

Customized Carbon Aerogels as positive electrode materials in Li-ion capacitors

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INTRODUCTION

Carbon Aerogels (CAs) are materials which structural and chemical properties can be easily tailored according with the required application. Between all the possibilities, these carbons have been widely used in different energy storage systems such as fuel cells¹ and mainly in supercapacitors² and Li-ion batteries³, showing competitive results with respect to those obtained with the already available commercial carbons. However, their performance in new emerging energy devices such as Li-ion capacitors (LICs) is still poorly known.

Li-ion capacitors are nowadays raising interest due to its ability to gather Li-ion batteries and supercapacitors advantages in a single device. This is achieved combining a capacitor-like positive electrode with a battery-like negative one.

In the present study, CAs with *ad-hoc* designed porous characteristics have been synthesized by an easy and straightforward methodology to be used as positive electrode in LICs. The way the porosity affects electrode performance has been evaluated. Moreover, a full-LIC was assembled with the best CA employing a commercial hard carbon as anode. The results have been compared with those of an analogous LIC but with a commercial activated carbon as the EDLC like electrode.

MATERIALS AND METHODS

Both pristine and hybrid organic aerogels were synthesized by a sol-gel process using resorcinol (R) and a solution of formaldehyde (F) as main reagents, water as solvent and a solution of NaOH 0.1 M as catalyst. The hybrid gel was easily obtained by the substitution of 100% of the water used as solvent by a GO suspension. The initial conditions of the precursor solution were a R/F ratio of 0.5, a dilution of 5.7 and a pH of 6.5. The precursor mixtures were then placed in a microwave oven at 85°C for 5h to undergo gelation, ageing and drying.

To obtain the respective activated carbons, the organic precursors were subjected to two one-step carbonization/activation process in a horizontal tubular reactor under a CO₂ flow of 50 ml min⁻¹ and a heating rate of 50 °C min⁻¹ up to 1000° C. The residence times were adjusted to obtain two different surface areas of ca. 1700 and 2300 m² g⁻¹. The nomenclature employed for the materials was: "CAS_{BET}" in the case of the pristine xerogels and "CAGOS_{BET}" for the hybrid one.

The textural properties of the carbons were estimated from N₂ adsorption-desorption isotherms at 77K (Micromeritics Tristar 3020). The electrochemical measurements were performed in a VMP3

potentiostat from Biologic using both two and three-electrode Swagelok testing cells and 1 M LiPF₆ (EC:DMC)(50:50 wt%) as electrolyte.

For the electrochemical characterization of the materials, self-standing electrodes were prepared by a 90 wt% of active material and 10 wt% of PVdF as binder. Electrodes made by 90/5/5 wt% of active material/C65/NMP and Al foil as current collector were employed for the Full-LIC evaluation.

RESULTS AND DISCUSSION

The rate capability of the carbon aerogels and YP80F (Figure 1), was firstly analysed in a half Swagelok cell configuration, employing metallic lithium as the counter electrode and self-standing electrodes as the working ones. Clear variations were observed, attributed mainly to the different porous characteristics of the materials under study (Table 1).

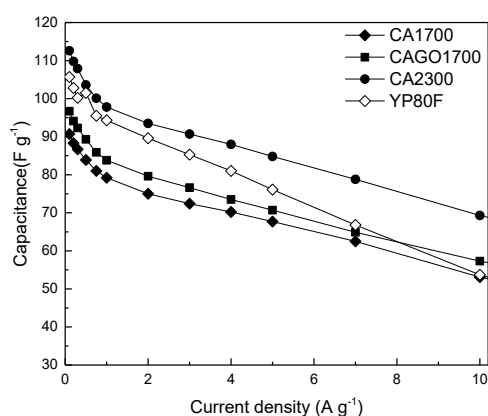


FIGURE 1. Specific capacitance of the carbons under a voltage window between 2,0-4,0 V vs Li⁺/Li.

TABLE 1. Porous characteristics of the carbons studied.

	V _p (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	D _{meso} (nm)	S _{BET} (m ² g ⁻¹)
CA1700	1,1	0,5	7,0	1796
CAGO1700	1,2	0,6	14,2	1652
CA2300	1,7	0,9	6,6	2248
YP80F	1,2	0,4	2,5	2312

At the range of low current densities, a relation between microporosity and charge storage was detected as micropores are the pores where the ions are stored². Hence, at 0.1 A g⁻¹, those materials with higher S_{BET} (AX2300 and YP80F) registered capacitances of 113 and 105 F g⁻¹, while the capacitances of CA1700 and CAGO1700 were 91 and 97 F g⁻¹, respectively.

As the current density increased, the capacitance decreased, however, a noticeable difference was observed in the curve slope between YP80F and all CAs, being the former more pronounced due to the narrow diameter of mesopores. Mesopores act as transport pores that enable a suitable movement of ions through the carbonaceous framework until they reach the micropores². Nevertheless, comparing the performances of CA1700 and CAGO1700 it can be concluded that there is a maximum mesopore diameter above which no improvements are attained, as even though the last one, has a D_{meso} double that of CA1700, the capacitance decay of both materials was of ca. 50%. CA2300 was the most stable carbon at all range of current densities applied, due to its high content of micropores and a suitable volume and diameter of mesopores.

Consequently, CA2300 was the one used as positive electrode to assemble a full LIC with a commercial HC as anode and a disc of Li metal as reference. The full device was analysed by a rate capability study under a cell voltage window between 2.2-3.8 V vs Li⁺/Li. As it is observed in Figure 2, the device registered a really stable performance even at a high current density of 5 A g⁻¹, that corresponds to 9 s of discharge time.

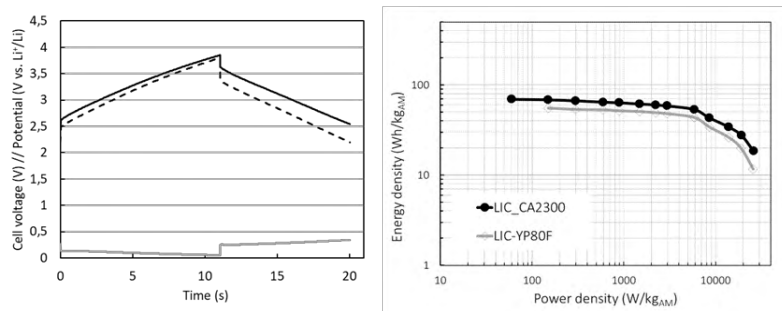


FIGURE 2. GA charge/discharge profiles of LIC-CA2300 at 5 A g^{-1} and Ragone plot of both LICs.

At these demanding conditions, the CA potential swings from 2,5 to 4,0 vs Li^+/Li , coupling perfectly with the cell voltage swing. That, allows to exploit the maximum capacitance the HC is able to provide, avoiding Li-plating as it swings above 0 V, specifically between 200-50 mV vs Li^+/Li .

This suitable performance was also reflected in the Ragone plot (Figure 2), where it is evidenced that the LIC made by CA2300 is able to store high energy densities even when high power densities are required. What is more, the values obtain are competitive to those of the LIC made with the already available commercial carbon YP80F.

CONCLUSIONS

Carbon aerogels are potential candidates to be used in energy storage devices due to the possibility to tailor their porous characteristics. So far, they have been mainly employed in Li-ion batteries and supercapacitors, however an in-depth study is required for their used in novel energy devices such as Li-ion capacitors. In the present study, it was found that the presence of micropores plays an important role for the positive electrode to reach high capacitances mainly at low current densities. Nevertheless, a suitable diameter of mesopores is the clue to obtain a stable device able to retain these high values at more demanding conditions without penalizing power delivery. By synthesizing CAs with the same volume of micropores but different diameter of mesopores, it could be concluded that it is a maximum diameter of mesopore above which the capacity retention does not improve anymore. The CA with a S_{BET} of $2248 \text{ m}^2 \text{ g}^{-1}$ and V_{meso} of $0,9 \text{ cm}^3 \text{ g}^{-1}$ with a diameter of 6,6 nm, was the material that delivered the best performance at all range of current densities studied. When this carbon was used in a full LIC as positive electrode versus a HC as anode, the device showed really stable performance with energy and power density values similar to those of a LIC made by commercial carbons.

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