

HIGH ENERGY SYMMETRIC AND ASYMMETRIC CARBON BASED CAPACITORS IN NEUTRAL AQUEOUS ELECTROLYTE

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Introduction

When applied to supercapacitors, the aqueous electrolytes present several advantages over the organic ones. The systems are cheaper, environment friendly and easy to construct. Moreover, with activated carbons (AC), the capacitance can be enhanced through pseudo-faradic charge transfer reactions between the surface functionalities and the aqueous electrolyte [1-2]. Recently, other pseudo-faradic contributions related with reversible hydrogen storage [3] 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 the maximum voltage U is less than 1 V [4], while it reaches 2.7 V in organic medium [5]. Consequently, the energy density $E = \frac{1}{2} CU^2$ is higher in organic than in aqueous electrolyte.

Recently, an asymmetric carbon/carbon supercapacitor able to be reversibly charged/discharged up to 1.6 V in acidic medium (1 mol L⁻¹ H₂SO₄) has been presented [6]. This system is based on two different carbon electrodes with different stability potential windows. However, a less corrosive neutral electrolyte would be a better choice.

In this contribution, we show for the first time that high voltage values can be obtained with an AC/AC supercapacitor in Na₂SO₄. The system could operate reversibly during 10,000 charge/discharge cycles up to 1.6 V.

Experimental

The electrodes were manufactured with a capacitor grade commercial activated carbon (AC, 2250 m² g⁻¹, O = 2.5 at%) provided by MeadWestvaco (USA). Pellets (1 cm diameter, 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.

Teflon Swagelok® type 2-electrode cells were built with gold current collectors and glassy fibrous separator. A special two-electrode cell equipped with a reference electrode (Hg/Hg₂SO₄ - SME) was also used. For the experiments carried out in three-electrode cell, the auxiliary electrode was a graphite rod and the reference was the SME. All potential values are further expressed versus 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 Na₂SO₄ 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.

Results and Discussion

Fig. 1 shows the cyclic voltammograms (CV) of AC in a three electrode cell with 1 mol L⁻¹ H₂SO₄, 6 mol L⁻¹ KOH and 0.5 mol L⁻¹ Na₂SO₄, respectively. The stability potential window is about twice larger in Na₂SO₄ than in acidic or basic electrolyte. Actually, in the neutral electrolyte, it 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 reduction, e.g., -0.38 V vs. NHE in 0.5 mol L⁻¹ Na₂SO₄ [3]. 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.

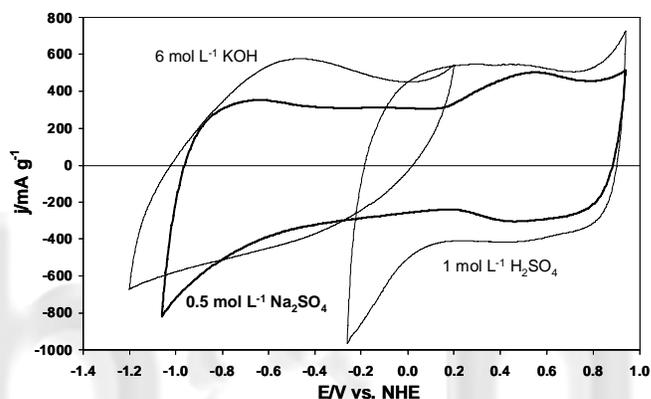


Fig. 1 Cyclic voltammograms (2 mV s⁻¹) showing the potential stability window of AC in 6 mol L⁻¹ KOH, 1 mol L⁻¹ H₂SO₄ and 0.5 mol L⁻¹ Na₂SO₄.

Cyclic voltammograms (CVs) and galvanostatic charge/discharge of a symmetric AC/AC supercapacitor in Na₂SO₄ suggested that the system should be able to operate up to 1.6 V with a specific capacitance of 135 F g⁻¹ at a current density of 200 mA g⁻¹. The evolution of the discharge capacitance during cycling of the symmetric AC/AC capacitor in Na₂SO₄ at different values of maximum voltage is presented in fig. 2. Typically for a system with a noticeable pseudo-faradic contribution, the capacitance increases when the maximum voltage increases from 1 to 1.6 V. Fig. 2 also confirms the possibility of operating up to 1.6 V when using this electrolyte. In fact, at 1.6 V, the capacitance slightly decreases by 7% during the first 2,000 cycles, and it further keeps constant at around 110 F g⁻¹ up to 10,000 cycles at a current density of 1 A g⁻¹. However, if the cell voltage is increased up to 1.7 V, the capacitance continuously decreases and the loss after 10,000 cycles is already 24%.

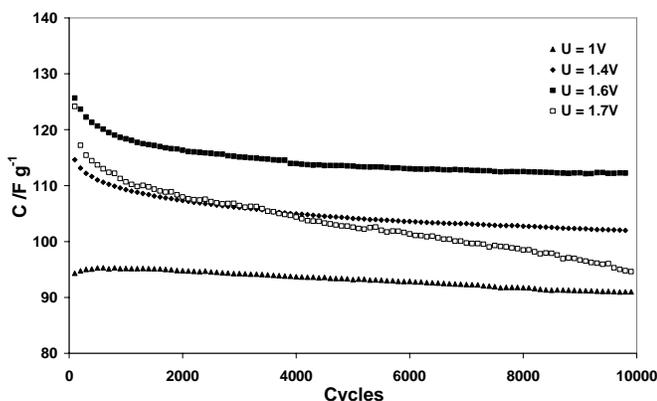


Fig. 2 Specific discharge capacitance of symmetric AC/AC supercapacitors during cycling at a current density of 1 A g^{-1} in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ for different values of maximum voltage.

Notwithstanding the fact that 1.6 V is the highest cell voltage ever presented for a symmetric carbon/carbon capacitor working in an aqueous electrolyte, this value is smaller than the total stability potential window of 2.0 V determined for AC in three-electrode cell. In order to determine the reasons of this underuse of the carbon potential window with a supercapacitor in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, experiments were carried out in a special two-electrode cell equipped with a reference electrode. Such configuration allows the positive and negative electrode potentials to be recorded separately during cycling the supercapacitor between zero and a given maximum voltage.

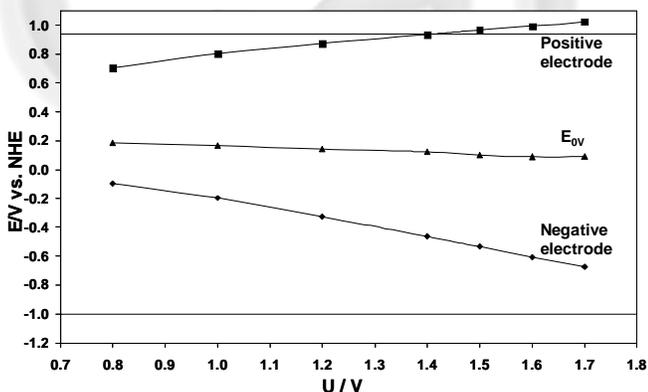


Fig. 3 Potential reached by the positive and the negative electrode during the operation of a 2-electrode cell (equipped with a reference electrode) at different values of maximum voltage and at 0 V (E_{0V}). Electrolyte: $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. The horizontal lines represent the extreme potential values determined for AC in 3-electrode cell (see fig. 1).

The results presented in fig. 3 show that, if the supercapacitor is charged between 0 V and the maximum stability voltage of 1.6 V, the operating potential windows for the negative and the positive electrode are [0.09; -0.61] and [0.09; 0.99] V vs. NHE, respectively. According to fig. 1, the lowest potential for a negative electrode in Na_2SO_4 before di-

hydrogen production is around -1 V vs. NHE and the highest one for a positive electrode in order to avoid an irreversible oxidation is around 0.9 V vs. NHE (see the horizontal lines included in fig. 3). Hence, fig. 3 clearly shows that the maximum voltage of the supercapacitor is limited by the positive electrode. In fact, the maximum potential reached by the positive electrode at $U = 1.6 \text{ V}$ is slightly beyond the limit, whereas the minimum potential reached by the negative electrode is still far away, ca. 0.4 V, from the limit imposed by gas evolution.

From the foregoing, the strategy to follow for taking profit of the whole stability potential window of 2.0 V in Na_2SO_4 , and for enhancing the energy density of an AC/AC capacitor, would consist in broadening the potential range of the negative electrode. In sulphuric acid medium, it has been shown that this kind of shift of the electrodes potential range is possible by building asymmetric systems with a mass balance of the positive and negative electrodes [6].

Conclusions

For the first time, we have demonstrated a high stability potential window of 2.0 V for an activated carbon in neutral Na_2SO_4 solution; such value is twice higher than in KOH or H_2SO_4 . Consequently, a symmetric AC/AC supercapacitor in Na_2SO_4 could operate up to $U = 1.6 \text{ V}$ with a good charge/discharge cycle life.

By introducing a reference electrode between the two AC electrodes, we established that, at $U = 1.6 \text{ V}$, the potential of the positive electrode is slightly beyond its irreversible oxidation limit, while the limit for di-hydrogen production is not reached at the negative electrode. Since the AC/AC symmetric capacitor in Na_2SO_4 largely outperforms all the symmetric systems in other aqueous electrolytes, further breakthroughs can be expected in this medium by using asymmetric configurations allowing the negative electrode potential to be pushed towards smaller values. This work will be detailed in our presentation.

References

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