

## Redox-active electrolytes as a new route to obtain high-energy carbon-based supercapacitors

S.Roldán, Z. González, M. Granda, R. Menéndez, R. Santamaría, C. Blanco

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011, Oviedo, Spain

silviarl@incar.csic.es

Supercapacitors (SCs) have attracted much interest as energy storage systems due to their high power density, long cycle life, short charging time, low maintenance, and good safety record (1). These factors make them highly attractive for use in electric devices and vehicles (2). However, for such applications it is first necessary to increase the amount of energy that can be stored by the SCs (3). Carbon materials are the most commonly used materials for electrodes in SCs because of their relatively low cost, good electrical conductivity and high surface area, being therefore ideal materials for the rapid storage and release of energy (4). There are two energy storage mechanisms for SCs: double-layer formation and pseudocapacitance. Although most of the capacitance of carbon materials arises from the formation of the double-layer, many of these materials reach an increase in their capacities thanks to pseudocapacitive effects, resulting from the quick faradaic reactions of surface functionalities, polymers or transition metal particles present in the electrodes (5). However, it is known that pseudocapacitance limits the lifetime of the SCs due to the instability of the functionalities with cycling and the degradation of the polymer and the composites.

Herein, we describe an alternative route to promote quick faradaic reactions **in order** to improve the specific capacitance ( $C_e$ ) of carbon-based SCs through the use of redox-active electrolytes (6, 7). The combination of the capacitance of the SC with that provided by the redox reaction of the electrolyte will lead an increase in overall capacitance. This concept is demonstrated by showing the effects of adding electrochemically active compounds to carbon-based SCs.

Indigo carmine (IC), methylene blue (MB) and hydroquinone (HQ) were utilized as electrochemically active compounds, and their pseudocapacitance effects were studied in MWCNT-based SCs. Furthermore, four carbon materials were tested with the HQ solution: multiwalled carbon nanotubes (MWCNTs), a carbon aerogel (CA), and two chemically activated carbon materials from coke, prepared with KOH (AC-KOH) or NaOH (AC-NaOH). The working solutions were prepared using 1 M  $H_2SO_4$  as supporting electrolyte in concentrations of 0.05 M, 0.07 M and 0.38 M for IC, MB and HQ, respectively. The electrochemical behaviour was studied in a Swagelok<sup>®</sup>-type cells by using a two-electrode configuration. Chrono-potentiometric studies of galvanostatic charge-discharge ( $0.88\text{-}88\text{ mA cm}^{-2}$ ) and cyclic voltammetry experiments ( $1\text{-}50\text{ mV s}^{-1}$ ) were carried out in an operating voltage window of 0-1 V using a VPM multichannel generator (Biologic, France).

All redox-active solutions studied in MWCNT-based SCs showed a great increase in the  $C_e$  values after the addition of the electrochemically active compound to the supporting electrolyte (Fig. 1a). A maximum value of  $180\text{ F g}^{-1}$  was obtained in HQ solution at a constant current density of  $0.88\text{ mA cm}^{-2}$ , and the use of IC and MB solutions led to  $C_e$  values 2.8 and 4.6 times higher, respectively, than those obtained in  $H_2SO_4$ . Obviously, these increases are due to the additional capacitive contribution of the faradaic reactions of the electrochemically active compounds, as the voltammogram profiles show (Fig. 1b). The cyclic voltammograms obtained with redox-active electrolytes display well-defined redox peaks, while the voltammogram obtained for the MWCNTs in  $H_2SO_4$  shows an ideal rectangular shape characteristic of an electrical double layer capacitor.

As can be seen before, the pseudocapacitive effects of the HQ-redox system were studied employing four carbon materials as electrodes (Fig. 2). The  $C_e$  values were at least two times higher after the addition of the redox compound. The greatest increase corresponded to the AC-KOH, for

which the Ce values trebled, reaching the value of  $900 \text{ F g}^{-1}$  at  $2.7 \text{ mA cm}^{-2}$ . It is worth mentioning that this value is much higher than the best value of Ce reported to date for SCs, which was obtained for the SC containing amorphous hydrated ruthenium oxide electrodes (8).

We can conclude therefore that these are innovative hybrid systems that combine two energy-storage processes: the double-layer formation characteristic of carbon-based SCs and faradaic reactions characteristic of batteries. This type of devices constitutes a breakthrough in the development of SCs, as it promises to be a highly efficient way to increase the storage of electrical energy.

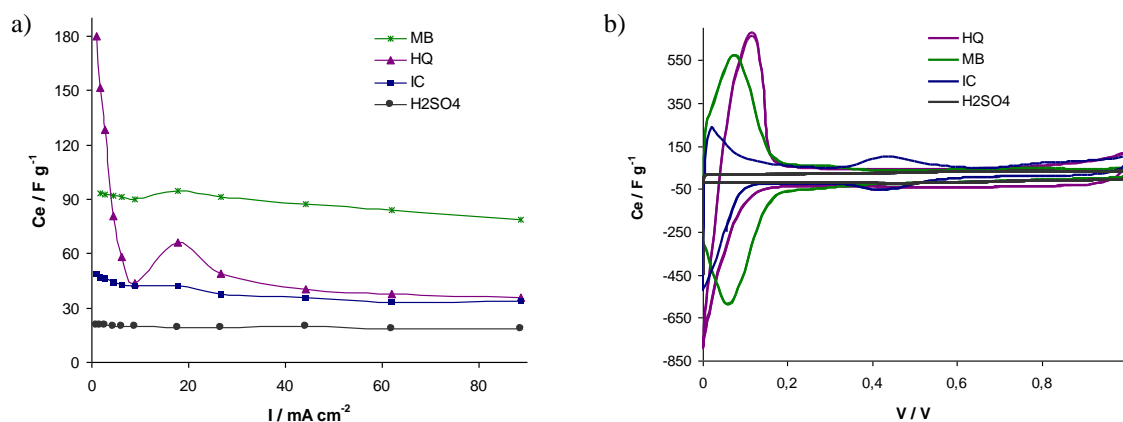
### Acknowledgements

This work was supported by MICINN (Project MAT2007-61467). S. Roldán thanks MICINN for an FPI predoctoral grant.

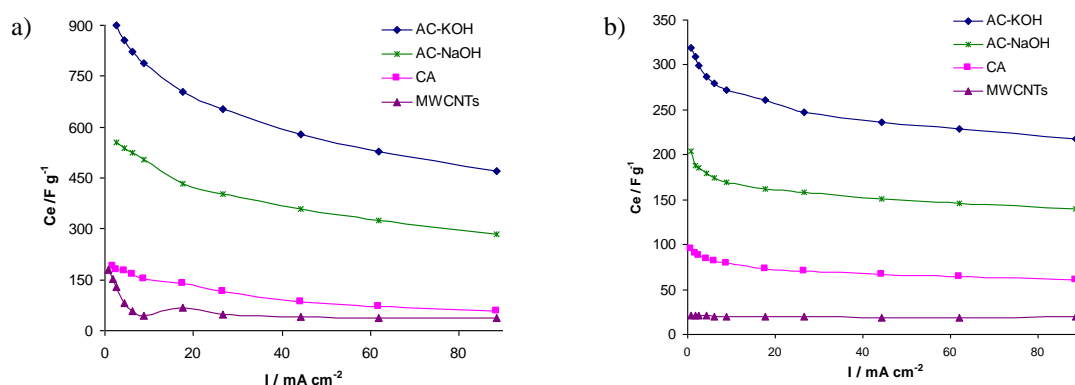
### References

- [1] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Letters*, **8** (2008) 3498.
- [2] R. Kotz, M. Carlen, *Electrochim. Acta*, **45** (2000) 2483.
- [3] P. Simon, Y. Gogotsi, *Nat. Mater.*, **7** (2008) 845.
- [4] J. Huang, B. G. Sumpter, V. Meunier, *Angew. Chem.*, **120** (2008) 120.
- [5] K. Jurewicz, K. Babel, A. Ziokowski, H. Wachowska, *Electrochim. Acta*, **48** (2003) 1491.
- [6] S. Roldán, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, *Angew. Chem.*, **123** (2011), 1.
- [7] S. Roldán, Z. González, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, *Electrochim. Acta*, doi:10.1016/j.electacta.2010.10.017
- [8] J. P. Zheng, P. J. Cygan, T. R. Jow, *J. Electrochem. Soc.* **142** (1995) 2699.

### Figure captions



Variation of specific capacitance with current density and b) voltammetric profiles ( $1 \text{ mV s}^{-1}$ ) obtained in MB, HQ and IC solutions and in the supporting electrolyte. (Electrode active material: MWCNTs)



Variation of specific capacitance with current density in: a)  $\text{HQ}/\text{H}_2\text{SO}_4$  and b)  $\text{H}_2\text{SO}_4$  (1V).