INFLUENCE OF MESOPHASE ACTIVATION CONDITIONS ON ITS SPECIFIC CAPACITANCE

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Introduction

In the last years, supercapacitors have been presented as an important alternative or complement to other energy storage devices such as secondary batteries and fuel cells [1]. Carbon materials have been shown as the most attractive electrode materials for these supercapacitors, due to their relatively low cost, high surface area and easy availability [2]. Although hard carbons are usually preferred to produce high surface materials, the use of soft carbons could bring some advantages for this application, such as a lower electrical resistivity and a higher density. Despite the research in this field has significantly increased during the last years, there is still a strong need for understanding the role played by the porosity and the interactions between the carbon and the liquid electrolyte.

In this paper, mesophase pitch AR24 was chemically activated under different conditions to produce porous carbons to be studied as electrodes in supercapacitors. The influence that the activation conditions have on the type of porosity developed in the mesophase and the relationships between this porosity and the specific capacitance of the materials are investigated.

Experimental

Naphthalene-derived mesophase pitch AR24 was chemically activated with KOH at different conditions. A series of mesophase-derived activated carbons was obtained using a fixed KOH/carbon ratio (3:1) and activation temperatures of 600, 700 and 800°C for 1 h. A second series was obtained at 700 °C for 1 h but using different proportions of KOH and carbon (1:1 and 5:1). After activation, the resulting material was neutralized with 1M HCl and then washed with distilled water until pH=7. Finally, the carbon was dried at 110°C in a vacuum oven for 24 h. The resultant activated carbons were labeled AR.3.6.1, AR.3.7.1, AR.3.8.1, AR.1.7.1 and AR.5.7.1, respectively, where the first number indicates the ratio of KOH used, the second one corresponds to the activation temperature (6 for 600, etc.) and the third one indicates the soaking time.

The activated carbons were characterized by elemental analysis (with direct determination of oxygen), N_2 and CO_2 adsorption isotherms and immersion calorimetry using molecular probes of different dimensions to evaluate the characteristics of the

microporosity of the samples [3]. Additionally, immersion calorimetry in water was used as an indication about the hydrophilic/hydrophobic character of the carbon surface.

Electrochemical tests were performed on carbon electrodes prepared as pellets by mixing 90 wt. % of the activated carbon with 10 wt. % of PVDF as binder. Two electrodes were separated by a disc of glassy paper. Capacitance measurements were made in a Swagelok type cell made of Teflon using an aqueous solution of sulphuric acid (2M) as electrolyte. The current collectors were made from Hastelloy. Galvanostatic charge-discharge characteristics were measured in the range of 0-1 V at various current intensities (1-100 mA).

Results and Discussion

The activated carbons obtained at different temperatures showed a progressive decrease of the oxygen content with increasing the activation temperature. However, no clear trend in the oxygen content was observed for the samples obtained using different amounts of activating agent.

Table 1. Elemental analysis of the activated carbons.

Sample	O	$-\Delta_iH_{CH2Cl2}$	$-\Delta_iH_{C6H6}$	$-\Delta_iH_{CCl4}$	$-\Delta_iH_{TIPOT}$	$-\Delta_iH_{TBOT}$	$-\Delta_iH_{H2O}$
AR.3.6.1	13.93	237	232	198	171	31	100
AR.3.7.1	10.22	252	237	255	285	21	83
AR.3.8.1	3.74	261	261	251	260	31	69
AR.1.7.1	8.21	164	150	90	118	15	50
AR.5.7.1	4.87	241	255	239	267	85	79

O, oxygen content (wt. %)
$-\Delta_iH$, immersion enthalpy (J/g)
TIPOT, tetraisopropyl-o-titanate
TBOT, tetrabutyl-o-titanate

The BET surface areas of the samples activated at different temperatures were similar for samples AR.3.7.1 and AR.3.8.1 (around 2300 m^2/g), while the sample obtained at 600°C had higher surface area (around 3500 m^2/g). The enthalpy of immersion of the activated carbons into liquids of different critical dimensions (Table 1) provided further information on the size of the porosity present in these samples. The increase in the size of the molecular probe causes the immersion enthalpy to significantly decrease for sample AR.3.6.1, which indicates that the porosity in this sample mainly consists of small micropores (< 0.5 nm). On the other hand, AR.3.7.1 and AR.3.8.1 have pores of larger size (up to 1.0 nm), as indicated by the high immersion enthalpy of this samples in TIPOT.

In the series of samples obtained with different ratios of activating agent, the BET surface area is much lower for sample AR.1.7.1 (1000 m^2/g) than for samples AR.3.7.1 and AR.5.7.1 (around 2300 m^2/g). The total porosity in AR.1.7.1 is lower and is mainly formed of small micropores (< 0.5 nm). The other two samples have higher porosity,

composed of larger pores, specially AR.5.7.1 which contains a significant amount of pores larger than (1.3 nm). This results are in good agreement with the results obtained from the adsorption isotherms.

The electrochemical tests of the activated carbons studied showed very high values of specific capacitance (between 400 and 200 F/g for low current intensities). The results obtained by immersion calorimetry correlate with the electrochemical behavior much better than those obtained from BET, as there is no direct correlation between the surface area and the specific capacitance. The sample with the lowest surface area (AR.1.7.1) also has the lowest values of specific capacitance. However, sample AR.5.7.1 has similar values of BET surface area to samples AR.3.7.1 and AR.3.8.1, while its capacitance is much higher. This is probably due to the larger micropores present in this sample. Moreover, sample AR.3.6.1, with the highest surface area, shows intermediate values of specific capacitance, probably due to the small size of the micropores in this sample, which are inaccessible to the electrolyte. It is worth mentioning that this sample has an extremely high electric specific resistance (ESR), which made it not possible to measure the capacitance at intensities higher than 10 mA. This behavior could be related with the high content in oxygenated functional groups of this sample, as suggested by the elemental analysis results and the immersion enthalpy in water, which is significantly higher for this sample than for the others.
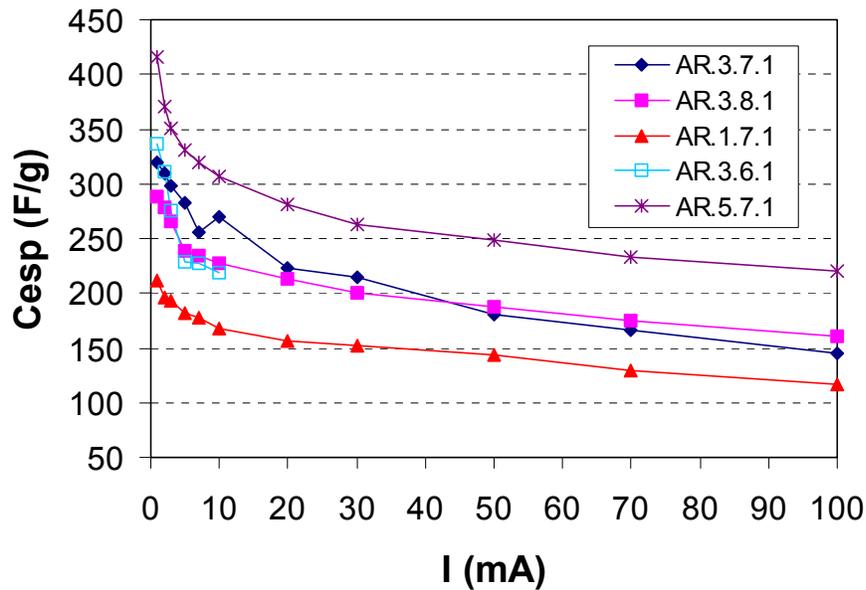

Figure 1. Specific capacitance of the activated carbons

Conclusions

The activated carbons obtained for this study showed extremely high values of specific capacitance (even higher than 400 F/g). Immersion calorimetry seems to be a very suitable technique for the characterization of the pore size distribution, as good correlation between the results obtained using it and the electrochemical behavior was observed. The use of different ratios of KOH as activating agent seems to have a greater effect on the capacitance of the samples than the activating temperatures.

References

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