

# ENHANCEMENT OF CAPACITANCE OF CARBON-BASED SUPERCAPACITORS BY THE QUINONE/HYDROQUINONE SYSTEM

Silvia Roldán, Clara Blanco, Marcos Granda, Rosa Menéndez, Ricardo Santamaría

Instituto Nacional del Carbón (CSIC), P. V. Box 73, 33080, Oviedo ((Spain)  
silviarl@incar.csic.es

## Introduction

Many efforts are being taken in order to increase the energy density of carbon-based supercapacitors (CBSCs). The incorporation of heteroatoms on the carbon surface by chemical treatments [1], the modification of carbon materials with conducting polymers [2] or transition metal oxides [3], and the use of ionic liquids [4] are examples of the enhancement of energy density by quick faradaic reactions. In this work, the enhancement of the specific capacitance values ( $C_e$ ) of CBSC by incorporating an electrochemically active system (quinone/hydroquinone) into the electrolyte was studied. An exceptional electrochemical behavior and an amazing  $C_e$  were obtained.

## Experimental

An activated carbon (E-AC) obtained by chemical activation of a coke with KOH was used as the electrode active material. The E-AC was characterized by adsorption of  $N_2$  at 77 K in an ASAP 2020 (Micromeritics). BET surface area was to  $1442 \text{ m}^2\text{g}^{-1}$ . The total pore volume was  $0.71 \text{ cm}^3\text{g}^{-1}$ , most of the pores being micropores (86 %), with an average pore diameter of 0.88 nm. The carbon content was 93 wt.%.

The electrochemical behavior was tested using a Swagelok<sup>®</sup>-type cell in a two-electrode configuration using a glassy fibrous separator and gold current collectors. Coin type carbon electrodes ( $\sim 33 \text{ mg}$ ) were prepared using 92 wt.% of the activated carbon and 8 wt.% of PVDF as binder. Tests were performed in 0.37 M hydroquinone dissolved in 1 M  $\text{H}_2\text{SO}_4$  (HQ/ $\text{H}_2\text{SO}_4$ ), and in the supporting electrolyte ( $\text{H}_2\text{SO}_4$ ) for comparison purposes. Galvanostatic cycling of the CBSC was carried out in the voltage window between 0 and 1 V at current densities of  $2.7\text{--}88 \text{ mA}\cdot\text{cm}^{-2}$  ( $100\text{--}3,400 \text{ mA}\cdot\text{g}^{-1}$ ) using a VPM (Biologic, France) multichannel generator. Voltammetry experiments were done in two and three-electrode cells in order to evidence the contribution of pseudocapacitance. In the three-electrode configuration, Pt was used as counter electrode and  $\text{Hg}/\text{Hg}_2\text{SO}_4$  as reference electrode. A synchronous experiment in a T-type Swagelok<sup>®</sup> cell was used to know the operating voltage of the cell. Impedance spectroscopy measurements were conducted at 0 V, varying frequencies between 1 mHz-100 kHz

## Results and Discussion

The influence of current density on the specific capacitance values was determined for E-AC in HQ/ $\text{H}_2\text{SO}_4$

and in the supporting electrolyte without any redox compound dissolved, from the charge-discharge experiments. As can be seen in Fig. 1, the addition of this electrochemically active compound to the supporting electrolyte caused to an amazing increase of the specific capacitance values. A maximum value of  $900 \text{ F}\cdot\text{g}^{-1}$  was achieved when a constant current density of  $2.7 \text{ mA}\cdot\text{cm}^{-2}$  (current load  $\sim 100 \text{ mA}\cdot\text{g}^{-1}$ ) was applied through the cell.

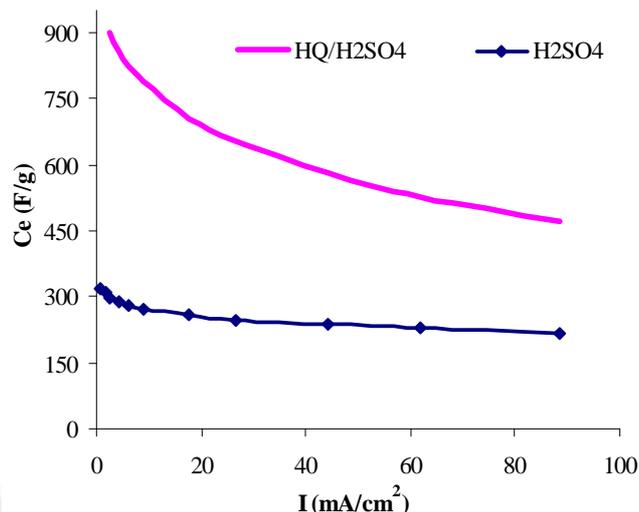


Fig. 1 Variation of the specific capacitance with the current density (two-electrode system).

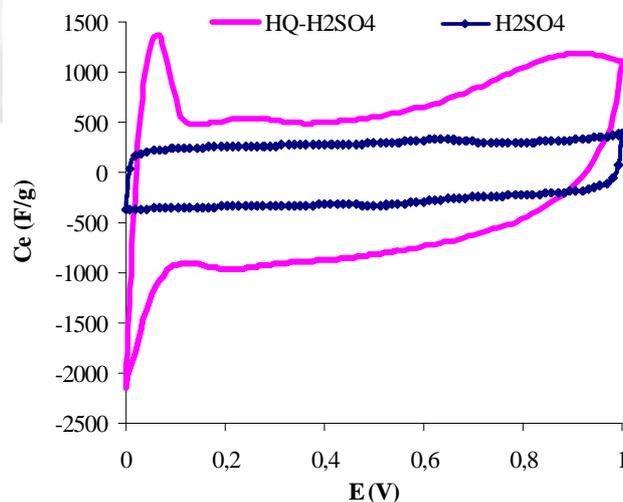


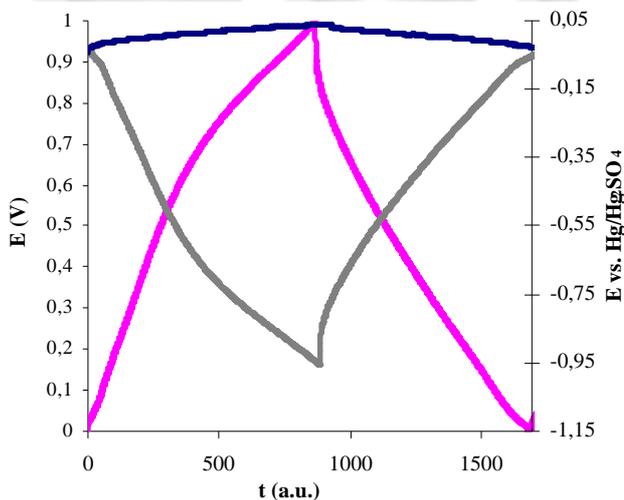
Fig. 2 Cyclic voltammetry performed at  $1 \text{ mV}\cdot\text{s}^{-1}$  (two-electrode configuration).

A capacity fall of  $\sim 48 \%$  with current density was observed, then the minimum  $C_e$  value reached was  $470 \text{ F}\cdot\text{g}^{-1}$ . This minimum value is significantly higher than the capacitance values published for carbon-based SC. It is important point out that the result of  $900 \text{ F}\cdot\text{g}^{-1}$  surpasses the

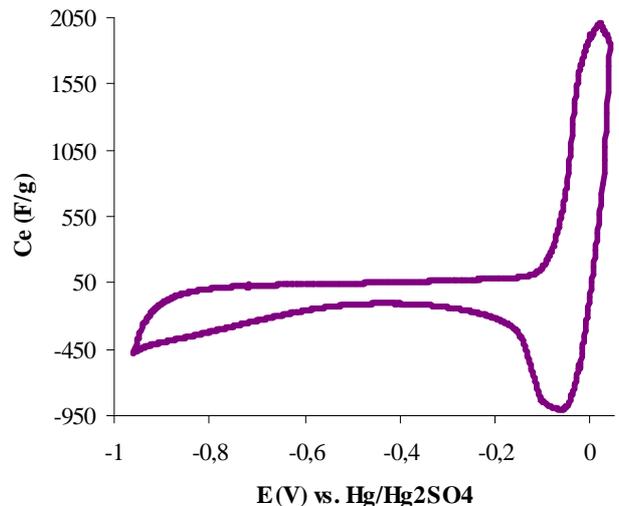
capacitive value obtained for the best example of the inorganic class of pseudocapacitive materials, ruthenium oxide ( $\sim 720 \text{ F}\cdot\text{g}^{-1}$  for its hydrous form) [5]. The resistance of the cell is quite similar after the addition of HQ to the supporting electrolyte (ESR:  $1.7 \Omega\cdot\text{cm}^{-2}$  in HQ/H<sub>2</sub>SO<sub>4</sub> and  $1.1 \Omega\cdot\text{cm}^{-2}$  in H<sub>2</sub>SO<sub>4</sub>). The coulombic efficiency was  $> 90\%$  for the whole range of current density applied, and it was  $> 99\%$  for values higher than  $8.8 \text{ mA}\cdot\text{cm}^{-2}$ , which could be related to the kinetic of the redox reaction.

The voltammetric profiles (Fig. 2) obtained in two-electrode configuration make evident the contribution of pseudocapacitance when the HQ/H<sub>2</sub>SO<sub>4</sub> solution is used as electrolyte. For a deeper understanding of the electrochemical behaviour of HQ/electrode pair behavior, synchronous charge-discharge galvanostatic experiments and a voltammetry study in three-electrode configuration were performed. A different behavior for the positive and negative electrodes was found (Fig. 3). The anode showed a potential profile constant with time, similar to the behavior of the batteries. Therefore, it is possible to conclude that the redox reactions of the quinone/hydroquinone pair occurs in the positive electrode. This was clearly observed when cyclic voltammetry was performed in the three-electrodes configuration (Fig. 4). Well-defined redox peaks appeared in the positive region, but it is worth noting that the redox reaction is not completed within the operating voltage window of the cell.

Cyclability experiments were performed in this novel redox-active electrolyte. The long-term cycling behavior in HQ/H<sub>2</sub>SO<sub>4</sub> was rather poor, with a reduction in the capacitance values of 61% after 600 cycles. This behavior was associated to the partial anodic oxidation of the hydroquinone, making the redox process irreversible.



**Fig. 3** Galvanostatic cycle for E-AC in HQ/H<sub>2</sub>SO<sub>4</sub> at 1 V (left Y-axis) and the potentials of work for the positive and negative electrodes (right Y-axis). Current density  $8.8 \text{ mA}\cdot\text{cm}^{-2}$  ( $340 \text{ mA}\cdot\text{g}^{-1}$ ).



**Fig. 4** Cyclic voltammetry performed at  $1 \text{ mV}\cdot\text{s}^{-1}$  in three-electrode cell using  $0.37 \text{ M HQ}/1 \text{ M H}_2\text{SO}_4$  as electrolyte.

## Conclusions

A novel route to increasing the Ce values has been opened through the incorporation of redox-active compounds to the commonly used electrolytes for SC applications.

Novel redox-active electrolyte obtained by dissolving HQ in H<sub>2</sub>SO<sub>4</sub> was tested on an activated carbon. The specific capacitance values obtained in this electrolyte was remarkably higher than values already published for carbon-based SC and even greater than values reached for ruthenium oxide SC. The resistance of the cell was not significantly modified with the addition of the HQ (ESR:  $1.7 \Omega\cdot\text{cm}^{-2}$  in HQ/H<sub>2</sub>SO<sub>4</sub>, and  $1.1 \Omega\cdot\text{cm}^{-2}$  in H<sub>2</sub>SO<sub>4</sub>).

Long-term cycling experiments performed on E-AC in HQ/H<sub>2</sub>SO<sub>4</sub> showed a poor behavior, with a total loss of the initial capacitance values of 61% after 600 galvanostatic charge-discharge cycles. These results are related with the irreversible character of the redox reaction of the quinone/hydroquinone pair within the operating potential window of the cell.

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