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A symmetric carbon/carbon supercapacitor operating at 1.6 V by using a neutral aqueous solution

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ABSTRACT

A high voltage symmetric carbon/carbon supercapacitor was built using a Na_2SO_4 aqueous solution. This system exhibits an excellent cycle life during thousands of cycles up to voltage values as high as 1.6 V. Three-electrode investigations show a particularly high potential window, ΔE = 2 V, for the considered activated carbon in Na_2SO_4. However, in a two-electrode cell, when the voltage is higher than 1.6 V, the potential of the positive electrode is beyond the oxidation potential of water, and AC is oxidized. These results demonstrate the potentialities of Na_2SO_4 for developing high energy density systems.

1. Introduction

The aqueous electrolytes, when applied to supercapacitors, present several advantages over the organic ones. The systems are cheaper, environment friendly and easy to construct. Moreover, with activated carbons (AC) enriched with heteroatoms (N, O, and P), the capacitance can be enhanced through pseudo-capacitive redox reactions between the surface functionalities and the aqueous electrolyte [1–3]. Recently, other pseudo-capacitive contributions, related either with reversible hydrogen storage [4] or the carbon–iodine interface [5], were found to considerably increase capacitance in aqueous medium.

Despite the previous listed advantages of aqueous electrolytes, they are not applied in industrial AC/AC capacitors, because their maximum voltage U is less than 1 V [6], while it reaches 2.7 V in organic medium [7]. Consequently, the energy density (E) expressed by Eq. (1):

$$E = \frac{1}{2}CU^2, \tag{1}$$

where C is the capacitance [8], is higher in organic than in aqueous electrolyte.

An effective strategy for increasing voltage in aqueous medium consists in building asymmetric cells with manganese oxide for the positive electrode and activated carbon for the negative one [9,10]. Although voltage values as high as 2 V were claimed for these systems, thin manganese oxide films are required to obtain high capacitance values [11]. Moreover, for ensuring a good stability of the positive electrode and a good cyclability of the system, it is preferable to limit the maximum voltage to 1.6 V [12]. Recently, a new approach of asymmetric carbon/carbon supercapacitor able to be reversibly charged/discharged up to 1.6 V in acidic medium (1 mol L^{-1} H_2SO_4) has been presented [13]. This system is based on two different carbon electrodes with different stability potential window. However, the highly corrosive character of H_2SO_4 precludes the industrial development of this device because finding cheap and light current collectors resistant to acidic corrosion remains a challenge. Actually, a less corrosive neutral electrolyte would be a better choice. In this sense, upon studying the asymmetric carbon/MnO_2 system in Na_2SO_4, we have previously observed a large stability potential window for the activated carbon electrode [12]. In this contribution, we show for the first time that high voltage values can be obtained with a carbon/carbon supercapacitor in Na_2SO_4. The system could operate reversibly during 10,000 charge/discharge cycles up to 1.6 V.

2. Experimental

The electrodes were manufactured with a capacitor grade commercial activated carbon (AC) provided by MeadWestvaco (USA). Pellets (1 cm diameter, thickness 300 nm ± 50 nm, and mass 8–10 mg) were prepared by pressing a homogeneous mixture of activated carbon (80 wt.%), acetylene black (Pure Black, Superior Graphite Co., USA; 10 wt.%) and PVDF (10 wt.%) as binder.

The symmetric AC/AC system was studied using teflon Swagelok® type 2-electrodes cells which were built with gold current collectors

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and glassy fibrous separator. A special two-electrode cell equipped with a reference electrode (Hg/Hg_2SO_4 — SME) was also used. For the experiments carried out in a three-electrode cell, the auxiliary electrode was a graphite rod and the reference electrode was the SME. All potential values are further expressed vs. the normal hydrogen electrode (NHE). Cyclic voltammetry, at a scan rate of 2 mV s^{-1}, and galvanostatic charge/discharge experiments were realized in 0.5 mol L^{-1} Na_2SO_4 aqueous electrolyte and using a VMP (Biologic) multichannel potentiostat/galvanostat. All the experiments were realized in a deaerated electrolyte in order to avoid side reactions between the carbon based electrodes and di-oxygen dissolved in the solution.

3. Results and discussion

A detailed physico-chemical characterization of the activated carbon (AC) can be found elsewhere [12]. In brief, AC exhibits a high purity (2.5 at.% O determined by XPS, no other heteroatom) and a specific surface area of 2250 m^2 g^{-1}.

Fig. 1 shows the cyclic voltammograms (CV) of AC in a three-electrode cell with 1 mol L^{-1} H_2SO_4, 6 mol L^{-1} KOH and 0.5 mol L^{-1} Na_2SO_4, respectively. The stability potential window is about twice larger in Na_2SO_4 than in acidic or basic electrolyte. Actually, in the neutral electrolyte, the potential window reaches 2.0 V due to the high over-potential for di-hydrogen evolution, e.g., 0.6 V. This over-potential is related with the storage of nascent hydrogen in AC below the thermodynamic potential for water decomposition, e. g., −0.38 V vs. NHE in 0.5 mol L^{-1} Na_2SO_4 [4]. The hump observed at 0.55 V during the anodic scan (see Fig. 1) is related to the electro-oxidation of hydrogen sorbed in AC. Comparable stability windows were observed for other ACs with different nanotexture and surface functionality, confirming that the wide potential window obtained in Na_2SO_4 is inherent to the nature of the electrolyte.

The cyclic voltammograms (CVs) and the galvanostatic charge/discharge of a symmetric AC/AC supercapacitor in Na_2SO_4 are presented in Fig. 2. For low values of maximum voltage, the CVs (Fig. 2A) exhibit a rectangular shape characteristic of a pure capacitive behaviour. When the maximum cell voltage increases, a current increase appears, which can be ascribed to redox reactions taking place at the positive and/or the negative electrode, and its counterpart is observed during the negative voltage scan. Galvanostatic charge/discharge cycles (Fig. 2B) recorded for small voltage windows show symmetric characteristics, confirming a pure capacitive behaviour, while some distortions related with the redox processes appear during the first cycles when the cell voltage increases. After few hundred cycles, the voltage vs. time curves become linear. These results suggest that the symmetric carbon/carbon system should be able to operate up to 1.6 V with a specific capacitance (C_S) of 135 F g^{-1}, determined following Eq. (2) [9]:

$$C_S = \frac{4 * C}{M}, \tag{2}$$

where C is the capacitance calculated from the galvanostatic discharge of the cell and M is the total mass of both electrodes.

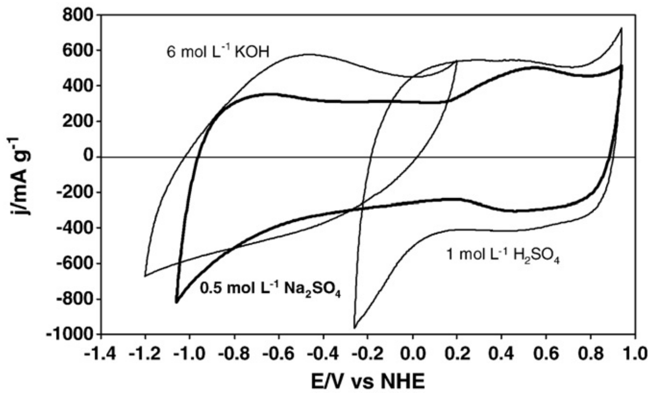

Fig. 1. Cyclic voltammograms (2 mV s^{-1}) showing the potential stability window of AC in 6 mol L^{-1} KOH, 1 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} Na_2SO_4.

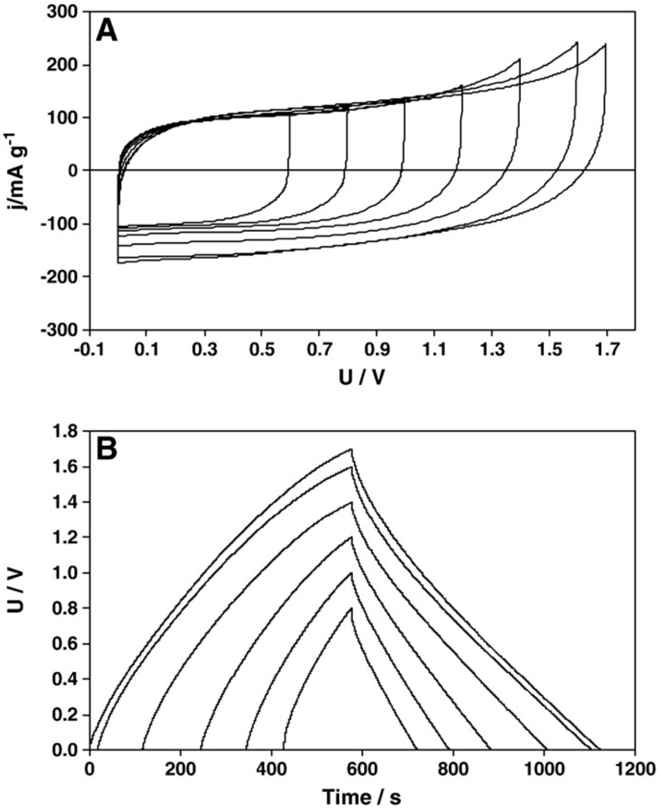

Fig. 2. Cyclic voltammograms (2 mV s^{-1}) (A) and galvanostatic (200 mA g^{-1}) charge/discharge (B) recorded for an AC/AC symmetric supercapacitor in 0.5 mol L^{-1} Na_2SO_4.

The galvanostatic charge/discharge cycling of the symmetric AC/AC capacitor in Na_2SO_4 at different values of maximum voltage is presented in Fig. 3. Typically of a system with a noticeable pseudo-capacitive contribution [9], the capacitance increases when the maximum voltage increases from 1 to 1.6 V. Fig. 3 also confirms the possibility of operating up to 1.6 V when using this electrolyte. In fact, at 1.6 V, the capacitance

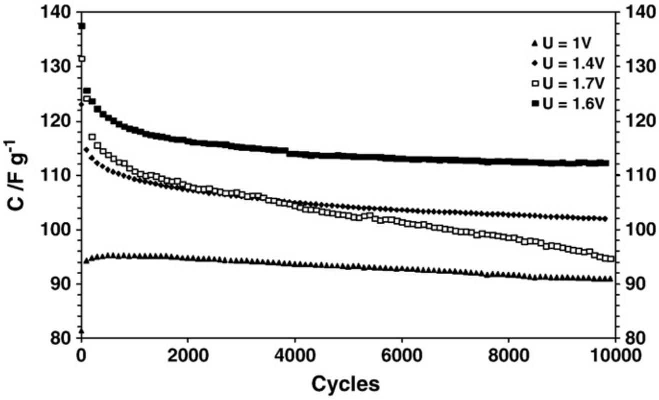

Fig. 3. Specific discharge capacitance of symmetric AC/AC supercapacitors during cycling at a current density of 1 A g^{-1} in 0.5 mol L^{-1} Na_2SO_4 for different values of maximum voltage.