

# CONTRIBUTION OF PSEUDOCAPACITANCE AND DOUBLE LAYER TO THE CAPACITANCE OF ACTIVATED CARBONS

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## Introduction

Carbon based supercapacitors store energy through two different mechanisms: double layer formation and pseudocapacitance. These two mechanisms are based on different physico-chemical phenomena but it is difficult to ascertain the contribution of each one to the total capacitance. In an ideal double layer capacitor the capacitance is independent of the applied potential. Other processes that contribute to capacitance but are potential dependent are defined as pseudocapacitive phenomena. This paper studies the behaviour of an activated carbon at different potential windows, in aqueous and organic media. The results obtained allow determining the contribution of each mechanism (double layer and pseudocapacitance) to the total capacitance. Moreover, it provides information about the kinetic dependence of the physico-chemical phenomena involved in energy storage.

## Experimental

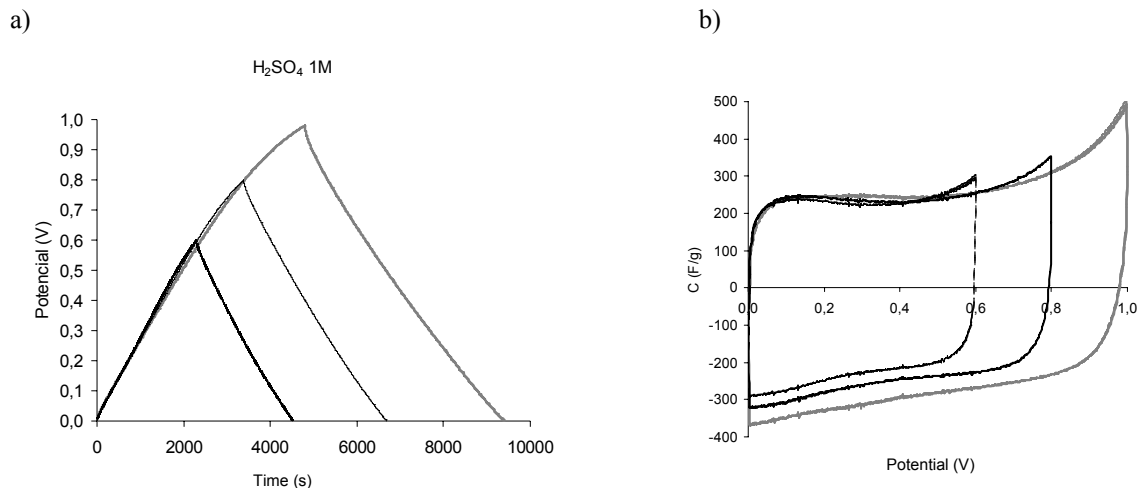
Naphthalene-derived mesophase pitch AR24 was chemically activated with KOH (3:1 KOH to carbon ratio) at 700°C for 1 h. The resultant activated carbon (AC) was used as electrode active material in this study. The textural properties of this highly microporous activated carbon were studied by nitrogen adsorption at 77 K, providing a total pore volume of 0.85 cm<sup>3</sup>/g and a BET area of 2000 m<sup>2</sup>/g. Sample AC has an important amount of oxygen functionalities, 3.5 wt. % obtained by elemental analysis and a low value of pH of 2.8. Additionally, it has a large amount of CO evolving groups, such as phenols, ethers and carbonyl groups.

Coin-type electrodes were prepared by mixing the activated carbon (90 wt. %) with polyvinylidene fluoride, PVDF (10 wt. %). The mixture was pressed into discs of 12 mm in diameter and of about 40 mg of weight. Two discs were mounted in a two-electrode cell to perform the electrochemical measurements. Tests were performed in an Autolab supplied by Eco Chemie. Cyclic voltammetry experiments were carried out at a sweep rate of 1 mV/s and galvanostatic charge-discharge cycles were performed with current densities ranging from 0.88 to 88 mA/cm<sup>2</sup>. Experiments were performed at different potential windows (0.6-1 V in aqueous media and 0.6-2.5 V in organic media).

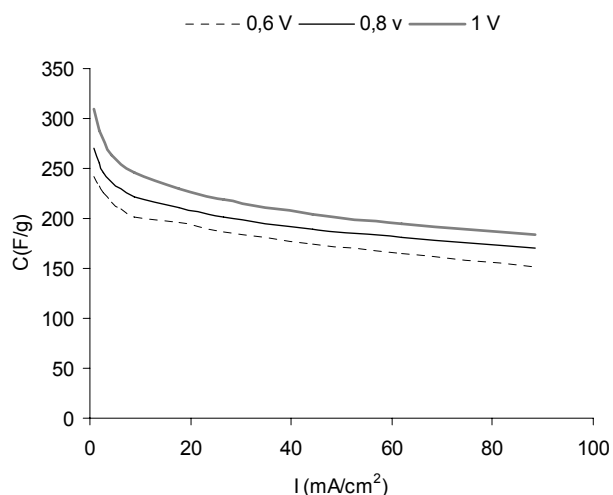
## Results and Discussion

Figure 1a shows the galvanostatic charge-discharge cycles for AC obtained at different potential windows in sulfuric acid. As the working potential increases there is a greater deviation from the ideal behaviour of a double layer capacitor, it being more significant at values close to 1 V. This is in agreement with a higher contribution of Faradaic currents at high potential windows, as the system is closer to the decomposition of the aqueous media, together with possible redox reactions in the carbon material. Similar information can be withdrawn from Figure 1b that shows the cyclic voltammograms obtained increasing the potential window at a constant sweep rate. In all cases there is an increase of the anodic current close to the cut-off potential, this situation being more pronounced at 1 V than at 0.6 or 0.8 V. This corroborates that the presence of Faradaic currents lead to a distortion of the ideal behaviour of the electrochemical capacitor. It is generally accepted that the perfect triangle in charge-discharge experiments or rectangular shape in voltammograms at 0.6 V it is due to the ideal behaviour of the double layer formation. However it cannot be discarded the existence of pseudocapacitance in the lowest voltage window as it will be demonstrated later on.

The results obtained from galvanostatic cycling (Figure 2) corroborate the fact that the capacitance values do not remain constant throughout the range of potential, as a clear increase in the capacitance values is observed with increasing the potential window. Therefore, it can be assessed that an important amount of pseudocapacitance is present in AC in this media.

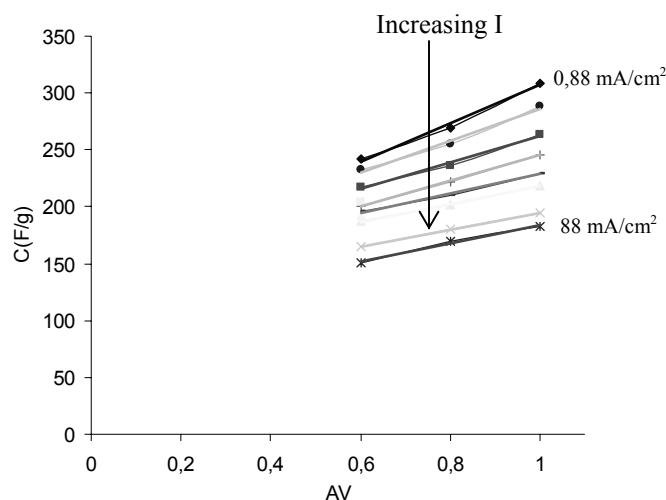


**Figure 1.-** Electrochemical characterization in H<sub>2</sub>SO<sub>4</sub> at different potential windows: a) charge-discharge cycles at 0,88 mA/cm<sup>2</sup> b) Cyclic voltamograms at 1 mV/s.



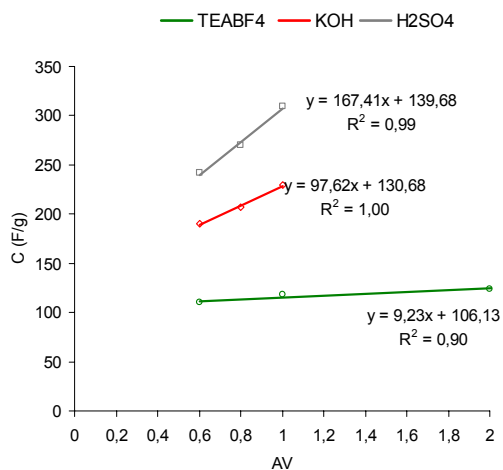
**Figure 2.-** Variation of specific capacitance with current density in H<sub>2</sub>SO<sub>4</sub> at different potential windows.

To obtain further information about the contribution of pseudocapacitance at various potentials, the variation of the specific capacitance at different current densities was represented in Figure 3. A linear tendency can be observed for all the current densities used. The slope gives information about the dependency of capacitance with the potential window. Therefore, it can be considered as an indication of pseudocapacitive phenomena in the capacitor. An ideal capacitor would have a slope value of zero. For voltages approaching zero volts, the value of capacitance would correspond exclusively to the formation of the electric double layer. At low current densities the slope values are higher than at high current densities, probably due to the greater contribution of slow kinetic processes, like Faradaic reactions. Differences found in the ordinate of origin should arise from diffusion limitations at the highest current densities.



**Figure 3.-** Variation of specific capacitance with potential window at different current densities in  $H_2SO_4$ .

A similar study was carried out in different electrolytes (Figure 4). For all of them the capacitance values at each current density perfectly fit to a straight line. The slope is much higher in the aqueous media than in the organic one, as a consequence of the minor contribution of pseudocapacitance effects in the organic media. Comparing the two aqueous electrolytes, the slope obtained in the acidic media is higher. This is in agreement with the general assumption that the pseudocapacitance effects are more pronounced for acidic media. The ordinates at origin are similar for the aqueous media and higher than for the organic one ( $\sim 135$  vs  $106$  F/Vg). These differences can be assigned to the restricted accessibility of the large ions of the organic media to form the double layer.



**Figure 4.-** Variation of capacitance with potential window in  $H_2SO_4$  1M, KOH 6M and TEABF<sub>4</sub>-ACN 1M at 1 V. 0,88 mA/cm<sup>2</sup>

## Conclusions

The results obtained determined the contribution of the different mechanisms of energy storage. Moreover provides information about the kinetical dependence of the physico-chemical processes involved in electrochemical capacitors.

## Acknowledgements

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