

THE ESSENTIAL ROLE OF ACTIVATED CARBON ALLOWING ASYMMETRIC CAPACITORS TO OPERATE AT 2V IN AQUEOUS MEDIUM

Volodymyr Khomenko, Encarnación Raymundo-Piñero, François Béguin
CRMD, CNRS-University, 1b Rue de la Férollerie, 45071 Orléans Cedex 02, France

Corresponding author e-mail address: beguin@cnrs-orleans.fr

Introduction

The amount of electrical energy accumulated in an electrochemical capacitor is proportional to the capacitance of the electrode material and to the square of the working voltage. The operating voltage is determined by the electrolyte potential window. In this sense, despite a good conductivity, aqueous electrolytes can work in a maximum potential window of 1V (the thermodynamic electrochemical window of water is 1.23V), while organic electrolytes can reach 3V. Therefore, some tentative works tried to find solutions for increasing the operating voltage in aqueous medium. One interesting approach is the so-called asymmetric capacitor where the positive and negative electrodes are from different nature, being polarized in a different range of potentials [1-3]. The asymmetric system using amorphous manganese oxide and activated carbon as positive and negative electrode, respectively, has been proposed with promising results [4], but the role of activated carbon is not clearly understood.

Activated carbons (AC) are usually used for symmetric electrochemical double layer capacitors due to the possibility of obtaining materials with a high specific surface area [5]. In the present work, pseudocapacitance properties of AC in aqueous medium under negative polarization will be demonstrated. The knowledge of the charge storage mechanism for AC will allow us to optimize the asymmetric manganese oxide/activated carbon capacitor in order to allow both electrodes to operate in an optimal potential range, that broadens the voltage window of the device up to 2 V in aqueous medium.

Experimental

The commercial activated carbon PX21 (Maxsorb, Kansai, Japan) with a BET surface area of 2500 m²/g was used in the present study as negative electrode material. Amorphous and hydrated manganese oxide (α -MnO₂·nH₂O) was prepared by a chemical method in the presence of 15 wt% of carbon nanotubes (CNTs) to obtain composites α -MnO₂·nH₂O/CNTs to be used as positive electrode material. A detailed chemical and electrochemical characterization of this material can be found elsewhere [6,7].

The capacitor electrodes were films formed by a mixture of the active material (α -MnO₂·nH₂O/CNTs composite or activated carbon, 90 wt%) with a binder solution (Teflon, 10%). The mixture was thoroughly homogenized in an agate mortar and dried

at room temperature before being rolled into a thin film of uniform thickness. Electrode pellets were cut with a surface of 1 cm^2 which corresponds approximately to a mass of 10 mg. Two electrode capacitors were built with a glassy fibrous separator and gold current collectors, using a teflon Swagelok[®] type system. The aqueous electrolytic solution used was $2 \text{ mol.L}^{-1} \text{ KNO}_3$ with a pH of 6.4. The values of capacitance were estimated by cyclic voltammetry (VMP-Biologic-France). Experiments were also done in teflon three electrode cells by using Pt and Hg/Hg₂SO₄ as auxiliary and reference electrode, respectively. All potentials are reported against normal hydrogen electrode (NHE).

Results and Discussion

Figure 1 shows cyclic voltammograms recorded with the three-electrode cell for the carbon electrode in 2M KNO₃ with a pH of 6.4 at different negative cut-off polarization values. The quite rectangular shape of the CV down to a potential cut-off of -0.4 V , with comparable values of positive and negative current, proves a pure capacitive and reversible behavior in this potential range. However, when the potential cut-off is decreased down to -0.8 V or -1 V , the anodic current increases with lowering the polarization potential. In addition, the fast current leap observed in Figure 1 shows that H₂ evolution from water decomposition starts at potentials close to -1 V , according to equation (1):



Taking into account that the thermodynamic value for H₂ evolution at pH=6.4 is -0.38 V , it indicates that activated carbon presents a high H₂ overpotential in the present conditions.

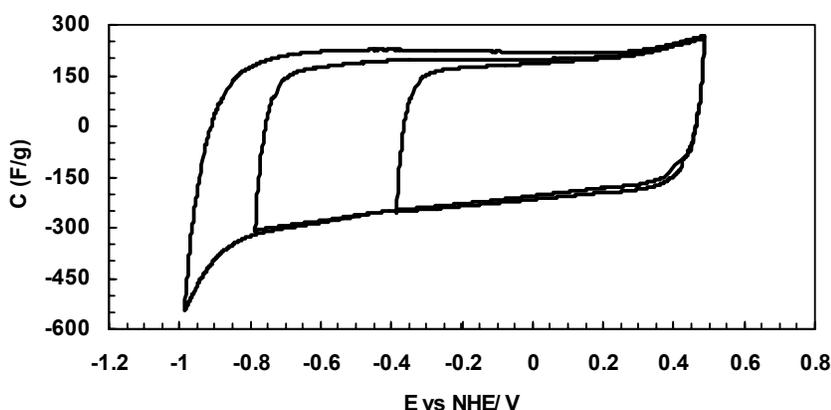


Figure 1. Cyclic voltammograms of the activated carbon PX21 electrode in the 2M KNO₃ electrolyte.

Therefore, there are enough evidences to affirm, as it was proposed in a previous work [8], that during the polarization of the activated carbon electrode at potentials lower than the one of water reduction, the hydrogen produced is immediately absorbed in the pores. Later, during the anodic scan, this adsorbed hydrogen is reversibly

electrooxidized and, for this reason, an increase of the anodic current is observed (see Figure 1).

Hence, down to potential cut-off higher than the thermodynamic value for the H_2 evolution, the storage mechanism of the activated carbon is simply by charging the electrical double-layer in the electrode-electrolyte interface. When the cut-off potential is decreased down to more negative values, there is a contribution of a pseudocapacitive effect due to a fast and reversible redox reaction, which is more extensive for low potential values and is traduced by an increase of the total specific capacitance of the electrode.

The overvoltage of H_2 evolution on the activated carbon is responsible of the very negative values to which it can be polarized. Figure 2 shows that, due to this unique behavior, it is very interesting to develop a full capacitor where the activated carbon is used as negative electrode and another material c.a. the manganese oxide/CNTs composite is used as positive electrode. Manganese oxide has also a pseudocapacitive behavior and can be polarized up to high positive values as 1.2 V with a high reversibility, but its lower potential limit is limited by irreversible redox reactions at 0.47 V [6,7]. Considering the characteristics of both electrodes in Figure 2, it is theoretically possible to obtain a working potential window of 2.2 V by combining the two materials in the same capacitor.

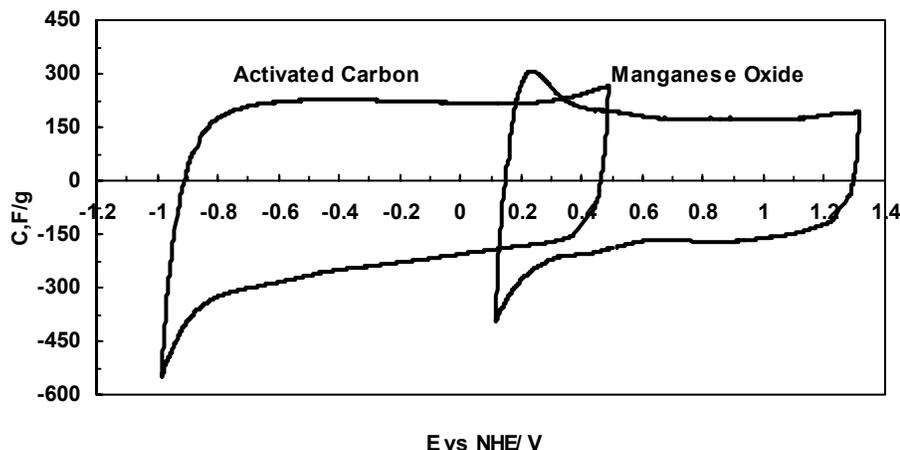


Figure 2. Cyclic voltammograms of the activated carbon PX21 and the manganese oxide/CNTs composite in 2M KNO_3

Figure 3 presenting the voltammetry curve for this kind of asymmetric capacitor, done in a real two-electrode system, confirms a quite rectangular shape characteristic of an ideal capacitive behavior up to 2.2 V. In practice, after optimizing the system, it was possible to obtain a working voltage window of 2 V in aqueous medium, while keeping an excellent cyclability. In these conditions, the energy density of the hybrid capacitor reaches 12.6 Wh.kg^{-1} of both electrodes, that is 10 times higher than in symmetric systems with activated carbon or manganese oxide in aqueous medium, and relatively close to the values of electric double layer capacitors working in organic electrolytes.

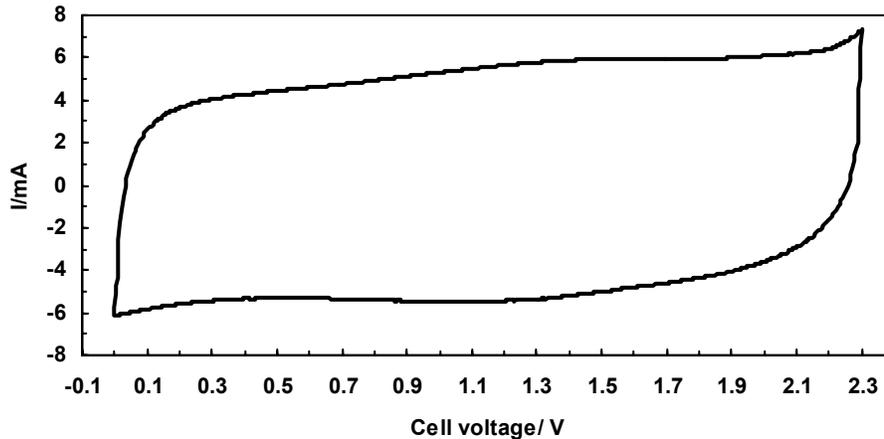


Figure 3. Cyclic Voltammogram of an asymmetric capacitor with the activated carbon PX21 and the manganese oxide/CNTs composite as negative and positive electrodes, respectively, in 2M KNO_3

Conclusions

The activated carbon was showing a unique behavior at negative polarizations. Its ability to reversibly adsorb hydrogen allows to polarize carbon to values far from the thermodynamic window of the electrolyte and is at the origin of a pseudocapacitive behavior.

As a consequence, a hybrid capacitor could be optimized by combining two materials with a pseudocapacitive behavior in aqueous medium, i.e. activated carbon and manganese oxide/CNTs composite, as negative and positive electrodes, respectively. The optimized system gives a practical cell voltage of 2 V in aqueous medium, with energy densities close to the values obtained with electric double layer capacitors working in organic electrolytes. Due to the various advantages of the aqueous electrolyte medium, it is worth to deeply investigate the systems based on this concept.

Acknowledgements

This research was supported by a Marie Curie fellowship of the European Community programme “Improving Human Research Potential and the Socio-Economic Knowledge Base” under contract number HPMF-CT-2001-01453.

References

[1] Park JH, Park OO. Hybrid electrochemical capacitor based on polyaniline and activated carbon electrodes. *J. Power Sources* 2002;111:185-190.

- [2] Laforgue A, Simon P, Fauvarque JF, Mastragostino M, Soavi F, Sarrau JF, Lailier P, Conte M, Rossi E, Sanguatti S. Activated carbon/conducting polymer hybrid supercapacitor. *J.Electrochem.Soc.* 2003 ;150 :A645-A651.
- [3] Brousse T, Bélanger D. A Hybrid $\text{Fe}_3\text{O}_4\text{-MnO}_2$ capacitor in mild aqueous electrolyte. *Electrochem. Solid State Lett.* 2003;6(11):A244-A248.
- [4] Hong MS, Lee SH, Kim SW. Use of aqueous electrolyte for 2 V manganese oxide/activated carbon hybrid capacitor. *Electrochem. Solid State Lett.* 2002;5(10):A227-A-230.
- [5] Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* 2001;39:937-950.
- [6] Raymundo-Piñero E, Khomenko V, Frackowiak E, Béguin F. Performance of manganese oxide/carbon nanotubes composites as electrode materials for real electrochemical capacitors. *J.Electrochem.Soc.* 2004, submitted.
- [7] Khomenko V, Raymundo-Piñero E, Béguin F. Developement of high performance hybrid supercapacitors based on a- MnO_2 /carbon nanotubes composites. NATO Science Series, II- Mathematics, Physics and Chemistry 2004, submitted.
- [8] Jurewicz K, Frackowiak E, Béguin. Towards the mechanism of electrochemical hydrogen storage in nanostructured carbon materials. *Appl.Phys.A*, in press.