

COMPARATIVE STUDY OF THREE-ELECTRODE CELL WITH SINGLE PARTICLE MICROELECTRODE

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Introduction

Three-electrode cell configuration is generally used for the characterisation of the performance of electrode active materials, as it provides detailed information about the faradic phenomena that occur within the range of thermodynamic stability of the electrolyte. In this configuration, the active material usually requires a polymer to form a manageable electrode, which acts as working electrode. This addition of the polymer to the activated carbon, causes a reduction of the surface area accessible to the electrolyte due to the blockage of part of the porosity of the activated carbon, an effect that is strongly influenced by the way in which the polymer and the carbon are mixed [1]. The polymer also causes a significant reduction of the electrical conductivity of the electrode. Therefore, the electrochemical behaviour obtained using a three-electrode cell configuration is always influenced by the presence of the polymer and not only by the activated carbon itself.

In the microelectrode technique [2], a single carbon particle is used as working electrode. This means that all the information obtained corresponds exclusively to the activated carbon, avoiding the reduction of surface area and electrical conductivity explained before for the macroscopic configuration. Two key aspects in the cyclic voltammetry experiments performed in the microscopic configuration are the low current intensities registered, with the subsequent reduction of the ohmic drop (IR), and the increased sensibility against faradic currents. As the size of the electrode increases, the charge current decreases exponentially, while the faradic currents do it linearly. Therefore, there is an improvement of the relationship between faradic and non-faradic currents when the microelectrode is used, which makes this technique much more sensitive than the macroscopic systems generally used.

The aim of this paper is to study the electrochemical behaviour of a chemically activated carbon using the conventional three-electrode cell configuration and the single particle microelectrode and compare the results obtained from each one.

Experimental

Materials

Naphthalene-derived mesophase pitch AR24 was chemically activated with KOH (3:1 KOH to carbon ratio) at 700°C for 1 h. The activation procedure followed and the textural characteristics of the activated carbon obtained have been previously described [3]. The resultant activated carbon (AC) was used as electrode active material in this study. The textural properties of this highly microporous activated carbon was studied by nitrogen adsorption at 77 K, providing a total pore volume of 0.85 cm³/g and a BET area of 2000 m²/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.

Three-electrode cell configuration

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 8 mm in diameter and of about 30 mg of weight which were used as working electrodes. Platinum and Hg/HgO work as the counter and reference electrodes, respectively.

Single particle microelectrode

The single particle microelectrode technique is mounted above a microscope, where a single particle of the activated carbon is contacted with a highly conductive carbon fibre attached to a gold probe surrounded by de-aired electrolyte. This acts as the working electrode. A Ni felt with a significantly larger surface area than the working electrode was used as counter electrode. Hg/HgO was used as reference electrode. Individual particles, sizes around 100 microns, of the activated carbon were used for the single particle experiments. A detailed description of the single particle microelectrode technique has been done previously [4].

The electrochemical measurements were performed in both cases 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 at a current density of 230 mA/g. The potential window used was maintained inside the limits of the thermodynamic stability of the electrolytic medium, 6 M KOH.

In order to compare the capacitance values provided for each technique, the estimation of the volume of the particle of carbon is needed, together with the density of the active material.

Results and Discussion

Figure 1 shows the results obtained in cyclic voltammetry experiments using both configurations. In the smallest potential window studied (0 to -0.2 V), the typical rectangular behaviour of a double layer capacitor is observed. The capacitance values estimated in both cases are fairly coincident, despite the possible errors that can be introduced in the estimation of the mass of the particle used in the three microelectrode. As could be expected, the resistance shown by the microscopic device is lower. This could be due to a better contact between the fibre and the particle in relation to the contact between the disc and the current collector, accompanied by the significantly lower currents measured in the microelectrode and the presence of polymer in the macroelectrode.

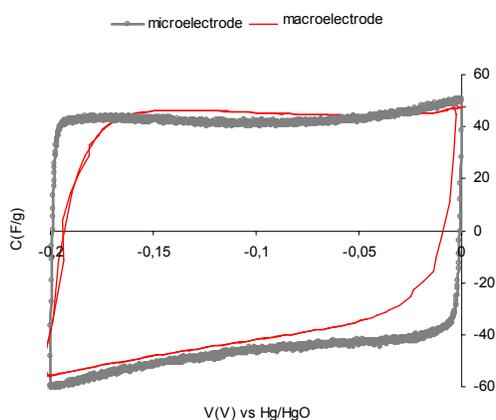


Figure 1.- Cyclic voltammogram for both configurations in the potential window from 0 to -0.2 V.

Figure 2 shows a comparison of the charge-discharge cycles obtained in both cases for the same potential window discussed before (0.2 V). Both cycles show the triangular shape typical of electrochemical capacitors where the storage of energy comes only due to the formation of the electric double layer. As observed before in the voltammograms, the equivalent series resistance is higher for the macroscopic device.

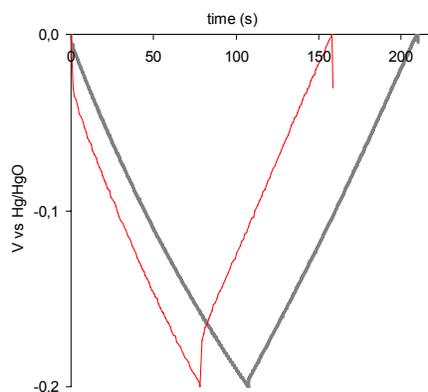
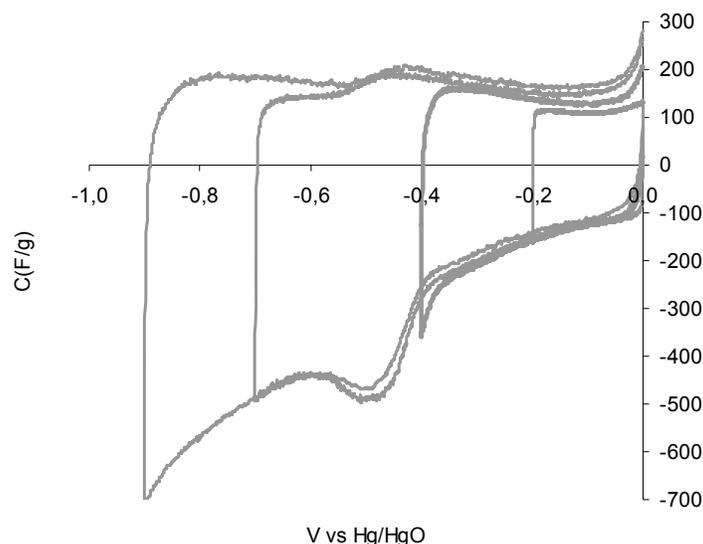


Figure 2.- Galvanostatic charge-discharge cycles for both configurations in the potential window from 0 to -0.2 V.

When the potential window is progressively increased in the direction of negative potentials, the voltammograms show significant differences for each configuration (Figures 3 a and b). The main difference can be observed at potentials between -0.4 and -0.5 V. In the microscopic system, the redox couple attributed to the reaction of quinone-type groups is clearly observed, whereas only a much more diffused effect is observed for the conventional three-electrode configuration. However, it is worth noting that the hump is much more significant in the anodic branch. The presence of potential gradients in the larger electrode may be the reason for the absence of detail found in the voltammograms.

It is clearly visible that the values of the positive and the negative currents are different in both configurations, as an indication of a contribution of faradaic currents, more pronounced when increasing the potential range into more negative values. Voltammograms also show a slight increase in the cathodic current as the potential window moves towards the cut off value, indicative of reversible hydrogen adsorption [5]. Additionally, a fast current leap in the anodic current is observed at around -0.9 V, which is assigned to solution decomposition (e.g., H_2 evolution). As could be expected, this effect is more significant the microelectrode device.

a)



b)

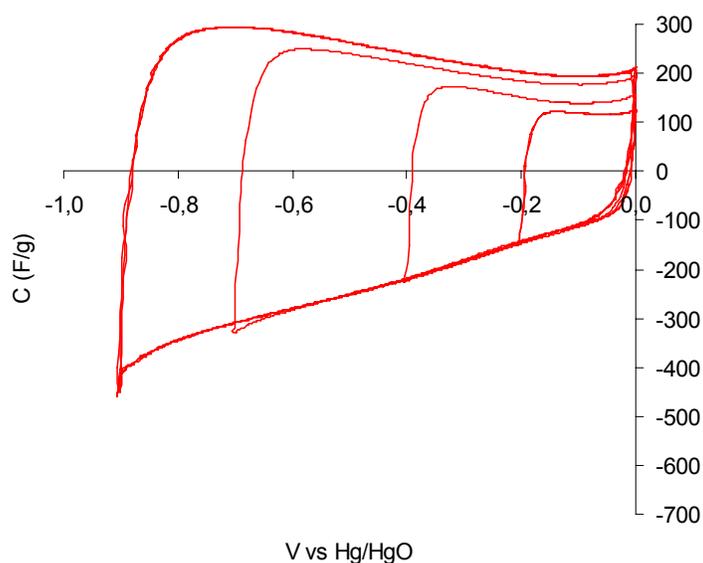


Figure 3.- Cyclic voltammograms when increasing the negative potential window for the a) the microelectrode configuration and b) the macroscopic electrode configuration

The galvanostatic charge-discharge cycles also show significant differences between both devices (Figure 4). While the discharge branch is linear, and quite similar in slope for both cases, the charge branch for the single-particle device shows two distinct parts, with a sharp change in slope. In the cycle corresponding to the macroscopic device, only a slight curvature of the charge branch is observed. This non-capacitive behaviour comes from the participation of faradaic currents simultaneously to the double layer charging current [6]. These faradaic currents are usually attributed to both reversible (such as reversible redox reactions of surface functional groups of the activated carbon or hydrogen adsorption) and irreversible processes (such as hydrogen evolution or irreversible reduction of functional groups in the carbon surface). The fact that the discharge branch is linear seems to indicate that there are irreversible processes involved in the charge. This is also in agreement with the asymmetry of the humps observed in the voltammograms at potential around -0.5 V (see Figure 3a). It is therefore likely that both reversible and irreversible phenomena are occurring simultaneously at these potentials.

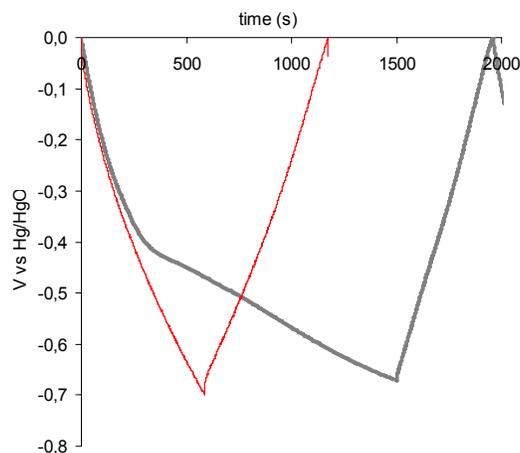


Figure 4.- Galvanostatic charge-discharge cycles for both configurations in the potential window from 0 to -0.7 V.

The study of the behaviour of the activated carbon at positive potentials is limited by the thermodynamic stability of the KOH used as electrolyte (+0.3 V vs Hg/HgO). Figure 5 shows the curves obtained when cycling the material, in both configurations, up to the limit of solution decomposition. There is a great asymmetry, resultant from the worse behaviour of the carbon material in the positive region, comparing to the negative [7], together with the oxygen evolution. The electrochemical processes taking place at positive polarization in carbon materials have been deeply studied in literature [8,9]. When moderate oxidation takes place, the morphology of the carbon material do not change, but some oxygen functional groups can be created at the surface of the material (i.e., hydroxyl groups) leading to an improvement in wettability [10]. However a strong oxidation can cause the degradation of the carbon material, with evolution of CO and CO₂.

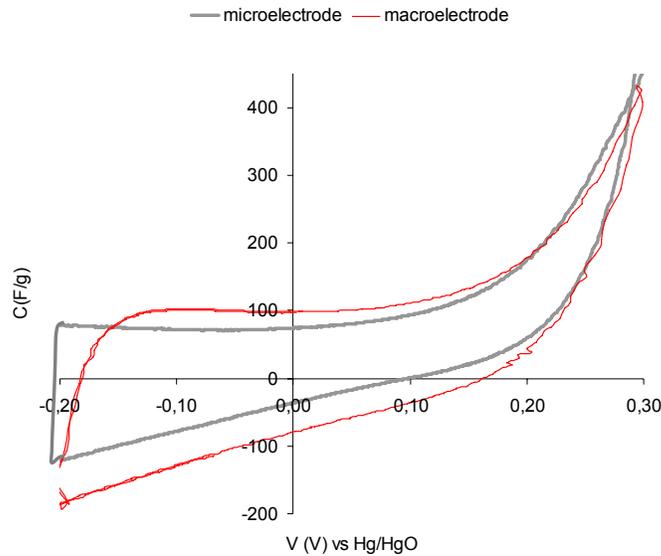
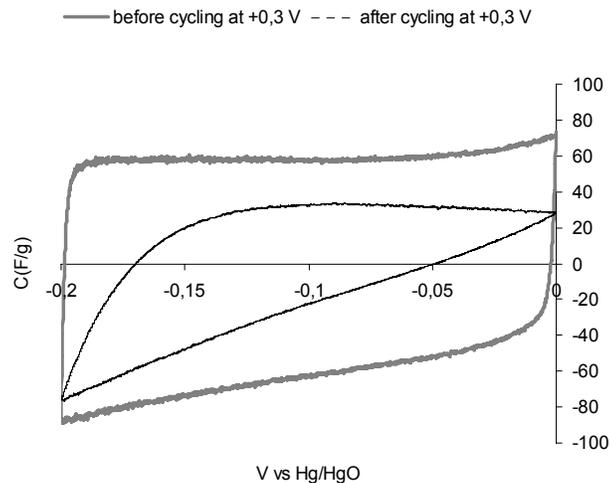


Figure 5.- Cyclic voltammograms obtained in both configurations in the potential window from -0.2 to 0.30 V.

In order to study the effect that positive polarization could cause on the carbon material, cycling into the capacitive region was performed after subjecting the electrode to +0.3V. The curves obtained are shown in Figure 6. In the case of the microelectrode (Figure 6a), irreversible damages are caused in the activated carbon, as the cycling ability is completely lost after submitting the particle to +0.3 V due to an irreversible oxidation of the carbon. A similar effect is observed in the macroscopic electrode (Figure 6b), although in this case the degradation of the carbon begins to be evident after submitting the electrode to +0.4 V. This fact indicates the higher sensitivity of the microelectrode technique comparing to the macroscopic device.

a)



b)

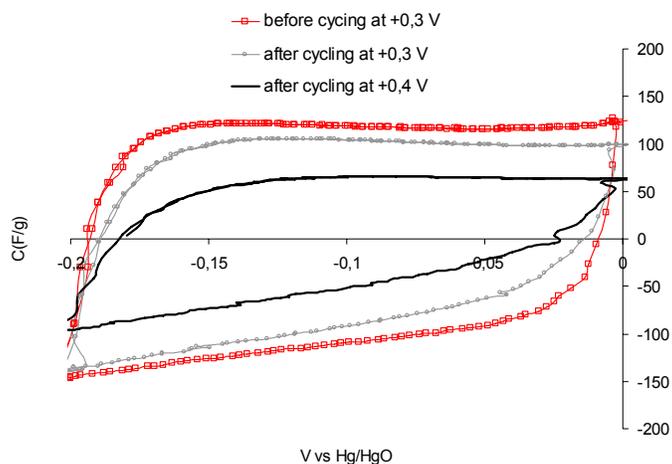


Figure 6.- Cyclic voltammograms performed in a) microelectrode configuration and b) in the macroscopic configuration, after cycling up to +0.3V.

Conclusions

The characterization of an activated carbon by using two different techniques, micro and macro-electrode setup has lead to a better knowledge of the electrochemical performance of the material. The higher sensitivity of the microelectrode device has shown the presence of a pseudocapacitance phenomena in the basic media, that can be hardly observed in the disc electrodes. The oxidation of the carbon surface destroys the capacitative behaviour of the material as the pores are blocked hindering the access of the electrolyte into the pore network.

Acknowledgements

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