

THE ASYMMETRIC CONFIGURATION: A SOLUTION FOR ENHANCING THE OPERATING VOLTAGE OF SUPERCAPACITORS

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Introduction

Recently, the interest in electrochemical capacitors has considerably increased as they are able to boost the power of systems. Nowadays, capacitors based on an organic electrolyte are mainly developed at the industrial scale. The reason is that voltage values up to 2.7 V can be reached in organic medium, whereas the existing systems in aqueous electrolyte cannot operate at more than 0.6-0.7 V. Since the stored energy and power are proportional to the square of voltage, one easily understands the reasons for being more interested by the organic electrolyte. Although this solution is the most currently adopted by companies, it is not satisfactory for the following reasons: i) the conductivity of organic electrolytes is very low, and as a consequence the power of capacitors based on these electrolytes is not high enough; ii) the capacitance of the electrode materials is lower in organic than in aqueous medium; iii) electrochemical capacitors operating in these media have a poor cycle life, i.e., they demonstrate an important performance fading with time of operation; iv) these systems must be built in moisture-free atmosphere, that increases their cost; v) due to the presence of organic compounds, they are unsafe and ecologically unfriendly. All these disadvantages could be eliminated by the use of an aqueous electrolyte, provided that the voltage window is enhanced.

An asymmetric configuration, with two electrodes of different nature, has been proposed in literature to enhance the voltage window in aqueous solution. These systems associate redox materials as nickel oxide (Beliakov, 1997), lead oxide (Volkovich, 1998), manganese oxide (Hong, 2002; Brousse, 2004; Khomenko, 2006) for the positive electrode and activated carbon for the negative electrode. The highly positive potential of the metal oxide electrode allows the cell voltage to be increased up to 2 V in some cases. However, the performance of such devices is more comparable to a battery than a capacitor, due to the presence of the redox compounds. Consequently, they present a number of disadvantages as i) an insufficient specific energy; ii) the use of ecologically dangerous compounds as lead; iii) a limited cycle life due to the use of a battery-like positive electrode; iv) a moderate power density.

In this work, we have developed a new type of supercapacitor based on only activated carbon (AC) materials for both electrodes in an environment friendly electrolyte (sulphuric acid). The novelty consists in using different activated carbons adapted for the positive and negative electrode, respectively, in a non symmetric configuration. According to this simple construction, either the capacitance value or the voltage window of the capacitor is enhanced, resulting in a high energy density device. For adapting the performance of an activated carbon, either as positive or as negative electrode, very simple processes have been followed in order to have materials in which the double layer capacitance and pseudocapacitance are combined.

Experimental

The starting materials were two commercial activated carbons named A and B. The porous texture was analyzed by N₂ adsorption at 77 K (Autosorb-1MP, Quantachrome). The values of the BET specific surface area were 1650 m²/g and 3490 m²/g for A and B, respectively.

The electrodes were 1 cm² pellets obtained by pressing a mixture of the activated carbon (85 wt%) together with 5 wt% carbon black and 10 wt% binder. The electrochemical characteristics were determined in 1 mol.L⁻¹ H₂SO₄ electrolytic medium, either in two or three-electrode cells, using the galvanostatic, voltammetric and impedance spectroscopy techniques (VMP multichannel potentiostat-galvanostat, Biologic, France). The capacitance values determined in a symmetric system using sulphuric acid as electrolyte were 110 F/g and 230 F/g for A and B, respectively.

Results and discussion

Carbon for positive electrode

The activated carbons were oxidized by 30% HNO₃ and their specific capacitance was measured using a three-electrode cell in 1 mol.L⁻¹ H₂SO₄. Figure 1 shows the cyclic voltammograms of as-received A and of A after chemical oxidation. One can observe that the capacitance of the activated carbon A increases from 110 F/g to 214 F/g, due to the redox processes involving the oxygenated functionalities. By contrast, the specific capacitance of B decreased from 230 to 180 F/g due to the destruction of the porous texture.

Interestingly, after chemical oxidation, the oxidized A activated carbon may operate in a higher potential range than as-

received A. However this carbon is not interesting for performing symmetric systems. The reason is that the redox reactions involving the oxygenated functionalities control simultaneously the equilibrium potential at 0 V (EP) and the ΔE for the positive and negative electrodes when working in a symmetric two-electrode system (arrows included in Figure 1). For the oxidized sample, the ΔE of the positive electrode is displaced to very positive potentials. Consequently, the positive electrode of the symmetric capacitor based on oxidized A works only partly in the range where redox reactions take place. Thus, the capacitance of the positive electrode is smaller than for the negative one and, due to the series dependence for the real capacitor, the positive electrode determines the total cell capacitance. In sum, the strong chemical oxidation of A provides a carbon perfectly adapted for operating in the positive potential range.

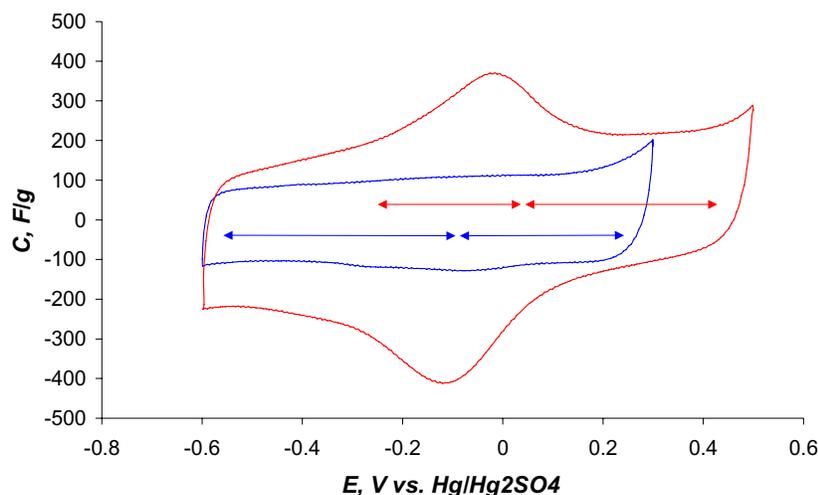


Figure 1. Voltammograms using a three-electrode cell in 1 mol.L⁻¹ H₂SO₄ for the activated carbon A (in blue) and for oxidized A (red). The arrows represent the ΔE values for the positive and negative electrodes when a two-electrode cell is charged up to 0.8 V.

Carbon for negative electrode

Activated carbons present unique pseudocapacitance properties under negative polarisation in aqueous medium (Jurewicz, 2004). The voltammograms presented in Figure 2 for the activated carbon B show that high overpotential values for H₂ evolution can be reached, that allows the potential window to be significantly increased. Hydrogen produced by water decomposition at potentials lower than the thermodynamic value is immediately adsorbed in the carbon porosity, being reversibly electro-oxidized during the anodic scan. In this case, the pseudocapacitive properties of activated carbon are related with the redox mechanism of hydrogen in the pores giving an additional capacitance. It should be mentioned that the hydrogen evolution overpotentials for the activated carbon B are higher than for A.

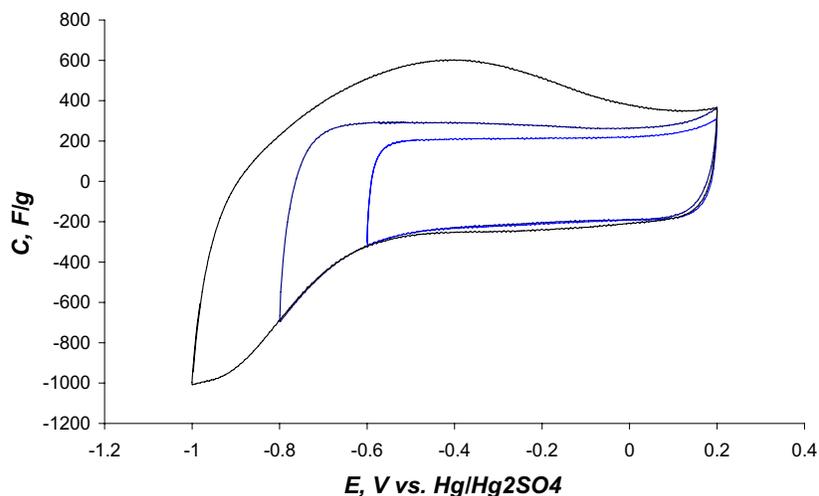


Figure 2. Voltammograms using a three-electrode cell in 1 mol.L⁻¹ H₂SO₄ for the activated carbon B.

Construction of the asymmetric capacitor

From the foregoing, different pseudocapacitive properties of activated carbon can be used in order to optimise its behaviour as positive or negative electrode. As an example, the cyclic voltammograms of the activated carbons B and oxidized A obtained in a three electrode cell are shown together on figure 3. From this figure, it is obvious that B is more adapted for the negative electrode, whereas oxidized A is typically a positive electrode material. Combining the two electrodes should allow a total cell voltage of 1.8 V to be reached without electrolyte decomposition or destructive oxidation of the activated carbon, as shown by the arrows indicating the potential range for each electrode. Also the capacitance of the electrochemical capacitor would be increased because the redox reactions of the positive and negative electrodes occur in different potential range.

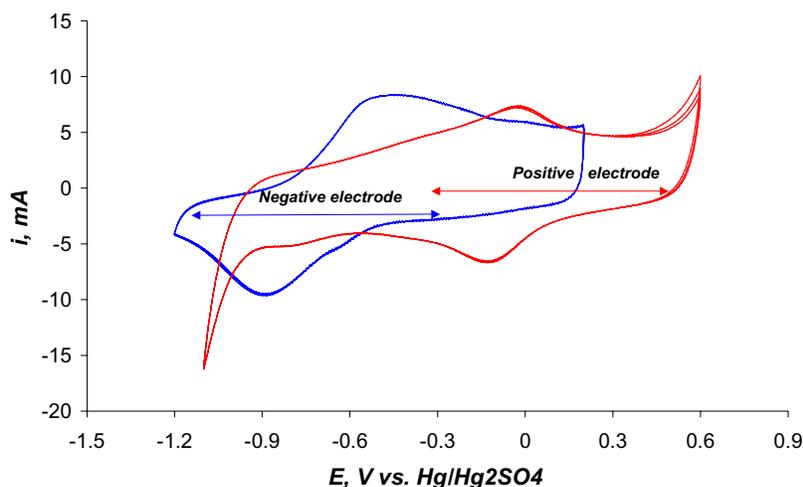


Figure 3. Voltammograms using a three-electrode cell in 1 mol.L⁻¹ H₂SO₄ for the activated carbon B (blue) and for oxidized A (red). Values of the real ΔE are included for both electrodes of an asymmetric capacitor combining B and oxidized A for the negative and positive electrodes, respectively.

Figure 4 shows the resultant CV obtained in a real two-electrode cell using an asymmetric configuration with the two materials presented in Figure 3 as positive and negative electrode. The test on this cell shows that it is possible to achieve a maximum voltage of 1.8 V in aqueous medium. The sharp current leap above 1.6 V may correspond to the beginning of gas evolution.

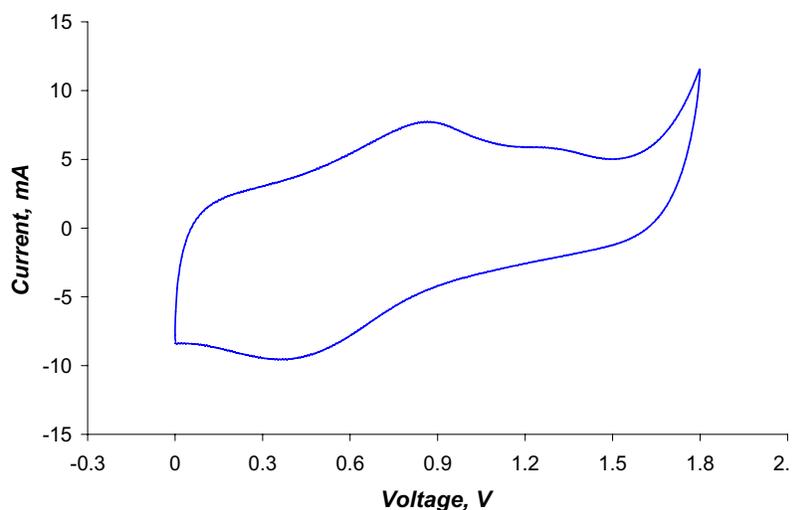


Figure 4. Cyclic voltammogram of an electrochemical capacitor using the activated carbon B and chemically pre-oxidized A as negative and positive electrode, respectively.

Figure 5 shows the cycle life of the asymmetric capacitor at a maximum voltage of 1.6 V and a current density of 1 A/g for about 10,000 cycles. The small 15% decrease of the discharge capacitance value during the first 2,000 cycles corresponds to the conditioning of the system. Thereafter, the specific capacitance remains almost constant during the subsequent 8,000

cycles, indicating a high cycling stability of the supercapacitor.

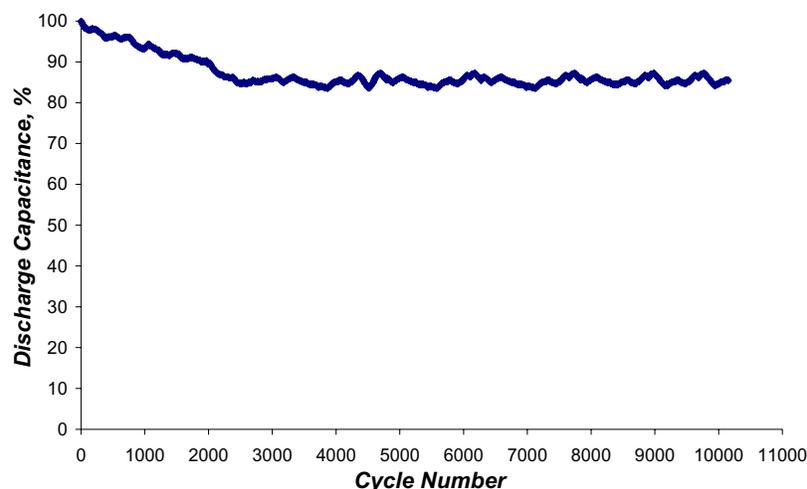


Figure 5. Variation of the discharge capacitance during the cycling of the asymmetric capacitor using the activated carbon B and chemically pre-oxidized A as negative and positive electrodes, respectively. Current density 1A/g.

The specific energy of the asymmetric capacitor is about 10 times higher than for a symmetric carbon based electrochemical capacitor using an aqueous electrolyte. It reaches values of about 30 Wh/kg of carbon, typical of an electrical double layer capacitor using an organic electrolyte. Hence, the electrochemical characteristics over-perform all existing electrochemical capacitors based on activated carbon in aqueous electrolytes (Khomeenko, 2006).

Conclusion

An asymmetric capacitor has been fabricated with two different activated carbon based electrodes using sulphuric acid as electrolyte. Both electrode materials store the electrochemical charges by involving together the charge/discharge of the double layer and redox reactions of pseudo-faradic nature, respectively. Due to the selective chemical treatment of the activated carbon, the nature of the oxidation/reduction reactions which take part on the negative and positive electrodes is different. This fact was used to increase the capacitance of the electrochemical capacitor. The working voltage of the electrochemical capacitor was extended by shifting the potentials of water decomposition and destructive oxidation of activated carbon through selective chemical treatments of the activated carbon. With this system operating in aqueous medium, most of the disadvantages of the organic electrolyte are eliminated. Due to the use of the water solution, the asymmetric capacitor with activated carbon electrodes of different nature is safe and environment friendly, and it can be produced at a low cost.

References

- Beliakov, A.L., Brintsev, A.M., 7th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1997.
- Volkovich, Y.M., Shmatko, P.A., 8th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1998.
- Hong, M.S., Lee, S.H., Kim, S.W., *Electrochem. Solid State Lett.*, 5 (2002) A227.
- Brousse, T., Toupin, M., Bélanger, D., *J. Electrochem. Soc.*, 151 (2004) A614.
- Khomeenko, V., Raymundo-Pinero, E., Béguin, F., *J. Power Sourc.*, 153 (2006) 183.
- Jurewicz, K., Frackowiak, E., Béguin, F., *Appl. Phys. A*, 78 (2004) 981.
- Khomeenko, V., Raymundo-Pinero, E., Béguin, F., French Patent FR 06 10483 (30 November 2006).