



## The importance of electrode characterization to assess the supercapacitor performance of ordered mesoporous carbons



Ángela Sánchez-Sánchez, Teresa A. Centeno<sup>\*</sup>, Fabián Suárez-García<sup>\*\*</sup>,  
Amelia Martínez-Alonso, Juan Manuel D. Tascón

*Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080, Oviedo, Spain*

### ARTICLE INFO

#### Article history:

Received 26 April 2016

Received in revised form

14 July 2016

Accepted 31 July 2016

Available online 1 August 2016

#### Keywords:

Ordered mesoporous carbon

Doped carbon

Supercapacitor

Electrode characterization

### 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 2 M H<sub>2</sub>SO<sub>4</sub> 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.

© 2016 Published by Elsevier Inc.

### 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

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: [teresa@incar.csic.es](mailto:teresa@incar.csic.es) (T.A. Centeno), [fabian@incar.csic.es](mailto:fabian@incar.csic.es) (F. Suárez-García).

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  $N_2$  and  $CO_2$  adsorption.

As reported elsewhere [26], nanocasting of 3-aminobenzoic acid (MABA) inside the porosity of an SBA-15 template in the presence of  $H_3PO_4$  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  $H_3PO_4$  and carbonization temperature [26–28].  $H_3PO_4$  influences the pyrolysis mechanism of the MABA precursor and a progressive degradation of the structural order and the mesopore arrangement was observed for high  $H_3PO_4$  concentrations. In general, larger pore volumes and wider mesopore size distributions were obtained for samples prepared at 800 and 900 °C and concentrations of  $H_3PO_4$  above 50 wt%. On the contrary, low amounts of  $H_3PO_4$  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  $m^2/g$  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 2 M  $H_2SO_4$  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  $H_3PO_4$  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%  $H_3PO_4$ ) 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  $N_2$  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  $K\alpha$  radiation; scanning range  $2\theta = 0.5$ – $5^\circ$ ; step width =  $0.01^\circ$ ; time per step = 1 s) and a Carl Zeiss DMS-942 microscope.

Chemical characterization was performed by XPS in a SPECS system using a monochromatic Al  $K\alpha$  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  $\sim 300$   $\mu m$ , punched into a diameter of 8 mm and dried in an oven at 100 °C for 24 h. The electrolyte was 2 M  $H_2SO_4$  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/cm<sup>2</sup>, the cell voltage ranging from 0 to 0.8 V. Electrochemical impedance spectroscopy (EIS) measurements were performed by using a sinusoidal signal of  $\pm 15$  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  $m^2/g$ , average pore size around 1.41 nm and limiting capacitance of 154 F/g (1 mA/cm<sup>2</sup>) was used as reference.

## 3. Results and discussion

### 3.1. Characterization of the ordered mesoporous carbons

As illustrated by the SEM micrographs in Fig. 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  $\mu m$  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 (Fig. 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%  $H_3PO_4$  gives slightly broader signals which are shifted to higher angles. In the case of the sample obtained with 50 wt% of  $H_3PO_4$  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 (Fig. 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

Download English Version:

<https://daneshyari.com/en/article/4758597>

Download Persian Version:

<https://daneshyari.com/article/4758597>

[Daneshyari.com](https://daneshyari.com)