Influence of mesophase activation conditions on the specific capacitance of the resulting carbons

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Abstract

Mesophase pitch AR24 was directly activated with KOH using different proportions of the activating agent and activation temperatures, to study the effect on the textural characteristics of the resultant activated carbons and how these characteristics influence their behaviour as electrodes in supercapacitors. The textural properties of the activated carbons were studied by gas adsorption and immersion calorimetry. The results indicate that all the carbons produced were mainly microporous, with pore size around 1 nm. The behaviour of these carbons as electrodes in supercapacitors was studied from galvanostatic charge–discharge cycles. The specific capacitance values obtained were very high, reaching 400 and 200 $F\,g^{-1}$ at low and high current densities respectively, for the sample activated with (5:1) KOH to mesophase ratio. Nevertheless, the reasons for this high capacitance values cannot be explained only on the basis of the textural characteristics of the activated carbons, as the results indicated that other factors might be also playing a significant role in their electrochemical behaviour.
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1. Introduction

Supercapacitors have been presented in the last years as an important alternative or complement to other energy storage or generation devices such as secondary batteries and fuel cells [1]. Carbon materials have been shown as the most attractive electrode materials for these supercapacitors, as a consequence of their relatively low cost, high surface area and availability [2]. Although non-graphitizable carbons are usually preferred to produce high surface area materials, the use of graphitizable carbons could bring some advantages for this application, such as a lower electrical resistivity and a higher density.

Despite intensive research in this field has significantly increased along the last years, there is still a strong need for understanding the role played by the porosity and the interactions between the porous carbon and the liquid electrolyte. The situation is complex because of the large variety of carbon precursors. The classical activated carbons are based on lignocellulosic or coal-derived materials [3], which are characterised by a low crystalline order, while other high surface carbon materials can be derived from such diverse materials as nanotubes [4] or graphitic carbon fibres [5], which present a much higher crystalline order. In addition to the different nature of the precursors, the activation procedures used to develop surface area in each case may be different (i.e. physical or chemical activation) [3–7], which can still generate further differences in the characteristics of the surface. Therefore, the textural study of the carbons (including the surface area and pore volume or pore size distribution) might be necessary but not sufficient to fully understand the behaviour of the carbon electrodes in the supercapacitors. Detailed analysis of the carbon chemistry is needed to achieve a better

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understanding of the interaction of the carbon and the electrolyte during the double layer formation.

In this paper, mesophase pitch AR24 was chemically activated with KOH under different conditions to produce porous carbons that were then used 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.

2. Experimental

2.1. Preparation of activated carbons

Naphthalene-derived mesophase pitch produced by Mitsubishi Gas Chemicals, AR24, was chemically activated with KOH under different conditions. As-received mesophase pitch was mixed with the activating agent (1:1 to 5:1 KOH to carbon mass ratio) by grinding in a mortar and then carbonised at temperatures between 600 and 800 °C for 1 h, under a nitrogen flow of 62 mL min^{-1}. The heating rate used was 2.5 °C min^{-1}. After completing the treatment the sample was allowed to cool freely to room temperature. The resultant material was neutralized with 1 M 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. A series of mesophase-derived activated carbons was obtained using a fixed KOH to 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, 3:1 and 5:1). The resultant activated carbons were labelled AR.3.6, AR.3.7, AR.3.8, AR.1.7 and AR.5.7, respectively, where the first number indicates the ratio of KOH used and the second one refers to the activation temperature (six for 600 °C, etc.). Table 1 summarises the activation conditions used to activate the mesophase pitch.

2.2. Characterisation of activated carbons

The resultant activated carbons were characterized by elemental analysis, with direct determination of oxygen, using a LECO-TF-900 furnace coupled to a LECO-CHNS-932 microanalyser.

Physical adsorption of gases (N$_2$ at 77 K and CO$_2$ at 273 K) was carried out in order to characterise the porous structure of the activated carbons. Apparent surface areas were determined by BET equation from the N$_2$ adsorption isotherm. The total micropore volume was calculated from the application of the Dubinin–Radushkevich (DR) equation to the N$_2$ adsorption at 77 K. The volume of narrow micropores (pore size smaller than 0.7 nm) was assessed from CO$_2$ adsorption at 273 K [8]. The total pore volume was obtained from the N$_2$ adsorption at $P/P_0 = 0.99$. The volume of mesopores was calculated by substracting the total micropore volume from the total pore volume.

The microporosity of the activated carbons was further characterised by measuring the enthalpy of immersion of the samples into liquids of different critical dimensions [9]. Measurements were carried out at 20 °C using dichloromethane (CH$_2$Cl$_2$, $L = 0.33$ nm), benzene (C$_6$H$_6$, $L = 0.41$ nm), carbon tetrachoride (CCl$_4$, $L = 0.63$ nm), tetraisopropyl-o-titanate (TIPOT, $L = 1.05$ nm) and tetrabutyl-o-titanate (TBOT, $L = 1.3$ nm). Additionally, immersion calorimetry into water was used as an indication of the hydrophilic/hydrophobic character of the carbon surface [10].

2.3. Electrochemical characterisation of activated carbons

The electrochemical performance of the activated carbons in supercapacitors was studied from galvanostatic charge–discharge cycles of a two electrode Swagelok type cell using an aqueous solution of sulphuric acid (2 M) as electrolyte. Coin type carbon electrodes (13 mm in diameter and about 500 μm in thickness) were prepared by mixing 90 wt.% of the activated carbon with 10 wt.% of PVDF as binder. The capacitor was constructed using two of these electrodes, separated by a disc of glassy paper. The specific capacitance was calculated from the linear region (~0.2–0.6 V) of the discharge branch, taking into account the mass of activated carbon used in the lightest electrode. Galvanostatic charge–discharge characteristics were measured in the range of 0–1 V at various current intensities (1–100 mA).

3. Results and discussion

3.1. Characteristics of activated carbons

The weight loss values obtained for the chemical activation of the mesophase pitch under the conditions studied are summarised in Table 1. The increase in the activation temperature caused the weight loss to increase slightly, from 22

Table 1
Activation conditions and characteristics of activated carbons

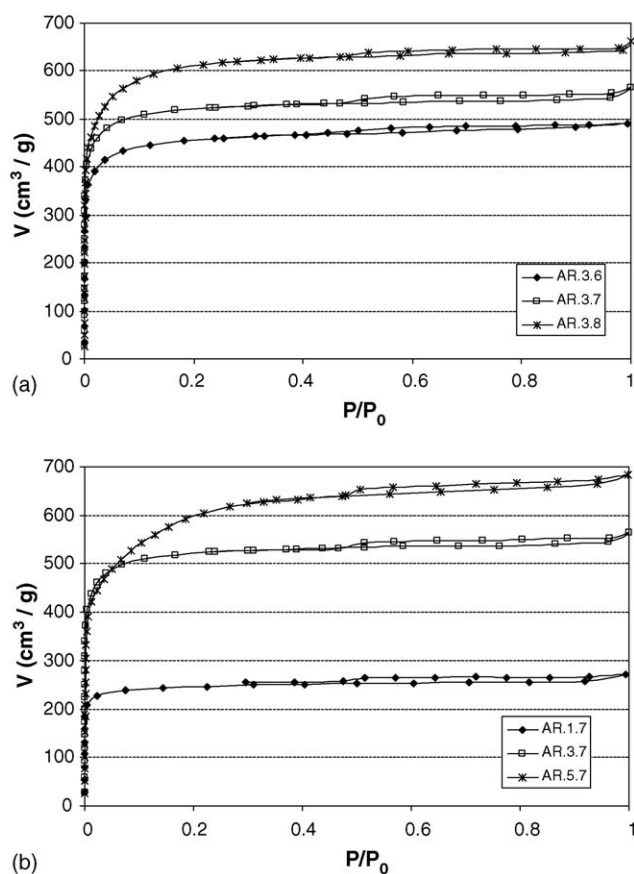| Sample	Temperature (°C)	KOH:mesofase ratio	Residence time (h)	Weight loss (wt.%)	O (wt.%)
AR.3.6	600	3:1	1	22	13.94
AR.3.7	700	3:1	1	24	10.31
AR.3.8	800	3:1	1	28	3.73
AR.1.7	700	1:1	1	16	8.28
AR.5.7	700	5:1	1	45	4.88

Fig. 1. N_2 adsorption isotherms of activated carbons obtained: (a) at different temperatures; (b) with different KOH to mesophase ratio.

to 28% for samples AR.3.6 and AR.3.8, respectively. The increase in the KOH to mesophase ratio also increased the weight loss of the samples, but in this case the changes are more significant (16 wt.% for AR.1.7 and 45 wt.% for AR.5.7). Activation also caused a significant amount of oxygen to be incorporated into the samples (Table 1), especially in the case of samples AR.3.6 (13.96 wt.%) and AR.3.7 (10.31 wt.%). Despite the low activation degree of sample AR.1.7, the oxygen content of this sample is significantly high (8.28 wt.%). As could be expected, the oxygen content decreases significantly when activation is carried out at 800 °C, as a result of the release of oxygenated compounds such as CO and CO_2.

Fig. 1 shows the nitrogen adsorption isotherms corresponding to the samples activated at different temperatures (Fig. 1a) and to those obtained using different amounts of KOH (Fig. 1b). All samples show type I isotherm profiles, characteristic of microporous carbons. The increase in the activation temperature and the amount of activating agent used enhance the uptake of nitrogen at 77 K. This is reflected in the total pore volume developed in the samples (Table 2), which increased from 0.76 to 0.99 $cm^3 \, g^{-1}$ in the activation temperature series and more significantly in the series obtained with different amounts of KOH, increasing from 0.42 to 1.05 $cm^3 \, g^{-1}$ for samples AR.1.7 and AR.5.7, respectively. The shape of the isotherms does not change significantly in the temperature series, the knee being only slightly wider for sample AR.3.8 (Fig. 1a). On the contrary, the increase in the amount of KOH caused the knee of the isotherm to widen to a great extent (Fig. 1b), this indicating that the micropore size distribution is widening from AR1.7 to AR5.7. These results are in agreement with those obtained by Kim et al. [5], when studying the activation of carbon fibres with different amounts of KOH.

The total micropore volume (up to 2 nm) increases with increasing activation temperature (0.70–0.88 for AR.3.6 and AR.3.8, respectively). On the other hand, the behaviour is different when the amount of KOH is increased. Increasing the KOH to mesophase ratio from 1:1 to 3:1 caused the micropore volume to increase significantly (from 0.39 to 0.83 $cm^3 \, g^{-1}$). However, when the ratio of KOH is 5:1, the micropore volume decreased despite the total pore volume in this sample increased. This indicates that not only micropores but also larger pores have been developed in this sample, in agreement with the shape of the isotherm discussed before. In fact, the contribution of mesopores in this sample is 0.25 $cm^3 \, g^{-1}$ (Table 2). A small contribution of mesopores is also present in sample AR.3.8 (0.11 $cm^3 \, g^{-1}$), but it is negligible for the other three samples. The CO_2 adsorption isotherms confirmed the results obtained by the N_2 adsorption, indicating that there are no diffusion problems in the samples [11]. The micropore volumes calculated from the CO_2 adsorption isotherms are very similar to the values obtained from the N_2 adsorption isotherms, the differences between these values being almost negligible (Table 2). AR.1.7 is the only sample where the values obtained from the CO_2 isotherm are higher than those obtained from the N_2 one, indicating the existence of narrow microporosity for which

Table 2
Textural characteristics of activated carbons

Sample	BET ($m^2 \, g^{-1}$)	V_T ($cm^3 \, g^{-1}$)	V_{N_2} ($cm^3 \, g^{-1}$)	V_{CO_2} ($cm^3 \, g^{-1}$)	$V_{N_2} - V_{CO_2}$ ($cm^3 \, g^{-1}$)	V_{meso} ($cm^3 \, g^{-1}$)
AR.3.6	1776	0.76	0.70	0.68	0.02	0.06
AR.3.7	2044	0.84	0.83	0.80	0.03	0.01
AR.3.8	2307	0.99	0.88	0.84	0.04	0.11
AR.1.7	963	0.42	0.39	0.43	−0.04	0.03
AR.5.7	2173	1.05	0.80	0.71	0.09	0.25

BET, BET surface area; V_T, total pore volume; V_{N_2}, micropore volume determined from the N_2 isotherms; V_{CO_2}, micropore volume determined from the CO_2 isotherms; V_{meso}, mesopore volume.

Table 3
Immersion enthalpies into different liquids

Sample	$-\Delta_i H_{CH_2Cl_2}$	$-\Delta_i H_{C_6H_6}$	$-\Delta_i H_{CCl_4}$	$-\Delta_i H_{TIPOT}$	$-\Delta_i H_{TBOT}$	$-\Delta_i H_{H_2O}$	n_{Hyd}
AR.3.6	237	232	198	171	31	100	5.1
AR.3.7	252	237	255	285	21	83	3.3
AR.3.8	261	261	251	260	31	69	1.4
AR.1.7	164	150	90	118	15	50	1.8
AR.5.7	241	255	239	267	85	79	2.5

$-\Delta_i H$, immersion enthalpy ($J\,g^{-1}$); n_{Hyd}, number of hydrophilic sites ($meq\,g^{-1}$).

the access of N_2 at 77 K is kinetically restricted. On the other hand, AR.5.7 is the only sample with a significant positive value ($V_{N_2} - V_{CO_2} = 0.09\,cm^3\,g^{-1}$) confirming the widening of the pores with the highest KOH to carbon ratio studied.

The apparent BET surface areas of the activated carbons (Table 2) increased with increasing activation temperature (from 1776 to 2307 $m^2\,g^{-1}$) and also with increasing amount of KOH used (from 963 to 2173 $m^2\,g^{-1}$). However, it is worth noting that although AR.5.7 is the sample with the larger volume of pores, the highest surface area corresponds to sample AR.3.8, due to the widening of the micropores observed in AR.5.7, as discussed before.

Immersion calorimetry into liquids of different size provides further information on the microporosity present in the samples [9]. The immersion enthalpies obtained for the activated carbons studied are summarised in Table 3. In general, the immersion enthalpies obtained are very high, even higher than for activated carbons of similar micropore volumes [12], as expected in view of the high volume of narrow micropores. The data shown in Table 3 reveal that most carbons have micropore sizes around 1.0 nm, as high immersion enthalpies were still obtained for TIPOT (nominal molecular diameter 1.03 nm), while a dramatic decrease is observed for the largest molecular probe used (TBOT diameter is 1.3 nm). A more detailed observation of the data shows significant differences between the samples. AR.1.7 shows the lowest heats of immersion in all the different liquids due to its lowest activation degree, as demonstrated above with the data derived from the isotherms. The presence of pores larger than 0.7 nm is limited in this sample, as a significant decreased of the heat of immersion is already noticeable for the CCl_4 (0.63 nm). This is in good agreement with the data obtained from the adsorption isotherms, where this sample presented a volume of CO_2 slightly higher than the volume of N_2. The sample less activated in the temperature series, AR.3.6, also shows a clear decrease in the heats of immersion as the size of the molecular probes increase, which indicates the presence of pores of smaller size. This was not clearly observed from the adsorption data. Finally, AR.5.7 has the highest value of immersion enthalpy in TBOT, confirming the widening of the pores as the KOH/carbon ratio is increased.

The enthalpies of immersion into water were used to estimate the number of hydrophilic groups [10] present in the activated carbons (Table 3). As could be expected, sample AR.3.6, which has the highest oxygen content, also has the highest content of hydrophilic groups, while the sample heat

treated to 800 °C is the less hydrophilic, in agreement with its lowest oxygen content. However, it is worth noting that sample AR.1.7 has a relatively low content in hydrophilic groups, despite the high oxygen content (8.28 wt.%). This suggests that the type of oxygen functionalities present in this activated carbon could be different to those present in the rest of the samples studied, with a higher degree of activation.

3.2. Electrochemical performance of activated carbons

The capacitance of the activated carbons prepared was studied from the galvanostatic charge–discharge cycles of a two-electrode cell at different current densities. An example of the charge–discharge profiles obtained for the different samples at 5 mA is shown in Fig. 2. All samples except AR.3.6 show triangular chronopotentiograms, indicating a typical behaviour of capacitive electrodes. In general, the initial voltage rise/drop observed in the charge/discharge profiles, which correspond to the ESR, is relatively small except for sample AR.3.6. Additionally, the voltage drop corresponding to this sample is followed by a non-linear decrease of the voltage with time. This made it difficult to calculate the capacitance values for sample AR.3.6, and the values plotted in Fig. 3 are only indicative. As the ESR increases with increasing current density, it was not possible to calculate capacitance values at current densities higher than 7.4 $mA\,cm^{-2}$ for this sample. The behaviour observed could be related to the extremely high oxygen content of this sample (nearly 14 wt.%) or to the lower temperature at which this activated carbon was obtained, which could have made the resistivity to be higher. Another reason that could explain this anomalous behaviour of AR.3.6, which is usually described in the literature, could be the difficulties of the electrolyte diffusion in the narrow microporosity. In this case this argument has to be refuted as it has been demonstrated the AR.1.7 has pores of smaller size while its electrochemical behaviour does present neither a significant ESR nor a deviation from linearity.

The variation of the specific capacitance of the activated carbons with current density is shown in Fig. 3. It is worth noting the high values of specific capacitance obtained for the different samples, reaching 400 $F\,g^{-1}$ at low current densities in the case of sample AR.5.7. The behaviour of samples AR.3.7 and AR.3.8 is very similar both at low and high current densities. The specific capacitance in these samples varies from around 320 $F\,g^{-1}$ (at 0.75 $mA\,cm^{-2}$) to around
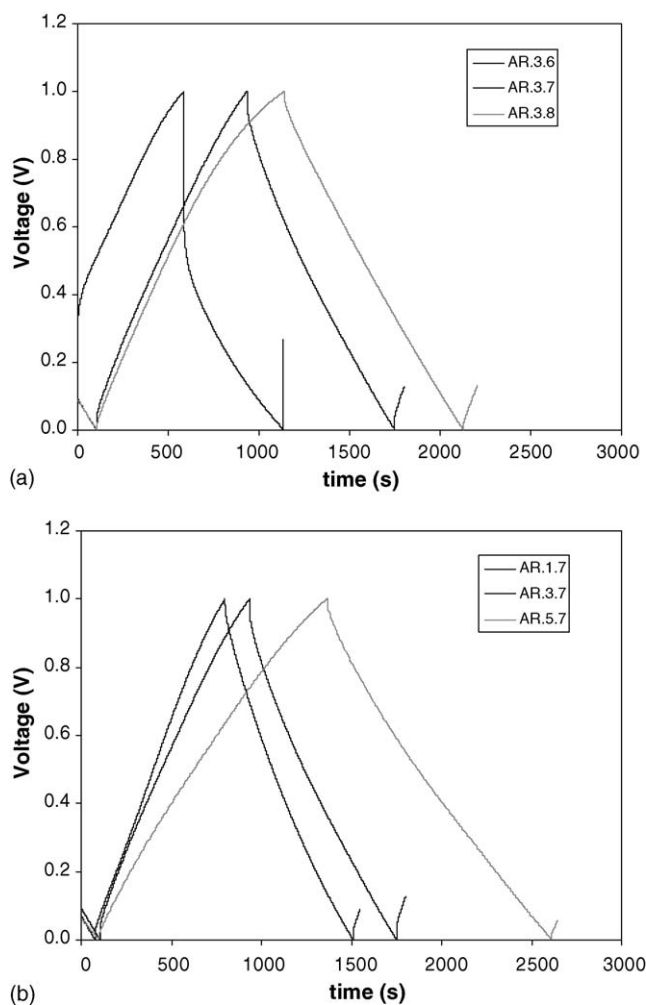
Fig. 2. Charge–discharge profiles at 5 mA of supercapacitors prepared with activated carbons obtained: (a) at different temperatures; (b) with different KOH to mesophase ratio. Electrode mass: 50 mg.
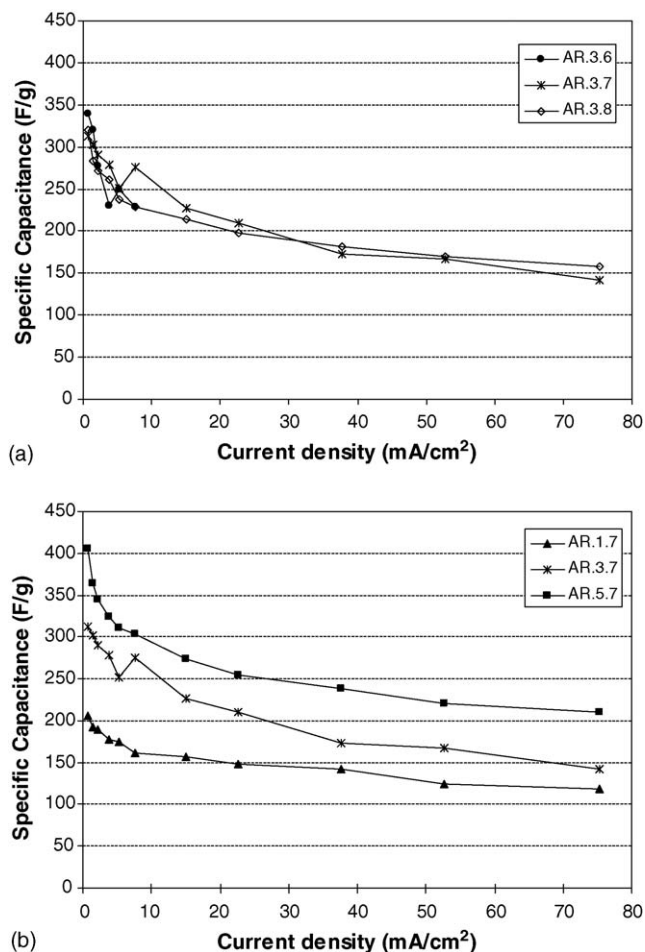

Fig. 3. Variation of the specific capacitance with the current density of activated carbons obtained: (a) at different temperatures; (b) with different KOH to mesophase ratio. Electrode mass: 50 mg.

$150\,\mathrm{F\,g^{-1}}$ (at $75\,\mathrm{mA\,cm^{-2}}$). The sample activated with the lowest amount of KOH (AR.1.7) has the lowest specific capacitance ($200\,\mathrm{F\,g^{-1}}$ at low current densities), which is due to the significantly lower surface area developed in this sample. The higher values of capacitance obtained for sample AR.5.7 (406 and $210\,\mathrm{F\,g^{-1}}$ for low and high current densities, respectively) could be related both to the high surface area developed and also to the larger pores of this sample (it contains larger micropores and a higher proportion of mesopores than the rest of the samples).

Although the explanations based on the textural characteristics of the samples might be satisfactory in the series of samples obtained varying the KOH to carbon ratio, a more complex situation arises in the temperature series. The electrochemical behaviour of these samples is very similar but significant differences were found in their textural characteristics (Table 2), both in surface area and pore volumes. These samples also showed important differences in their chemical composition, like oxygen content (Table 1) or hydrophilic character (Table 3). Although these factors

might be important in the formation of the double layer, there might be other properties of the carbon or carbon–electrolyte interactions that could be contributing to the high specific capacitance observed. The need for new research focusing on properties of the carbon materials other than the textural ones can be demonstrated with the recent work of Inagaki et al. [13], where very high specific capacitances ($450\,\mathrm{F\,g^{-1}}$) where obtained in materials of relatively low surface area ($320\,\mathrm{m^2\,g^{-1}}$).

The high values of specific capacitance obtained in this study are close to the highest values ever found for carbon materials, although the textural properties of our carbons cannot be considered exceptional. Other authors working with activated carbons based on anisotropic precursors have found similar results [14,15], which seems to indicate that activated carbons obtained from these precursors have some advantages for the storage of energy in the double layer when compared to other carbons. Furthermore, the results presented here indicate that it is possible to obtain high capacitance values from samples that are mainly microporous, with pore size around 1 nm. It is worth noting that, although a significant

decrease of the specific capacitance with increasing current density was observed (Fig. 3), the values obtained at high current densities are still significantly high ($\sim$150–200 F g^{-1}). The causes of this dependence of the capacitance with the current density are not clear. This variation cannot be exclusively attributed to the presence of microporosity, as suggested by many authors, as the loss of capacitance is similar for all the samples independently of the textural characteristics. This can be clearly deduced from the behaviour of samples AR.1.7 and AR.5.7 (Fig. 3). The decrease in specific capacitance is about 50% in both cases, despite the pores in sample AR.5.7 are significantly larger than in sample AR.1.7, as discussed above.

4. Conclusions

Activated carbons with high surface areas have been developed from the direct activation of mesophase pitch with KOH under different conditions. The increase in the activation temperature caused the surface area and micropore volume to increase. Meanwhile, the activation with the highest KOH to mesophase ratio (5:1) also caused the widening of the pores with no substantial increase in the surface area.

Immersion calorimetry into liquids of different molecular size confirmed the results obtained by gas adsorption. Additionally, the number of hydrophilic sites in the samples, estimated by immersion into water, was higher for those samples with higher oxygen content, except for the least activated sample (AR.1.7). The combination of both techniques shows that the size of the pores are around 1.0 nm for most of the activated carbons, with few pores over 1.3 nm (except for sample AR.3.5) or under 0.7 nm.

The activated carbons studied showed very high values of specific capacitance, reaching in some cases 400 F g^{-1} for low current densities and values around 150–200 F g^{-1} for high current densities, values which are relatively high in comparison with other described in the literature. In the series of carbons obtained with increasing the KOH to mesophase ratio, the capacitance increased with increasing the surface area and pore volume of the samples. However, in the temperature series, the capacitance was rather similar, despite the different textural characteristics observed. This, together with the fact that the dependance of the capacitance with current density was similar for all the samples, suggest that there are other factors in addition to surface area and pore size that might be contributing to the formation of the double layer and the amount of energy stored in it. A significant effort is needed for the elucidation of the mechanism of the double layer formation.

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