Energy Storage

Towards a Further Generation of High-Energy Carbon-Based Capacitors by Using Redox-Active Electrolytes**

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The growing interest in supercapacitors (SCs), also called electrochemical capacitors or ultracapacitors, is due to their high power density, long cycle life, short charging time, and good safety record. These factors make them highly attractive for use in electric devices and vehicles.[1,2] For such applications it is first necessary to increase the amount of energy that can be stored by the SC.[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. They are therefore ideal materials for the rapid storage and release of energy.[4] Most of the capacitance of carbon materials arises from the formation of an electrical double layer. Nonetheless, many of these materials owe their increased capacitance to the pseudocapacitive contribution of quick faradaic reactions resulting from surface functionalities, mainly oxygen and nitrogen.[5] These reactions can be stimulated by increasing the surface functionalities of the carbon material through chemical treatments, by using carbon/polymer composites, or by inserting electroactive particles from transition metals.[6–8] However, some negative effects may occur as a result of the instability of these functionalities with cycling, degradation of the composites, or their high cost.

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

The addition of HQ to the supporting electrolyte caused a great increase in the capacitance values for all the carbon materials tested (Figure 1). The C_e values were at least two times higher after the addition of the redox compound. The greatest increase corresponded to the chemically activated carbon material AC-KOH, for which the C_e values trebled,
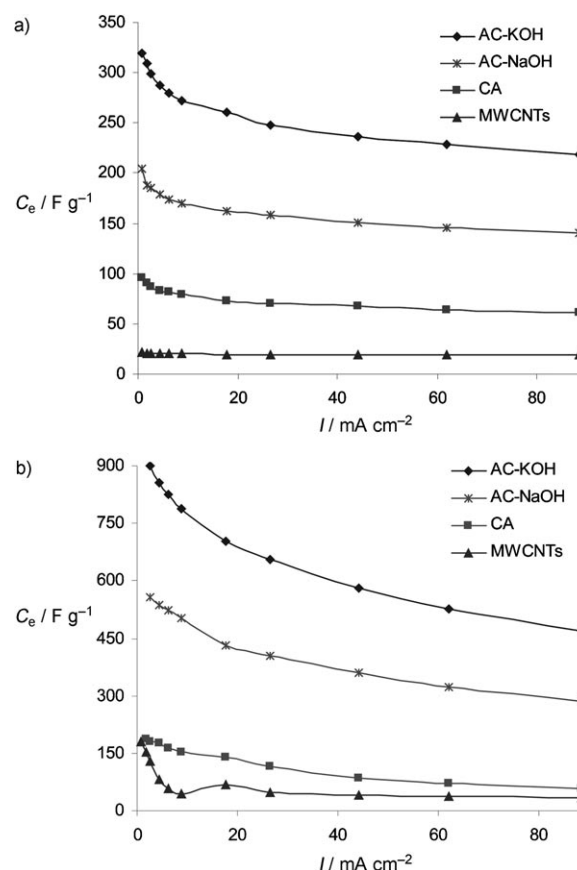
[*] S. Roldán, Dr. C. Blanco, Dr. M. Granda, Prof. R. Menéndez,
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Figure 1. Variation of specific capacitance with current density in: a) H_2SO_4 and b) HQ/H_2SO_4 (1 V).

reaching the value of 901 F g^{-1} at 2.65 mA cm^{-2}. This value is much higher than those previously reported for carbon-based capacitors and is even greater than the best value reported to date for SCs (720 F g^{-1}), which was obtained for a SC containing amorphous hydrated ruthenium oxide electrodes.[9] Also worth mentioning is the significant enhancement of capacitance achieved by multiwalled carbon nanotubes (MWCNTs) at the lowest current density (from 21 to 180 F g^{-1}). This result is comparable to the best reported values obtained by MWCNTs modified with electroconducting polymers.[8]

The increase in capacitance achieved by using this novel redox electrolyte is attributed to the additional pseudocapacitive contribution from the faradaic reactions of the hydroquinone/quinone system (Figure 2). The presence of pseudocapacitance is evidenced by the charge/discharge cycles and the voltammogram profiles. Figure 3 shows an example of the

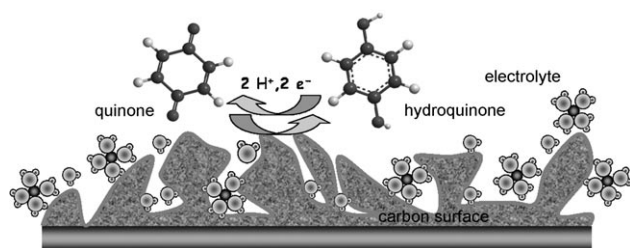**Figure 2.** Representation of the processes occurring on the carbon surface: double-layer formation and redox reaction.

Figure 4. Cyclic voltammograms obtained at 1 mVs^{-1} in HQ/H$_2$SO$_4$ and H$_2$SO$_4$ for AC-KOH.
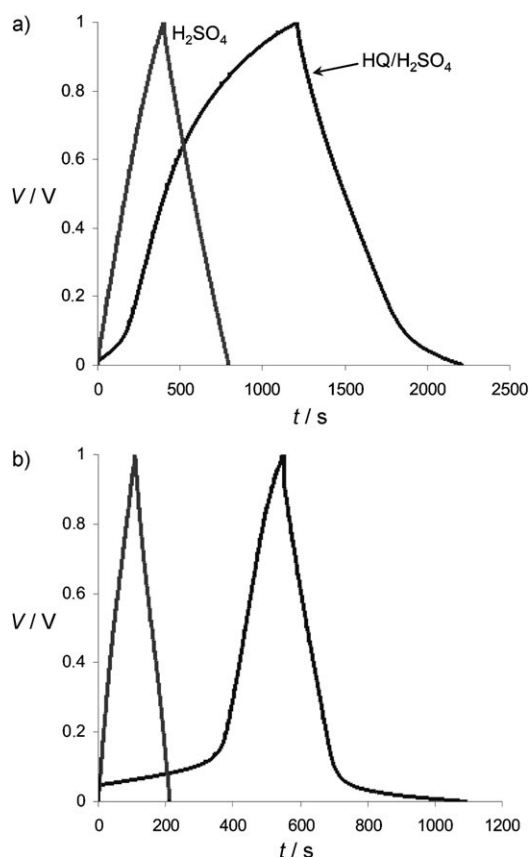

Figure 3. Charge and discharge profiles of: a) CA and b) MWCNTs, at 2 mA (1.77 mAcm^{-2}) in HQ/H$_2$SO$_4$ and H$_2$SO$_4$.

charge/discharge cycles for a carbon aerogel (CA) and MWCNTs. As can be seen, a clear deviation from the ideal triangular shape is observed in HQ/H$_2$SO$_4$. Plateaus characteristic of redox reactions that occur at constant potential appeared after HQ had been incorporated into the cell. These plateaus were especially evident in the case of the MWCNT-based capacitor. Moreover, a significant hump in the charge branch of the cycles appeared in the case of CA and the activated carbon materials. Such characteristics represent a deviation from the ideal triangular shape and are known to be typical effects of pseudocapacitive contributions.

The effect of adding HQ to the electrolyte is also clearly observed in the cyclic voltammograms (CV; Figure 4). In all cases, the CVs obtained in HQ/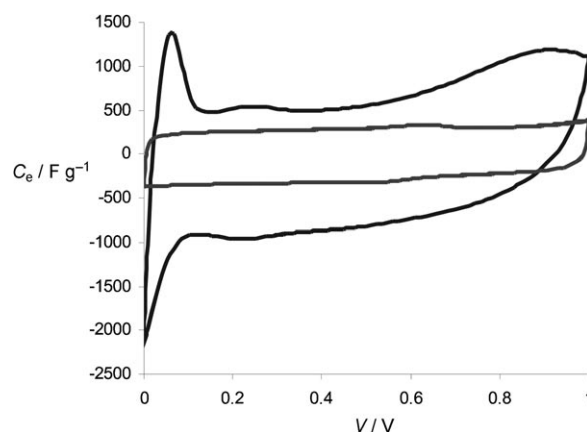H$_2$SO$_4$ display a set of anodic and cathodic peaks that are pseudocapacitive in nature, whereas the voltammograms obtained in H$_2$SO$_4$ show a rectangular shape, which is characteristic of electrostatic capacitors.

The electrochemical reactions of quinoid compounds have been widely characterized at various electrodes, such as platinum,[10] gold,[11] and glassy carbon,[12] and in different media.[13–15] It is generally accepted that the redox chemistry of these compounds involves elementary steps comprising 2H$^+$ and 2e$^-$ for the quinone/hydroquinone reaction.[12] However, these reactions are an oversimplification of a very complex mechanism that depends on the protic nature of the solvent, the presence of Brønsted acids or bases,[12] and the interrelations of the reactants, intermediates, and products by electron- and proton-transfer reactions. Moreover, as the quinone/hydroquinone reaction is an inner-sphere electron-transfer process,[16] the heterogeneous electron-transfer kinetics of this couple is also strongly influenced by the surface characteristics of the electrode.[16–18] Bearing this in mind, it is not surprising that in the present study the electrochemical response observed depends on the carbon electrode used. Whereas for AC-KOH the initial capacitance trebles, the surface of MWCNTs seems to be the most effective, as the C_e value increases by a factor of 9. Considering the increase in C_e values achieved (160 Fg^{-1} for MWCNTs and 600 Fg^{-1} for AC-KOH), the surface area (210 m^{2}g^{-1} for MWCNTs, 1442 m^{2}g^{-1} for AC-KOH) is a determining factor, as it limits the extension of the redox reaction and, therefore, the total pseudocapacitive contribution.

The long-term cycling behavior of AC-KOH in HQ/H$_2$SO$_4$ showed a decrease in the initial capacitance of 65% after 4000 cycles (Figure 5). The main loss occurred during the first 1000 cycles; after that the C_e value of the original capacitor is retained. This loss of capacity is directly connected with the fact that the HQ redox reaction is not completed within the operating voltage window of the cell. Nevertheless, it is important to point out that the long-term cycling behavior can be comparable to that of batteries.

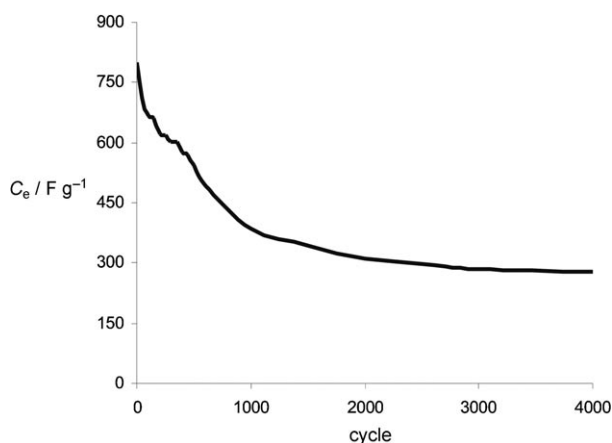In conclusion, the C_e value of carbon-based SCs was significantly improved by the addition of an electrochemically

Figure 5. Variation in the specific capacitance values with the number of cycles for AC-KOH in HQ solution (4.42 mA cm⁻²).

carbon materials from coke, prepared with KOH (AC-KOH) or NaOH (AC-NaOH).

The electrochemical behavior was studied in Swagelok-type cells by using a two-electrode configuration. 1 M H_2SO_4 was employed as the electrolyte in the conventional SCs. 0.38 M Hydroquinone dissolved in 1 M H_2SO_4 (HQ/H_2SO_4) made up the redox-active electrolyte.

Chrono-potentiometric studies of galvanostatic charge–discharge (0.88–88 mA cm⁻²) and cyclic voltammetry experiments (1–50 mV s⁻¹) were carried out in an operating voltage window of 0–1 V.

active compound (HQ) to the supporting electrolyte. Capacitance values were observed to be at least two times higher after the addition of the redox compound. The most outstanding increase corresponded to an activated carbon-based SC, for which an energy density of 31.3 W h kg⁻¹ was achieved, which is comparable to that of some batteries.

This is an innovative hybrid system that combines two energy-storage processes: the double-layer formation characteristic of carbon-based SCs and the faradaic reactions characteristic of batteries. This system constitutes a breakthrough in the development of SCs, as it promises to be a highly efficient way to increase the storage of electrical energy. Further research is necessary to optimize the performance of system by finding the most energy-efficient redox compound for a particular carbon material and electrolyte (aqueous or organic).

Experimental Section

Four carbon materials were studied: multiwalled carbon nanotubes (MWCNTs), supplied by Sigma–Aldrich; a carbon aerogel (CA), supplied by Marketech International; and two chemically activated

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