INFLUENCE OF PYROLYSIS CONDITIONS OF A MEDIUM TEMPERATURE PITCH ON ITS ELECTROCHEMICAL PERFORMANCE IN SUPERCAPACITORS

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Introduction

The development of energy storage devices is a very active field of research due to the needs associated to new applications such as portable electronics, where miniaturization and light weight challenge the existing technology. Moreover, the progress in high energy and power devices is demanded by the society to implant the electric vehicle and to reduce environmental impact of fossil fuels. In the last years, supercapacitors have been presented as an important alternative or complement to other energy storage devices such as secondary batteries [1]. Carbon materials have been shown as the most attractive active electrode materials for supercapacitors, due to their relatively low cost, high surface area and easy availability [2].

In this paper, a medium temperature pitch was pyrolised at different conditions. The products obtained were chemically activated with KOH to develop carbons of high surface area, suitable for their use in supercapacitors. The influence of the pyrolysis conditions on the electrochemical behaviour of the resultant carbons is studied.

Experimental

SASOL medium temperature pitch was pyrolised at 450°C for residence times varying from 0 to 6 h. Pyrolysis was performed on 6 g of sample, following the procedure described elsewhere [3]. Two series of samples were obtained, one at atmospheric pressure (S-0, S-2, S-4 and S-6), the other one at 1 MPa (SP-0, SP-2, SP-4 and SP6). Two additional samples were prepared by further heat treating sample S-6 to 600 and 1000°C (S-6(600) and S-6(1000), respectively). The samples were characterized by elemental analysis, solubility tests, optical microscopy and X-ray diffraction. Chemical activation was performed using KOH (3:1 to carbon) at 700°C for 1 h. 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 labelled S-0a, SP-0a, etc. These activated carbons were characterized by elemental analysis (with direct determination of oxygen) and immersion calorimetry using molecular probes of different dimensions to evaluate the characteristics of the microporosity of the samples [4].

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 yields of the pyrolysis treatments carried out at 1 MPa were around 25 wt. % higher than those obtained under atmospheric pressure (Table 1). As could be expected, the samples obtained at 1 MPa are more soluble in toluene, especially those treated for 0 and 2 h. For longer treatments, the resultant samples were almost completely insoluble. The oxygen content significantly decreased in the pyrolysis products as compared to the parent pitch (around 2 wt. % and 4.66 wt. %, respectively). Only after treatment at 1000°C the oxygen content decreased to 0.54 wt. %. The pyrolised samples were almost fully anisotropic, except for the samples treated for 0 h (S-0 and SP-0) and 2 h at 1 MPa (SP-2). The anisotropic features were a mixture of mosaics (around 20 vol. %) and domains (around 80 vol. %).

Table 1.- Main characteristics of the pyrolised samples

Sample	PY	AC	TI	O
SASOL	-	0	4.0	4.66
S-0	40.0	60.9	73.0	2.83
S-2	34.5	100	99.0	2.11
S-4	34.0	100	100.0	2.47
S-6	33.0	100	100.0	2.00
SP-0	64.0	37.2	59.2	2.23
SP-2	62.0	83.9	80.0	2.00
SP-4	57.0	97.3	98.1	1.89
SP-6	57.0	100	99.7	1.72
S-6(600)		100	100	2.66
S-6(1000)		100	100	0.54

PY, pyrolysis yield (wt. %) TI, toluene insoluble content (wt. %)
O, oxygen content (wt. %) AC, anisotropic content (vol. %)

The immersion calorimetry results are shown in Table 2. The immersion enthalpies in Cl_2H_2 and tri-2.4-xylylphosphate (TXP) are a good indication of the presence of small (around 0.33 nm) and large (around 1.5 nm) micropores, respectively, in the activated carbons. The relatively high values of immersion enthalpy in Cl_2H_2 shown by most of the

samples pyrolised at 450°C (above 200 J/g) indicate a considerable development of small microporosity. Attending to the large microporosity, the samples obtained under atmospheric pressure have a larger amount of large microporosity, as indicated by their higher values of immersion enthalpy in TXP. The sample activated after heat treatment to 1000°C (S-6(1000)a) has extremely low immersion enthalpies both in Cl_2H_2 and TXP, indicating that the activation treatment of this sample has not been very efficient. The sample heat treated to 600°C before activation (S-6(600)a) showed better results in comparison to the previous one, but the porosity developed seems to be lower than for the sample activated without any further heat treatment (S-6)a, specially the smaller microporosity.

Table 2.-Main characteristics of activated samples.

Sample	AY (wt. %)	$-\Delta_i H_{Cl2H2}$ (J/g)	$-\Delta_i H_{TXP}$ (J/g)
S-0a	65.6	-	83
S-4a	75.4	214	79
S-6a	75.9	248	92
SP-0a	68.6	172	11
SP-2a	67.6	232	44
SP-6a	72.8	232	39
S-6(600)a	83.5	193	66
S-6(1000)a	81.0	7	2

AY, activation yield
$-\Delta_i H_{Cl2H2}$, immersion enthalpy in Cl_2H_2
$-\Delta_i H_{TXP}$, immersion enthalpy in tri-2.4-xylylphosphate

All the samples pyrolised at 450°C had very high specific capacitances when tested as electrodes in supercapacitors (Figures 1 and 2). In general, the activated samples from the series pyrolised under atmospheric pressure showed higher specific capacitances both at low and high current intensities, reaching a plateau for intensities higher than about 40 mA. The significant decrease of the specific capacitance for high current intensities observed for samples SP-0a and SP-6a seems to be related to their lower content in small micropores, as discussed before. The electrochemical behaviour of the samples heat treated to higher temperatures is shown in Figure 3. Sample S-6(600)a showed a similar trend to S-6a for the different current intensities but with lower specific capacitances (especially at low intensities), which is in agreement with the porosity information obtained from immersion calorimetry. Meanwhile, the sample heat treated to 1000°C showed extremely low capacitance values (< 25 F/g), as a result of the low microporosity developed in the sample during activation.

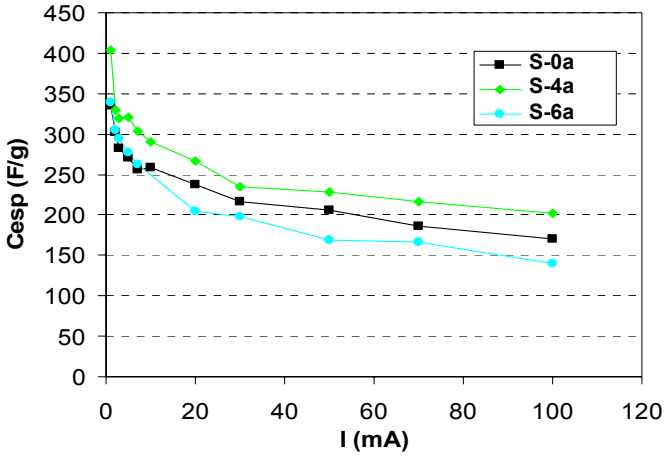

Figure 1.- Specific capacitance of samples pyrolised under atmospheric pressure.

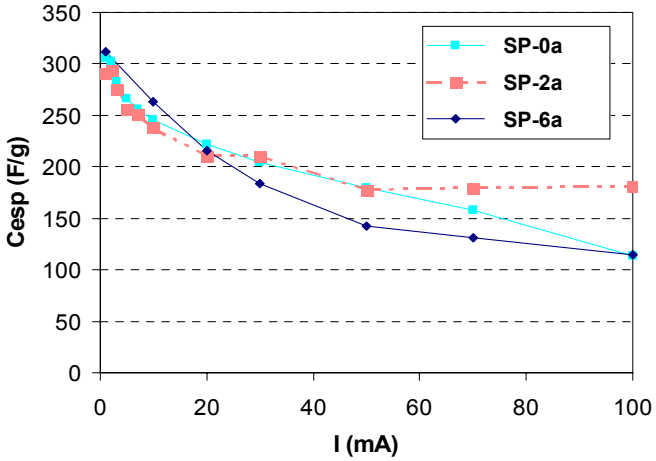

Figure 2.- Specific capacitance of samples pyrolised at 1 MPa.

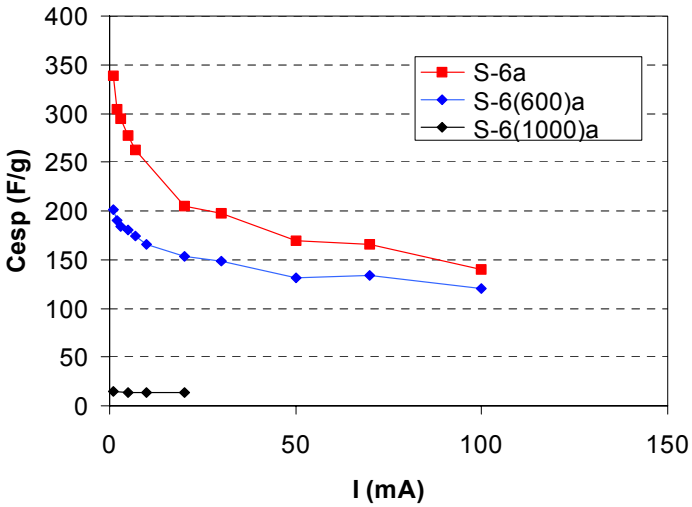

Figure 3.- Specific capacitance of samples treated to different temperatures before activation.

Conclusions

Activated carbons obtained from samples pyrolised at 450°C showed very high specific capacitances when tested as electrodes in supercapacitors, due to the high amount of microporosity developed in the samples during activation. Samples pyrolised under atmospheric pressure developed a larger amount of large micropores, this resulting in higher capacitance values at high current intensities than the samples pyrolised at 1 MPa. Heat treatment of samples to 600 and 1000°C before activation resulted in a very poor development of porosity during activation and, therefore, those samples showed lower specific capacitance, especially for the heat treatment to 1000°C.

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