

# PREPARATION AND CHARACTERIZATION OF MONOLITHS WITH HIERARCHICAL POROSITY FOR SUPERCAPACITOR APPLICATIONS

A.L. Tomás-García<sup>1</sup>, D.Lozano-Castello<sup>1</sup>, E.Morallón<sup>2</sup>,  
D.Cazorla-Amorós<sup>1</sup>, C.Barbero<sup>3</sup>

<sup>1</sup>Departamento de Química Inorgánica and <sup>2</sup> Departamento de Química Física, Universidad de Alicante, Ap. 99 E-03080. Spain

<sup>3</sup>Departamento de Química, Universidad Nacional de Río Cuarto, Agencia postal No 3, 5800 Río Cuarto, Argentina

## Introduction

High energy and high power electric double layer capacitors (EDLC) uses activated carbons or glassy carbons as electrodes. The reason of using activated carbon in EDLC manufacture is attributed to the recognized fact that the larger the surface area that an EDLC can provide for adsorption of ions on electrodes, the more energy can be stored in the EDLC [1,2]. High surface area carbon materials containing tailored microporosity, with a relatively wide micropore size distribution are particularly desirable for this application [2]. It has been also stated that regularly connected wide micropores and/or narrow mesopores are very effective at reducing ion-transfer resistance [3,4].

In a previous work it was shown that the carbonization of cationic resorcinol-formaldehyde (RF)-surfactant composites produces monolithic porous carbons containing micropores and mesopores (bimodal pore size distribution). This type of nanostructured carbon can be prepared with surface area up to 670 m<sup>2</sup>/g, presenting a total capacitance of around 145 F/g in sulphuric acid. The objective of the present study is to develop higher degree of porosity in this type of monolithic porous carbons, keeping the bimodal pore size distribution, in order to increase their capacitance. To do that, different activation procedures (chemical activation with KOH and "physical" activation with CO<sub>2</sub>) have been used.

## Experimental

Monolithic porous carbons have been prepared by carbonization of resorcinol-formaldehyde (RF) porous resins. The resins were produced from RF gels by conventional drying in air, using stabilizers to maintain the porous structure during drying. The procedure is similar to that described elsewhere [5]. Two different porous resins were prepared, and after carbonization two carbon monoliths were obtained (REF and PDA). These two monolithic carbons have been activated using CO<sub>2</sub> as activating agent. The activation conditions were selected from the results of thermogravimetric experiments, to obtain a burn-off around 50%. The activation conditions (heating rate, activation temperature and time, CO<sub>2</sub> flow rate) and the resulting burn-off for the REF and PDA monoliths were, respectively: (i) sample REF-CO<sub>2</sub>: 5 °C/min, 825 °C, 3 hours, 80 ml/min, 44% burn-off; (ii) sample PDA-CO<sub>2</sub>: 5

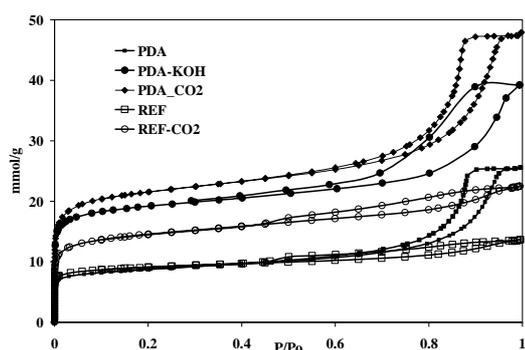
°C/min, 850 °C, 2.5 hours, 80 ml/min, 54% burn-off. Moreover, the PDA monolith was activated using KOH as activating agent and following the procedure described elsewhere [6]. The activation conditions of the sample PDA-KOH were: (i) KOH/monolith ratio equal to 3/1 in weight; (ii) heating rate 5 °C/min; (iii) activation temperature 750 °C; (iv) activation time 1h; (v) N<sub>2</sub> flow rate of 500 ml/min.

Surface area characterization of the two monoliths, before and after activation, was carried out by physical adsorption (N<sub>2</sub> at 77 K and CO<sub>2</sub> at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome). Temperature programmed desorption experiments were done in a DSC-TGA equipment (TA Instruments, SDT 2960 Simultaneous), coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3), to characterize the surface chemistry of the samples. To measure the electric double layer capacitance, composite electrodes were prepared from powder porous carbon material, using 5% teflon. A stainless steel mesh was used as a current collector. The standard three electrode cell configuration was employed. Reversible hydrogen electrode (RHE) was used as reference and a platinum wire was employed as a counter electrode. 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as aqueous electrolyte. The capacitance value was measured by the galvanostatic method at 1 mA.

## Results and Discussion

Figure 1 presents the N<sub>2</sub> adsorption isotherms at 77K for the two carbon monoliths, before and after activation. From the shape of the isotherm of the two carbon monoliths before activation (PDA and REF), it can be said that the carbon monoliths are mainly microporous materials, although they also contains mesopores, which is confirmed by the existence of a hysteresis cycle in the adsorption/desorption process (the exact shape of the hysteresis loop is different for each monolith). After activation with CO<sub>2</sub> or KOH, the shape of the isotherms remains quite similar and the adsorption capacity increases, indicating an increase in pore volume.

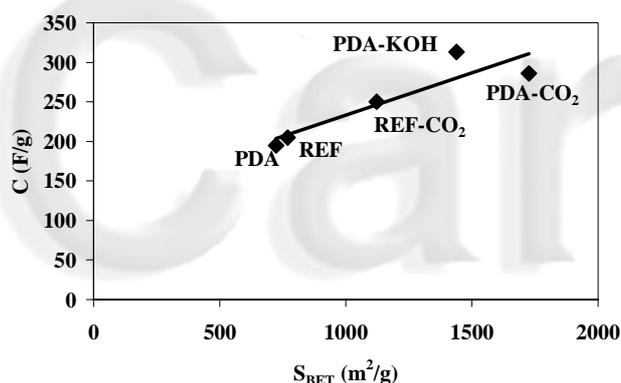
Table 1 collects, as an example, the calculated apparent BET surface areas ( $S_{BET}$ ) and the micropore volume calculated from the N<sub>2</sub> (77K) adsorption ( $V_{DR}(N_2)$ ) for the PDA carbon monolith before and after activation with CO<sub>2</sub> and KOH. The quantification of the amount of CO and CO<sub>2</sub> desorbed in TPD experiments is also displayed. It can be seen that the selection of the suitable activation conditions with CO<sub>2</sub> and KOH activation has allowed us to obtain materials with quite high development of porosity, increasing the apparent surface area from 725 m<sup>2</sup>/g up to 1725 m<sup>2</sup>/g. These activated materials still present bimodal porosity (microporosity and mesoporosity), as deduced from Figure 1. Moreover, the surface chemistry has been also modified (see Table 1), especially after the KOH activation process, obtaining materials with very high content of CO-type surface oxygen groups, which are very interesting for their performance as supercapacitors.



**Fig. 1**  $N_2$  adsorption isotherms at 77 K for the carbon monoliths before (PDA and REF) and after activation with  $CO_2$  or KOH.

**Table 1. BET Surface Area, Micropore volume, CO and  $CO_2$  Desorbed Amounts for PDA Carbon Monolith Before and After Activation**

Sample	$S_{BET}$ ( $m^2/g$ )	$V_{DR}(N_2)$ ( $cm^3/g$ )	CO ( $\mu mol/g$ )	$CO_2$ ( $\mu mol/g$ )
PDA	725	0.28	1209	461
PDA- $CO_2$	1725	0.70	1114	492
PDA-KOH	1440	0.66	2500	511



**Fig. 2** Capacitance values in acidic medium versus apparent BET surface area for the carbon monoliths before and after activation with  $CO_2$  or KOH.

The values of capacitance in acidic medium for the two carbon monoliths (PDA and REF) before and after activation are plotted in Figure 2 versus the BET surface area. This plot shows that a general trend between capacitance and BET surface area exists for all the samples, although it is not a perfect linear relationship. As it has been demonstrated in a previous work [7], the specific surface area is a key parameter for the porous carbon materials to be applied as supercapacitors, but other characteristics, such as surface chemistry, have an important contribution to the capacitance through faradic processes, or to increase the wettability of aqueous electrolyte. From Figure 2 it can be seen that the maximum capacitance value is obtained after activation of the carbon monolith PDA with KOH (sample PDA-KOH),

presenting a value as high as 313 F/g. This sample has higher capacitance than the sample PDA- $CO_2$  (prepared from the same carbon monolith (PDA) but with  $CO_2$ , instead of KOH activation), which has higher apparent surface area. This fact must be most probably due to the much higher content of CO-type surface oxygen groups for the sample PDA-KOH (see Table 1), which has been demonstrated to be very relevant for obtaining porous carbon materials with high performance as supercapacitors [7].

## Conclusions

Monolithic porous carbons have been prepared by carbonization of resorcinol-formaldehyde (RF) porous resins. The resins were produced from RF gels by conventional drying in air, using stabilizers to maintain the porous structure during drying. These monolithic carbons have been activated using different activating agents ( $CO_2$  and KOH). The materials obtained present bimodal porosity (micro and mesopores) and quite high development of porosity. The specific capacitance of a monolithic porous carbon before activation (e.g. 195 F/g) can be increased considerably after activation (e.g. activation with KOH (KOH/carbon ratio 3/1) gives materials with capacitance of 313 F/g). This approach offers viability to engineer new materials for use as supercapacitors.

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