 1054 m²/g, average pore size around 1.41 nm and limiting capacitance of 154 F/g (1 mA/cm²) was used as reference.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Ordered Mesoporous Carbons.

As illustrated by the SEM micrographs in Figure 1a, the OMCs show a similar morphology to the SBA-15 used as template (not shown here) [26], consisting in chains of particles with bean-like shape and less than 1 μ m in length. The materials PAC5/900 and especially PAC50/900 display a less defined morphology, with some fused particles due to the degradation of the silica template during the carbonization step in the presence of phosphoric acid [26,28].

The small-angle XRD diffractograms (Figure 1b) exhibit three peaks ascribed to the (100), (110) and (200) reflections of the bidimensional hexagonal space group p6mm, which is in agreement with a correct replication of the SBA-15 structure. Samples PAC800 and PAC900 show well-resolved peaks, while the material prepared in the presence of 5% H₃PO₄ gives slightly broader signals which are shifted to higher angles. In the case of the sample obtained with 50 wt.% of H₃PO₄ only the (100) peak can be observed. This is due to a partial loss of ordering of the mesoporous arrangement with increasing amount of phosphoric acid used in the synthesis.

Type-IV adsorption isotherms (Figure 2) reflect the high porosity development of the OMCs, which is centered in the mesopore range. The pore size distributions differ depending on the amount of H_3PO_4 used in their synthesis. Samples PAC800 and PAC900 possess uniform mesopores with diameters around 5.5 nm, which correspond to the space between hexagonally arranged carbon bars [26]. On the other hand, the presence of 5% H_3PO_4 produces a shift of the PSD to somewhat larger pores (6.1 nm), which is related to a slight activating effect. Whereas PAC800, PAC900 and PAC5/900 attain quite similar specific surface areas ranging from 1031 to 1178 m^2/g (Table 1), the addition of 50 wt.% H_3PO_4 enhances the activation process and PAC50/900 reaches a surface area of 1883 m^2/g . In this case, a remarkable degradation of both the structural order and mesopore arrangement [26,28] results in a wide PSD with a maximum around 6.5 nm (Figure 2).

It is noteworthy the retention of large amounts of nitrogen and oxygen after the carbonization of MABA. As previously reported [27,28], carbonization temperature and H_3PO_4 concentration exert diverse effects on the evolution of nitrogen, oxygen and phosphorus, whose surface concentration in the present OMCs ranges, respectively, between 2.9-4.5, 3.5-6.3 and 0-1.3 mmol/g (Table 1). Figure 3 summarizes the wide variety of N- and O-functionalities on the OMCs surface (obtained from the deconvolution of XPS spectra of N1s, O1s and P2p components (see also Figures S1 and S2 of the Supporting Information)). Briefly, nitrogen is mainly in the quaternary form (N3). Its density on the carbon surface increases with increasing carbonization temperature and decreases in the presence of H_3PO_4 . Pyridinic (N1), pyrrolic (N2) and N-oxide (N4 and N5) functionalities are less abundant as the carbonization temperature and the amount of H_3PO_4 are increased.

Increase in the carbonization temperature reduces the oxygen-group content, whereas their density on the carbon surface is enhanced by the addition of phosphoric acid. As illustrated in Figure 3, the use of an amount of phosphoric acid as high as 50 wt.% notably reduces components O1 (C=O bonds in carbonyl and carboxylic acid) and O3 (non-carbonylic C–O bonds in ester and anhydride functionalities), while a significant increase in the O2 peak takes place. The latter is associated with esters, anhydrides and hydroxyl functional groups and also to the bridging oxygen in phosphates/polyphosphates (C – O – PO₃) [32,33].

3.2. Electrochemical Performance.

At a first glance, the rectangular voltammograms and the symmetry and linear slopes of the charge-discharge cycles in Figure 4 a-b are indicative of efficient electrochemical double layer formation in the present carbons. Indeed, the specific capacitances of PAC800 and PAC900 are in the upper limit found for mesoporous carbons in 2M H₂SO₄ (200-220 F/g) and largely exceed those of typical templated mesoporous carbons with a similar specific surface area (generally in the range of 140-160 F/g) [10,17,20]. Surprisingly, PAC50/900 with a surface area as high as 1883 m²/g, reaches only 172 F/g, which is very similar to that shown by PAC5/900, whose surface area (1031 m²/g) slightly surpasses one half of the surface area of PAC50/900 (Figure 5a).

An overall assessment based on a variety of templated mesoporous carbons with a low content in surface functionalities suggested an average contribution from the carbon surface of around 0.14 F/m² in aqueous H₂SO₄ electrolyte [17]. Figure 5a illustrates the fact that the present materials do not follow such a general pattern. It is worth noting that the average contribution of the surface of PAC800, PAC900 and PAC5/900 provides around 0.16-0.19 F/m², whereas in the

case of PAC50/900 the contribution is only 0.09 F/m^2 . Taking into account the high surface functionalization of these carbon materials, a higher average contribution from their surface could be expected. Therefore, these low values could suggest that the functional groups are not electrochemically active and, therefore, 3-aminobenzoic acid, either with or without added H_3PO_4 , would not be an appropriate precursor of doped carbons for electrochemical capacitors.

Furthermore, contrary to what could be expected from their highly advantageous structure, Figures 4c and 4d reveal that some of the studied OMCs (specifically, PAC5/900 and PAC50/900) are not a good option for high power applications. Their high energy density drops with increasing power output and their operation is surpassed by that of the conventional microporous activated carbon (Figure 4c). Despite being a disordered microporous carbon with an average pore size around 1.4 nm, AC achieves capacitance saturation at a higher frequency and its response is much faster than that of the more advanced OMCs (Figure 4d).

A closer examination based on the N_2 adsorption isotherms measured on the electrodes (Figure 2) reveals that the studied OMCs may undergo a significant decrease in their surface when are processed in electrodes. Thus, the measured surface area of PAC800, PAC5/900 and PAC50/900 in the electrode is only 634, 717 and $1070 \text{ m}^2/\text{g}$, which, respectively, correspond to 54, 70 and 57% of the surface areas of the corresponding powders (Table 1). Such a loss is very high compared to the 8-9% decrease experienced by a standard activated carbon and a templated mesoporous carbon prepared from a mixture of thermoplastic poly(vinyl alcohol) with MgO particles [20] (Figure S3 of the Supporting Information). It is noticed that the extent of porosity reduction in the electrode depends on the OMC itself as the adsorption isotherm of PAC900 remains practically unchanged (Figure 2).

The small-angle X-ray diffractograms of the electrodes (Figure 6b) display a limited resolution due to the presence of the binder and the added carbon black, but the clear decrease in the intensity of the XRD peaks compared with those for the powders (Figure 1b) reflects the reduction of the OMC mesostructured order degree during electrode preparation. PAC900 retains the highest degree of ordering which suggests that the treatment at 900°C leads to a stronger structure, resulting less damaged in the electrode.

The different behavior of the OMCs during electrode processing is corroborated by SEM observations. As illustrated by the micrographs of the electrodes shown in Figure 6a, the carbon structure is partially destroyed. The chains are broken into individual bean-like particles which largely retain their integrity in the case of PAC800 and PAC900 electrodes. On the contrary, the materials prepared in the presence of H_3PO_4 (PAC5/900 and PAC50/900) are more brittle and their processing results in fragmented items.

Figure 6a also shows that a significant portion of the resulting carbon entities is embedded in the binder used for the electrode preparation. This explains the porosity loss observed for the studied OMCs when they are shaped into electrodes. It is worth noting that PAC900 does not undergo such a particle coating. Likely, the nature of the surface obtained at higher temperature hinders the interaction with the binder and as a consequence the area is maintained around 1000 m^2/g (Table 1). The somewhat wider PSD (Figure 2) may be due to the breakdown of some of the mesopore walls during the preparation of the electrode, which would produce the joining of adjacent mesopores giving rise to larger pores.

The study of the OMC-electrodes provides evidences for a remarkable participation of the surface complexes derived from 3-aminobenzoic acid in redox reactions, contrary to what was previously stated when the specific capacitance was related to the surface area of the powders.

Indeed, if one uses the surface area of the carbons in the corresponding electrodes as a normalizing parameter (Table 1), the surface-capacitance of PAC800 raises to 0.35 F/m^2 (Figure 5b) indicating a significant extra contribution in the form of a pseudocapacitance, to be added to the purely double layer behavior associated to the extent of the surface area. Taking into account a contribution from the double layer in 2M H_2SO_4 of around 0.105 F/m^2 (obtained by a systematic study of a large variety of carbon materials) [34], one obtains a pseudocapacitance of 157 F/g in PAC800, which corresponds to 71 % of its overall capacitance. PAC900, with a rather similar structure, achieves 192 F/g by a contribution of only 0.19 F/m^2 . The larger effective surface of the latter carbon in the electrode results in a higher double-layer capacitance (105 F/g) but the pseudocapacitance decreases to 87 F/g and accounts for 45% of the specific capacitance. This lower value may derive from the somewhat lower surface density of functionalities $(\text{O}+\text{N}+\text{P})/\text{S}_{\text{BET}}$ (Table 1) with a preferential elimination of pyridinic and pyrrolic nitrogen at higher temperature (900°C) (Figure 3).

The specific capacitance of PAC5/900 is only 15% lower than that of PAC900 although their surface areas in the corresponding electrodes are notably different from each other. The catalytic effect of H_3PO_4 promoting dehydration, cyclization and condensation of the carbon structure [27, 28] leads to a large variety of functionalities and, therefore, the loss in the double-layer contribution in PAC5/900 is partly compensated by a higher pseudocapacitance. The capacitance of PAC5/900 corresponds to 46% from EDL and 54% from redox-type processes.

The heat treatment of MABA with 50 wt.% H_3PO_4 increases the content in functionalities but their density (per m^2 of surface area) is similar to that in the material obtained without H_3PO_4 (Table 1). As PAC50/900 and PAC900 also display comparable surfaces in the electrode, their specific capacitances result to be quite similar to each other.

While the presence of functional groups is highly beneficial to increase the capacitance at low frequency, its effect on the high frequency operation is the opposite due to the participation of the functional groups in redox reactions [35], which slow down the ion mobility. Additionally, coating of the carbon particles by the binder may prevent good interaction with the electrolyte under dynamic conditions. As discussed previously, both effects appear to be less significant in PAC900 and Figure 4d clearly illustrates its faster response among the OMCs series. The maximum operating frequency $f_{\max}$ (at which the capacitance drops to 50% of its maximum value) of the electrode based on PAC900 is nearly 5 times higher than that for PAC800. Such a better performance in comparison with the other studied OMCs is related to (i) its higher conductivity as a consequence of being obtained at 900 °C [36], (ii) minor particle breakdown and limited loss of structural order during electrode processing, and (iii) lower degree of particle coating by the binder (Figure 6a).

Regarding the comparison with the activated carbon, the operation of the studied OMCs is more limited as far as the expected advantage of the ordered structure for better ion mobility cannot be exploited in the present case, because of the loss of the long-range structural order after processing the OMCs in the electrodes.

4. CONCLUSIONS

Due to the changes suffered by the studied advanced carbons when processed in electrodes, the interpretation of the supercapacitor performance based on the powdered carbon properties can be insufficient, or even misleading. A reliable assessment of the role of material features requires the characterization of the corresponding electrodes.

The study of electrodes made from materials obtained by the carbonization of 3-aminobenzoic acid allowed us to identify it as an attractive precursor of carbons for supercapacitors. The resulting highly-doped ordered mesoporous carbons achieve specific capacitances as high as 221-164 F/g in 2M H₂SO₄ aqueous electrolyte, the pseudocapacitance contribution ranging between 35 and 70% of the overall capacitance.

In spite of the ordered arrangement of mesopores in the obtained carbons, high-power performance is not achieved. The long-range structural order is not retained during electrode processing and, consequently, the great expectations based on the outstanding properties of the OMCs in powdered form cannot be fulfilled. This is a disadvantage over standard activated carbons, which virtually preserve their structure when processed as electrodes for supercapacitors.

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Figure 1. SEM micrographs (a) and small-angle X-ray diffraction patterns (b) of the ordered mesoporous carbons.

Figure 2. N₂ adsorption-desorption isotherms at -196°C for the ordered mesoporous carbons in powder and in the electrode. Inset: pore size distributions obtained by applying the NLDFT method. The adsorption capacity of samples in electrode is referred to the OMC mass.

Figure 3. Density of nitrogen (a) and oxygen (b) functionalities in the surface of the OMCs determined from the deconvolution of the high-resolution XPS spectra shown in Figure 1S of the Supporting Information. Nitrogen functionalities correspond to: (N1) pyridinic; (N2) pyrrolic; (N3) quaternary nitrogen and (N4 and N5) N-oxides. Oxygen functionalities correspond to: (O1) C=O bonds in carbonyl and carboxylic acid; (O2) ester, anhydride and hydroxyl functional groups and also to the bridging oxygen of phosphates/polyphosphates ($\text{C} - \text{O} - \text{PO}_3$) and (O3) non-carbonylic C – O bonds in ester and anhydride functional groups.

Figure 4. Electrochemical performance of the OMCs in 2M H₂SO₄. (a) Cyclic voltammograms at 1 mV/s, (b) Galvanostatic charge–discharge cycles at 1 mA/cm², (c) Ragone-type plot, (d) Evolution of the normalized capacitance $C/C_{\max}$ with the frequency (inset: EIS Nyquist plot (high-frequency range)). An activated carbon (AC) is used for comparison.

Figure 5. Variation of the specific capacitance at 1 mA/cm² with the total surface area of OMCs in powder (a) and in the electrode (b). For comparison, the line drawn through the origin corresponds to the best fit for templated mesoporous carbons obtained by different procedures ($\square$, [17]), ($\circ$, [20]).

Figure 6. SEM micrographs (a) and small-angle X-ray diffraction patterns (b) of the electrodes made from ordered mesoporous carbons.

Table 1. Characteristics of the ordered mesoporous carbons

Carbon	Specific area (S_{BET})		Surface concentrations of heteroatoms				Specific capacitance at 1 mV/s
	Powder (m^2/g)	In the electrode (m^2/g) [*]	N (mmol/g)	O (mmol/g)	P (mmol/g)	$[(\text{O}+\text{N}+\text{P})]/S_{\text{BET}}$ ($\mu\text{mol}/\text{m}^2$)	C (F/g) [*]
PAC800	1178	634	4.46	4.09	0.00	7.26	221
PAC900	1084	1027	3.95	3.51	0.00	6.88	192
PAC5/900	1031	717	2.88	5.02	0.95	8.58	164
PAC50/900	1883	1070	3.60	6.30	1.34	5.97	172

^{*} Referred to the mass of carbon in the electrode