



Chemical and electrochemical characterization of porous carbon materials

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Received 17 November 2005; accepted 11 April 2006

10 Abstract

11 Chemical and electrochemical techniques have been used in order to assess surface functionalities of porous carbon materials. An
12 anthracite has been chemically activated using both KOH and NaOH as activating agents. As a result, activated carbons with high
13 micropore volume (higher than 1 cm³/g) have been obtained. These samples were oxidized with HNO₃ and thermally treated in N₂ flow
14 at different temperatures in order to obtain porous carbon materials with different amounts of surface oxygen complexes. Thermal treat-
15 ment in H₂ was also carried out. The sample treated with H₂ was subsequently treated in air flow at 450 °C. Thus, materials with very
16 similar porous texture and widely different surface chemistry have been compared. The surface chemistry of the resulting materials was
17 systematically characterized by TPD experiments and XPS measurements. Galvanostatic and voltammetric techniques were used to deep-
18 en into the characterization of the surface oxygen complexes. The combination of both, chemical and electrochemical methods provide
19 unique information, regarding the key role of surface chemistry in improving carbon wettability in aqueous solution and the redox pro-
20 cesses undergone by the surface oxygen groups. Both contributions are of relevance to understand the use of porous carbons as electro-
21 chemical capacitors.

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23 *Keywords:* Activated carbon; Chemical treatment; Temperature programmed desorption; Electrochemical properties; Surface oxygen complexes

25 1. Introduction

26 Many applications of carbon materials are strongly
27 influenced by their surface chemistry. Thus, their use in
28 catalysis (either as catalyst or support), adsorption in solu-
29 tion or electrochemical processes are three examples in
30 which the surface chemistry can have an important rele-
31 vance in the materials performance [1–5]. Specially, any
32 discussion on the electrochemical behaviour of carbon,
33 such as its performance as double layer capacitor, which
34 is being very much studied nowadays, should take into
35 account the carbon electrode/electrolyte interface, where

functional groups play an important role, mainly in aque- 36
ous medium [1,3–16]. 37

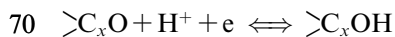
The presence of surface heteroatoms, especially oxygen 38
groups, affects the electrochemical response of the carbon 39
materials in two different ways. On one hand oxygen 40
groups may determine the wettability by the electrolyte 41
solution. It is known that the micropores of carbon cannot 42
be fully wetted in aqueous solutions because of their hydro- 43
phobic behaviour [5]. The increase in oxygen content mod- 44
ifies the electrostatic field in the surface, imparting certain 45
polarity, which makes easier the interaction with water 46
molecules [1]. On the other hand, the surface oxygen 47
groups may experience redox reactions [4,5] that can have 48
a significant contribution to different processes. 49

An interesting example of the relevance of surface oxy- 50
gen groups in electrochemical processes is the capacitance 51

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of porous carbons, used as a component of supercapacitors. As it was shown in previous studies [5,6], the faradic current is significantly increased with the content in surface oxygen groups, while the increase in the double layer is not so important. This remarks that the enhancement in capacitance is mainly based on pseudocapacitance or redox mechanisms. Recent results showed that the promotion of capacitance with the amount of oxygen surface complexes also takes place in non-aqueous electrolyte, where wettability is not a limiting factor [7]. This idea had already been exposed by some authors [7,9–12]. Further studies in our laboratory allowed us to conclude that CO-type desorbing groups are responsible for the enhancement in capacitance [8]. The CO-type surface complexes are mainly hydroxyl, carbonyl or quinone groups which can undergo the well-known mechanism for the quinone/hydroquinone redox pair:



The role of CO₂-desorbing groups is still unclear and it has been rarely reported [5]. Electron delocalization, which favours electrical conductivity is enhanced by the loss of strong electron-withdrawing groups, such as CO₂-type groups [4]. In that sense, the removal of CO₂-type groups should improve capacitance. This observation was previously reported [9]: the capacitance values reached a maximum after removal of the CO₂ groups at 450 °C. Thus, it was concluded that CO₂ complexes play a negative role in electrical energy storage. However this fact should be further analysed in detail.

The above comments show that to understand the electrochemical behaviour of materials, a deep characterization of the surface chemistry is necessary, which can be carried out by spectroscopic, chemical and electrochemical techniques. The characterization of surface oxygen groups is very often done by chemical or spectroscopic methods such as TPD, XPS, acid–base titration, FTIR, ... Although the measurements are, in many cases, easy, their interpretation is not simple due to the convolution of the contribution from the different functional groups. Moreover, in spite of the fact that electrochemical methods, like cyclic voltammetry, have a high surface sensitivity and the redox reactions from surface oxygen groups can be detected, it is difficult to assign the features observed to specific types of oxygen groups due to the overlapping of the different reactions and to the difficulties in the electrochemical measurements since materials with sufficient electrical conductivity should be used.

An integration of both chemical/spectroscopic methods and electrochemical techniques to deepen into the characterization of the surface chemistry could provide unique information. Unfortunately, this is not usually encountered in the literature, although there are exceptions such as Ref. [5].

Consequently, the objective of this work is to characterize activated carbons with very similar porous texture and widely different surface chemistry by chemical and electro-

chemical techniques, trying to deepen into the role of surface oxygen complexes in electrochemical properties such as the capacitance of porous carbons.

2. Experimental

2.1. Activation process

Chemical activation was done using KOH and NaOH as activating agents. An anthracite was the precursor used. Details of the preparation process are available elsewhere [17,18]. The preparation conditions for each sample are included in Table 1.

2.2. Chemical oxidation with HNO₃

The oxidation was carried out by mixing 1.5 g of activated carbon (AK and ANa) with 20 ml of concentrated nitric acid during 3 h at room temperature. After this treatment, the samples were washed several times with hot distilled water until the pH of the filtrate was the same as the washing water. Then, the samples were dried at 100 °C. The nomenclature includes an “N” to indicate this treatment in nitric acid (i.e., samples AKN and ANaN).

2.3. Thermal treatments in N₂

Carbons containing different amounts of surface oxygen complexes were obtained by subjecting the oxidized samples to thermal treatments at different temperatures (i.e., from 250 to 900 °C). These treatments were carried out in N₂ (200 ml/min) and using a heating rate of 3 °C/min. After reaching the heat-treatment temperature, it was kept for 1 h. Temperatures used are shown in Table 2. The nomenclature includes the treatment temperature (i.e., sample AKN-450 means sample AK treated in HNO₃ and heat-treated in N₂ up to 450 °C).

2.4. Thermal treatment in H₂

One sample (CA) was thermally treated in H₂ flow in order to remove most of the oxygen complexes. Before thermal treatment, the sample was purified (i.e., removal of inorganic impurities) by successive treatments with aqueous solutions (10 wt.%) of HCl, HNO₃ and HF, respectively, at room temperature for 48 h without stirring. After HCl and HNO₃ treatments, the sample was repeatedly washed with deionized water up to a final pH = 4.

Table 1
Preparation conditions in chemical activation

Sample	Activating agent	Activating agent/carbon ratio	Activation temperature (°C)	Activation time (h)	N ₂ flow rate (ml/min)
AK	KOH	3:1	750	1	800
ANa	NaOH	3:1	750	1	800
CA	KOH	3:1	750	2	800

Table 2

Thermal treatment temperature, porous texture, quantification of oxygen surface groups in activated carbons obtained from TPD experiments and capacitance values, in all the samples studied

Sample	T (thermal treatment) (°C)	$V_{DR}(N_2)$ (cm ³ /g)	Average pore size DR (N ₂) (nm)	$V_{DR}(CO_2)$ (cm ³ /g)	μmol CO/g	% CO	μmol CO ₂ /g	% CO ₂	C (F/g)
AK	–	1.10	1.54	0.73	2267	80	573	20	238
AKN	–	1.05	1.72	0.68	3550	63	2059	37	254
AKN-450	450 (N ₂)	1.11	1.70	0.66	3333	85	573	15	232
AKN-750	750 (N ₂)	1.09	1.85	0.68	327	76	104	24	189
AKN-900	900 (N ₂)	0.98	1.67	0.61	138	55	114	45	167
ANa	–	1.06	1.69	0.70	1733	76	560	24	193
ANaN	–	1.10	1.61	0.71	2380	58	1730	42	238
ANaN-250	250 (N ₂)	1.09	1.64	0.69	2191	63	1312	37	242
ANaN-450	450 (N ₂)	1.09	1.64	0.68	2128	77	652	23	202
ANaN-750	750 (N ₂)	1.00	1.59	0.61	324	69	148	31	171
ANaN-900	900 (N ₂)	0.93	1.58	0.57	68	22	240	78	148
CA	–	1.39	1.76	0.72	2817	73	1035	27	250
CAH	850 (H ₂)	1.33	1.71	0.63	133	46	156	54	0.03
CAHO _x	450 (air)	1.22	1.75	0.56	3708	81	889	19	191

148 After the HF treatment, it was washed with deionized
149 water up to the final pH of the washing water and dried
150 at 120 °C. Then, the sample was thermally treated under
151 a hydrogen flow of 5 ml/min g at 850 °C for 3 h. This sam-
152 ple is named as CAH. This procedure has been published in
153 the literature [19].

154 2.5. Thermal treatment in air

155 The sample CAH, previously treated in H₂, was sub-
156 jected to a thermal treatment in air flow in order to recover
157 part of the surface oxygen groups. The process was carried
158 out in a quartz tube fixed-bed reactor. The sample was
159 heated at 10 °C/min up to 450 °C. Then, the temperature
160 was kept for 12 h. This sample is named as CAHO_x.

161 2.6. Porous texture characterization

162 Porous texture of all samples was determined by physi-
163 cal adsorption (N₂ at 77 K and CO₂ at 273 K) using an
164 automatic adsorption system (Autosorb-6, Quantra-
165 chrome) after samples out-gassing at 523 K under vacuum
166 for 4 h. The total micropore volume (pore size below 2 nm)
167 and the average pore size were calculated from the applica-
168 tion of the Dubinin–Radushkevich equation to the N₂
169 adsorption at 77 K (range of relative pressures used for
170 the DR analysis was: $0.005 < P/P_0 < 0.17$). The narrow
171 micropore volume (pore size smaller than around 0.7 nm)
172 has been assessed from CO₂ adsorption at 273 K using
173 the DR equation and for relative pressures below 0.025
174 [20–24]. The densities of the adsorbed phases used for the
175 calculations, were 0.808 and 1.023 g/ml for N₂ and CO₂,
176 respectively.

177 2.7. Surface chemistry characterization

178 Temperature programmed desorption (TPD) experi-
179 ments were done in a DSC–TGA equipment (TA Instru-
180 ments, SDT 2960 Simultaneous) coupled to a mass

spectrometer (Thermostar, Balzers, GSD 300 T3), to char-
181 acterize the surface chemistry of all samples. In these exper-
182 iments, 10 mg of the sample were heated up to 950 °C
183 (heating rate 20 °C/min) under a helium flow rate of
184 100 ml/min.

XPS on the samples were obtained by using a VG-Mic-
186 rotech Multilab electron spectrometer. The source
187 employed was the MgK α (1253.6 eV) radiation of twin
188 anode in the constant analyser energy mode. Pressure of
189 the analysis chamber was maintained below 10^{–9} Torr.
190 The binding energy scale was regulated by setting the
191 C 1s transition. Peak areas were estimated by calculating
192 the integral of each peak after subtraction of the back-
193 ground and fitting the experimental peak by a Gaussian
194 curve. The binding energy values have been identified as
195 C–C at about 284.6 eV, C–O at about 286.1 eV, C=O at
196 about 287.3 eV and O–C=O at about 288.5 eV [25–33].
197

2.8. Electrochemical characterization

198 For the electrochemical characterization, composite
199 electrodes were prepared from powder porous carbon
200 material, acetylene black (Strem Chemicals) and binder
201 (PVDC copolymer, aqueous dispersion (55% solids), Sut-
202 ccliffe Speakman), in a ratio 77:10:13 wt.%, respectively. The
203 materials were mixed and pressed up to 100 bars for
204 10 min. The total electrode weight used for the measure-
205 ments was about 70–90 mg. After that, the composite elec-
206 trode was placed in a stainless steel mesh as a current
207 collector. In order to measure the electric double capaci-
208 tance of a single porous carbon electrode, the standard
209 three electrode cell configuration was employed. Reversible
210 hydrogen electrode (RHE) was used as reference and a
211 platinum wire was employed as a counterelectrode. 1 M
212 H₂SO₄ was used as aqueous electrolyte. The galvanostatic
213 method (at 2 mA), in a range of potentials between 0 and
214 1 V, has been used to measure the capacitance. The capaci-
215 tance values have been calculated from the interval
216 between 0.2 and 0.6 V, dividing the imposed current by
217

218 the slope of the lineal chronopotentiograms plot, taking the
219 average value between charge and discharge processes. The
220 result is then divided by the weight of porous carbon that is
221 about 77% of the total composite.

222 Cyclic voltammograms have been obtained in 1 M
223 H₂SO₄ solution in order to assess the redox behaviour of
224 the samples, since deviations from rectangular shape result-
225 ing in reversible peaks indicate pseudocapacitance. The
226 electrode and the electrochemical system employed were
227 the same as those referred before. The scan rate was
228 0.5 mV/s.

229 All electrochemical measurements were carried out with
230 an EG&G Potentionstat/Galvanostat model 273 controlled
231 by software EChem M270. All the solutions were pre-
232 pared with ultrapure water (Purelab ELGA).

233 3. Results and discussion

234 3.1. Porous texture characterization

235 The activated carbons prepared present type I iso-
236 therms, what is characteristic of microporous solids.

237 Table 2 contains the micropore volumes calculated from
238 N₂ adsorption data at 77 K [$V_{DR}(N_2)$] and CO₂ adsorption
239 data at 273 K [$V_{DR}(CO_2)$] for each sample. The compari-
240 son between the total micropore volume, $V_{DR}(N_2)$, and
241 the narrow micropore volume, $V_{DR}(CO_2)$, gives informa-
242 tion of the micropore size distribution [20–24]. Micropores
243 smaller than 0.7 nm in size are measured by $V_{DR}(CO_2)$, and
244 those smaller than 2 nm and bigger than 0.7 nm can be calcu-
245 lated by the difference between $V_{DR}(N_2)$ and $V_{DR}(CO_2)$.
246 The data show that narrow micropores are 65% of the total
247 microporosity, approximately.

248 Taking into account series AKN to AKN-900 and
249 ANaN to ANaN-900, it can be seen that little changes in
250 porosity occur when samples AK and ANa are oxidized
251 and thermally treated at different temperatures. Nitric acid
252 could either increase the porosity or block some micropo-
253 res. According to our results, the first effect is the main
254 one in the sample activated with NaOH, whereas the second
255 occurs in the sample activated with KOH. The samples
256 that have undergone the thermal treatment at higher tem-
257 peratures present a slight decrease in micropore volume.
258 This fact could be caused by certain structural rearrange-
259 ment in the material [34,35]. This effect is also observed
260 in the micropore volume reduction of sample CAH, which
261 was strongly purified and has undergone a thermal treat-
262 ment until 850 °C in H₂.

263 We can see that these changes in porosity caused by oxi-
264 dation and thermal treatments are very slight and hence,
265 they will not affect the electrochemical behaviour in an
266 important way.

267 3.2. Surface chemistry characterization by TPD and XPS

268 Surface oxygen groups on carbon materials decompose
269 upon heating producing CO and CO₂ at different tempera-

270 tures. It is known that CO₂ evolves at low temperatures as
271 a consequence of the decomposition of the acidic groups
272 such as carboxylic groups, anhydrides or lactones [24,36–
273 38]. The evolution of CO occurs at higher temperatures
274 and is originated by decomposition of basic or neutral
275 groups such as phenols, ethers and carbonyls [24,36–38].

276 Series AKN to AKN-900 and ANaN to ANaN-900
277 were characterized by TPD experiments. Figs. 1–4 show
278 the TPD profiles corresponding to all samples.

279 Table 2 contains the quantification of the amount of CO
280 and CO₂ desorbed in these experiments.

281 It can be observed that samples with different amounts
282 of surface oxides have been prepared (from 68 to
283 3550 μmol/g of CO and from 104 to 2059 μmol/g of CO₂).

284 TPD experiments contain different peaks in the CO and
285 CO₂ profiles, what indicates the presence of different types
286 of surface oxygen groups. In the CO spectra, several peaks
287 can be distinguished that come from the decomposition of

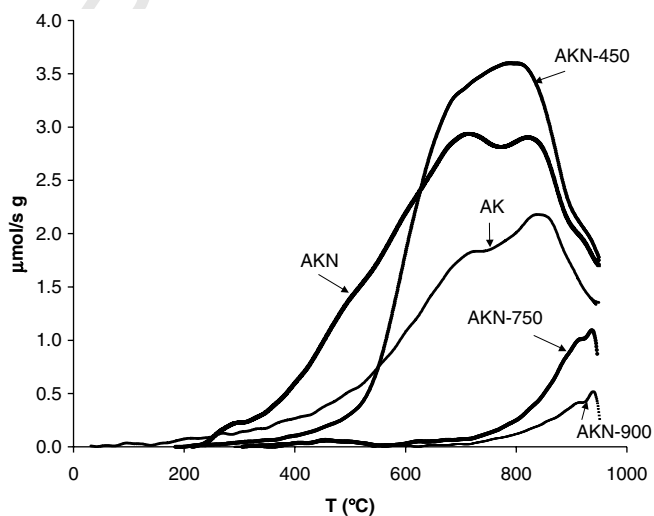


Fig. 1. TPD curves corresponding to CO desorption in AK samples.

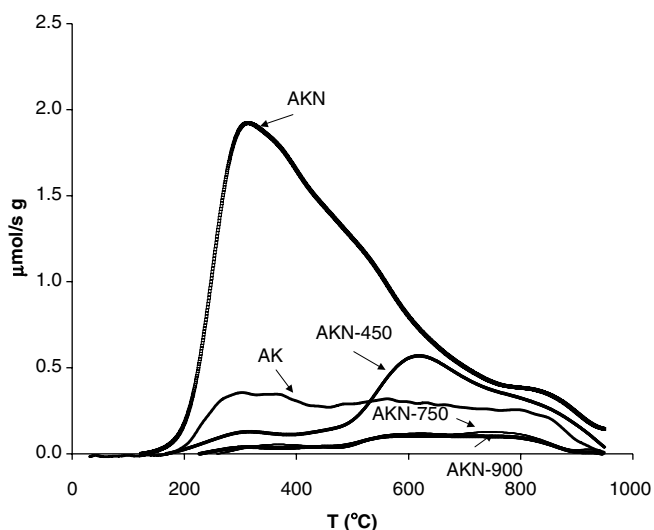


Fig. 2. TPD curves corresponding to CO₂ desorption in AK samples.

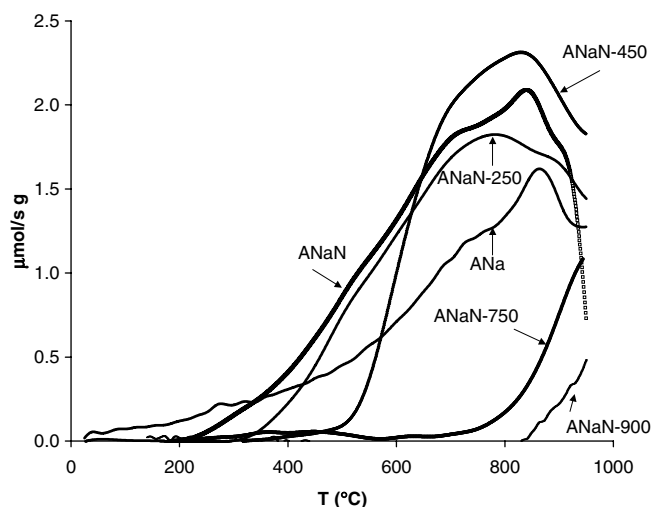


Fig. 3. TPD curves corresponding to CO desorption in ANa samples.

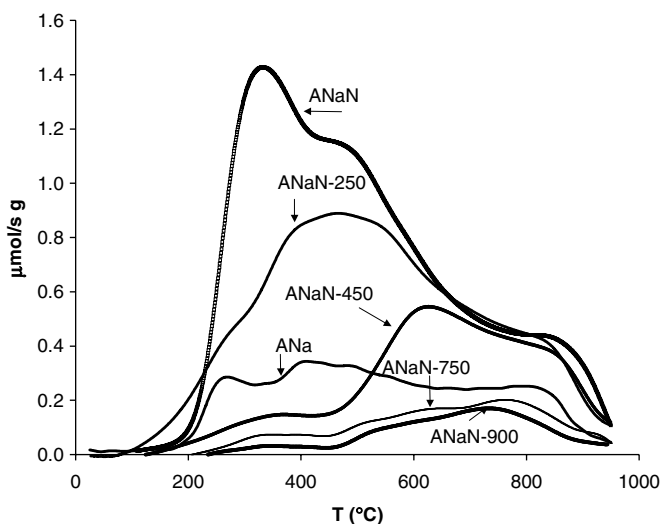


Fig. 4. TPD curves corresponding to CO₂ desorption in ANa sample.

288 carboxylic anhydrides (at about 500 °C) [24,37–40] and
 289 phenol, carbonyl, quinone and ether groups (at higher tem-
 290 peratures) [24,37–40]. In the CO₂ spectra, three peaks
 291 appear. The peak at 300 °C is usually associated to car-
 292 boxyl groups, the one at 500 °C is related to carboxylic
 293 anhydrides and the desorption above this temperature
 294 could be caused by lactone groups decomposition or CO₂
 295 coming from secondary reactions as these are substantially
 296 enhanced with porous carbon [5,37–39].

297 It is known that the thermal decomposition of each car-
 298 boxylic anhydride produces one CO molecule and one CO₂
 299 molecule at close temperatures [37–39]. In order to assess
 300 the amount of CO and CO₂ associated to different func-
 301 tional groups, the deconvolution of the CO and CO₂ spec-
 302 tra was made using a multi-Gaussian function. Table 3
 303 contains the results for the anhydride peak from the CO
 304 and CO₂-profiles deconvolution, respectively, since this
 305 specific information will be later used.

306 As it can be observed, the CO₂ peak tends to appear just
 307 a little before than CO peak. The reason why we observed
 308 this difference is that the decomposition of carboxylic
 309 anhydrides is not a simultaneous process. A CO₂ molecule
 310 desorbs first and then the CO one. However, these desorp-
 311 tions are very close and it is usually considered that they
 312 take place simultaneously.

313 XPS was employed for the analysis of the surface oxy-
 314 gen groups in the samples AKN and ANaN, since these
 315 ones have the highest amounts of surface oxygen groups.
 316 The distribution of oxygen complexes of each sample has
 317 been calculated by deconvolution of the XPS spectra, fixing
 318 the binding energy in the values presented in the experi-
 319 mental section. The results are included in Table 4.

320 It can be observed that the percentage of O–C=O spe-
 321 cies measured from XPS is of the same order of magnitude
 322 (but smaller) to the percentage of CO₂-type groups
 323 obtained from the TPD experiments (Table 2). Unambigu-
 324 ous interpretation of XPS spectra is difficult: the external
 325 and the internal composition of a solid carbon sample
 326 may differ and, additionally, carbon external voids can arti-
 327 ficially lower the measured concentration of surface species
 328 [4]. Taking into account that these two techniques are not
 329 quantitatively comparable, we can conclude that the results
 330 obtained by TPD and XPS are relatively consistent with
 331 each other.

332 Samples CA, CAH and CAHO_x were also subjected to
 333 TPD experiments. The TPD profiles are shown in Figs. 5
 334 and 6 and the quantifications are included in Table 2.

335 It is important to note the differences existing between
 336 the samples. The main difference between sample CA and

Table 4
 Distribution of oxygen complexes from the XPS spectra

Sample	C–O (%)	C=O (%)	CO ₂ (%)
AKN	22	47	30
ANaN	51	19	30

Table 3
 CO and CO₂ contribution to the TPD from carboxylic anhydride decomposition

Sample	CO data from anhydrides			CO ₂ data from anhydrides		
	μmol/g	Peak temperature (°C)	Width (°C)	μmol/g	Peak temperature (°C)	Width (°C)
AKN	810	505	198	843	487	161
ANaN	525	505	198	531	433	103
ANaN-250	513	545	176	507	499	200

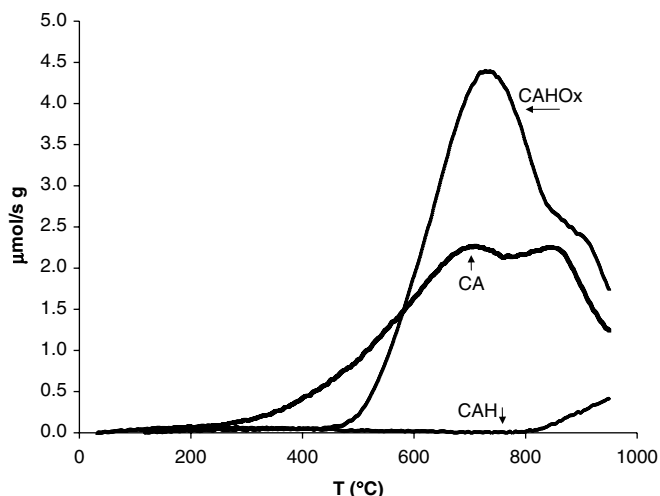


Fig. 5. TPD curves corresponding to CO desorption in CA samples.

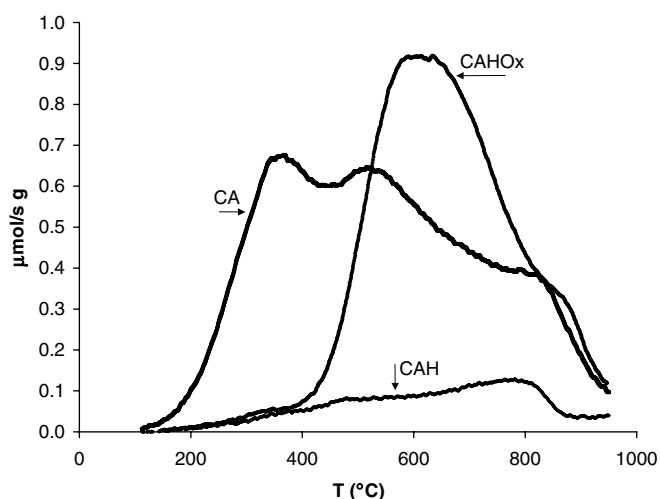


Fig. 6. TPD curves corresponding to CO₂ desorption in CA samples.

337 CAH is that the latter does not contain surface oxygen
 338 groups in a significant amount. In addition, sample CAH
 339 is different from AKN-900 and ANaN-900 from the point
 340 of view of thermal treatment although TPD profiles are
 341 similar: this happens because the treatment in H₂ has satu-
 342 rated carbon bonds, its reactivity towards oxygen is the
 343 lowest and it is the most hydrophobic. Then, this sample
 344 is very useful to test the role of surface chemistry in the
 345 wettability of the carbon material. Sample CAHO_x has a
 346 high amount of CO and CO₂ desorbing groups because
 347 the treatment in air at 450 °C has generated an important
 348 number of surface oxygen groups. However, it is important
 349 to note that the peaks corresponding to carboxylic acids
 350 and anhydrides do not appear in the CO₂ spectrum, being
 351 the lactone peak, at temperatures above 500 °C, the only
 352 one remaining. The CO spectrum has also changed consid-
 353 erably since the peak at 500 °C (anhydrides) has almost
 354 completely disappeared as expected because the heat treat-
 355 ment temperature is very close to the temperature of anhy-
 356 drides decomposition.

3.3. Electrochemical characterization: galvanostatic and voltammetric experiments

357
358

359 Table 2 contains the specific capacitance values for all
 360 the samples measured for a constant current intensity of
 361 2 mA (this corresponds to a current of about 30 mA/g).
 362 Samples from AKN to AKN-900 and from ANaN to
 363 ANaN-900 show that, as previously reported [8], the higher
 364 the amount of surface oxygen groups, the higher the
 365 capacitance.

366 Figs. 7 and 8 show the cyclic voltammograms for AKN to
 367 AKN-900 and ANaN to ANaN-900 samples.

368 An ideal double layer capacitance behaviour of an elec-
 369 trode material should consist of a rectangular shape of the
 370 cyclic voltammogram. The phenomenon, then, is purely
 371 electrostatic. On the other hand, materials with pseudoca-
 372 pacitance show redox peaks related to electron transfer
 373 reactions. Such redox processes can be observed in the vol-
 374 tammograms included in Figs. 7 and 8, especially for sam-
 375 ples AKN, AKN-450 (Fig. 7) and ANaN and ANaN-450
 376 (Fig. 8). If the voltammograms are observed carefully, sev-
 377 eral overlapping peaks from 0.5 to 0.65 V can be distin-
 378 guished, being the main features an oxidation peak at
 379 0.5 V and a second one at 0.63 V, approximately. The
 380 reduction peaks are less defined. The existence of this
 381 broad peak shows that different redox processes are
 382 involved. The peak at 0.63 V is more intense for the most
 383 oxidized samples (AKN, ANaN). In addition, it disappears
 384 almost completely after thermal treatment at 450 °C.
 385 Moreover, after thermal treatments at 750 °C or 900 °C,
 386 all the peaks seem to disappear, obtaining a quasi-rectan-
 387 gular shape in the voltammograms, indicating again that
 388 surface oxygen groups are contributing to capacitance by
 389 redox reactions.

390 In a previous work, an excellent correlation between
 391 CO-desorbing groups and capacitance (both referred to
 392 the porosity of the material) was observed [8]. The corre-
 393 sponding plot (capacitance vs. CO-type groups) was made

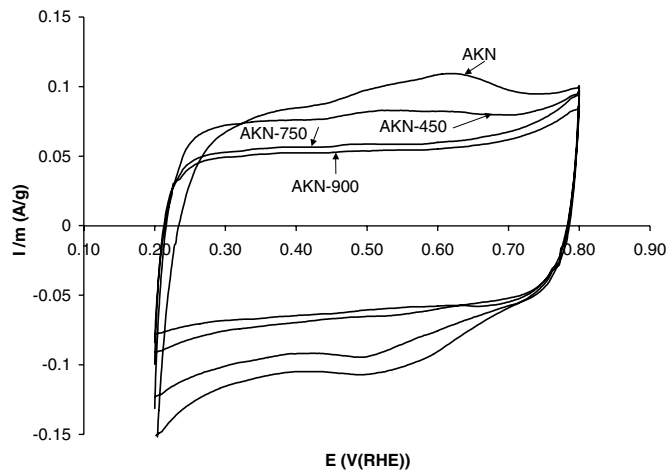


Fig. 7. Steady cyclic voltammograms of AK series. 1 M H₂SO₄, V = 0.5 mV/s.

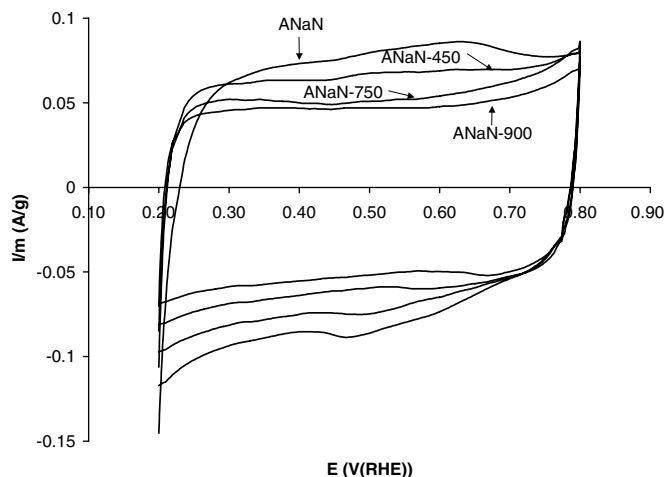


Fig. 8. Steady cyclic voltammograms of ANa series. 1 M H₂SO₄, $V = 0.5$ mV/s.

394 with these series of samples (Fig. 9). Let us note that in this
 395 case the plot has been done without dividing by the poros-
 396 ity of the materials, due to the very similar porous texture
 397 of these samples; however, if this parameter is taken into
 398 account (for example, by dividing by the VDR(N₂) in
 399 Table 2), a better correlation is obtained. In any case, a
 400 clear correlation between capacitance and the CO-type
 401 groups exists. The samples heat-treated at 450 °C or higher
 402 temperatures, follow a linear trend (except for sample
 403 ANaN-900 due to its lower porosity – Table 2), but the rest
 404 of the samples exhibit an upwards deviation. The main dif-
 405 ference between these two groups of samples is that those
 406 treated above 450 °C do not contain a significant amount
 407 of carboxyl groups and anhydrides. Then, either both type
 408 of surface oxygen groups or one of them is the responsible
 409 for the additional contribution to the capacitance.

410 To check this point, sample ANaN-250 was obtained by
 411 heat treatment up to 250 °C, in order to remove most of the
 412 carboxylic groups without decomposing the anhydrides.
 413 Interestingly, the capacitance of sample ANaN-250 is

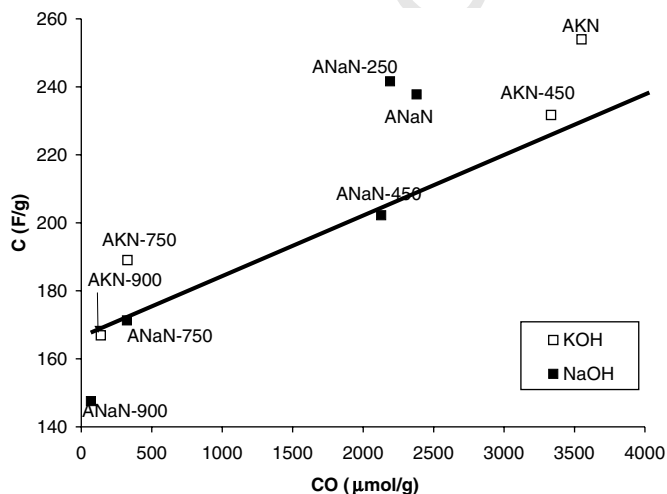
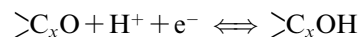


Fig. 9. Capacitance vs. CO content.

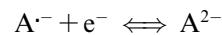
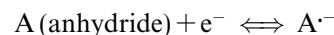
414 slightly better than that of sample ANaN. This suggests
 415 that carboxylic groups do not play an important role in
 416 the promotion of capacitance, although it seems that their
 417 contribution to this property is not positive, as previously
 418 proposed [4,9].

419 From the previous comments, it can be concluded that
 420 carboxylic anhydrides could be the responsible for the
 421 enhancement in capacitance, since these kinds of groups
 422 only exist in the samples not treated above 400–550 °C,
 423 which is the desorption temperature interval of anhydrides.

424 Taking into account that a redox peak at 0.63 V appears
 425 in cyclic voltammograms for samples treated at lower tem-
 426 peratures than 450 °C and that it almost disappears after
 427 treatment at 450 °C, it can be suggested that anhydrides
 428 undergo a redox reaction at this potential. This reaction
 429 should be somehow different from that occurring in carbo-
 430 nyls or quinone groups, which redox process should occur
 431 at lower potentials. According to our experiments they are
 432 mainly associated to the first peak in cyclic voltammo-
 433 grams. It is known that the reduction potential of the pair
 434 quinone/hydroquinone is located at, approximately, 0.7 V
 435 vs. NHE. However, as it has been previously published,
 436 an increase in the number of aromatic rings causes the for-
 437 mal potential to decrease [5] and can reach values close to
 438 0.5 V [1]. Taking into account that the basic structure of
 439 activated carbons is based on graphene layers, the decrease
 440 in the expected potential could be logical and the process
 441 located below 0.6 V presumably proceeds through a one
 442 electron transfer quinone/hydroquinone mechanism [4]:



445 The reaction mechanism for the oxidation/reduction of
 446 anhydrides (at about 0.63 V) is not very clear. Many elec-
 447 trochemistry textbooks indicate that carboxyl groups are
 448 inactive electrochemically. However, it must be considered
 449 that, on carbon materials, the nature of the substrate can
 450 have a substantial effect on the electrochemical behaviour
 451 of the available functional groups; for instance, large ara-
 452 matic substrates and activating functional neighbours can
 453 facilitate their reduction [4]. In organic chemistry literature,
 454 studies related to oxidation and reduction of anhydrides in
 455 organic medium can be found [41,42] and the following
 456 mechanism is proposed:



461 Despite the fact that anhydrides could be hydrolysed in
 462 aqueous medium, the thermodynamic and kinetic stability
 463 of these functional groups can be enhanced by electron
 464 delocalization in the $\pi\pi$ orbitals of the graphene layers.
 465 An experimental observation of this effect can be found
 466 in Ref. [38]. A sample oxidized in air which contained a
 467 large number of anhydrides was put in contact with a
 468 wet atmosphere for a long period of time, and after drying
 469 at low temperatures, the TPD experiment still revealed the
 470 presence of an important amount of this type of groups.

471 Thus, the hydrolysis of these groups linked to graphene
472 layers, seems to be slow.

473 According to the redox scheme presented above, each
474 anhydride group will contribute with two electrons in the
475 redox process. If we consider this aspect in the capacitance
476 vs. CO-type groups plot presented in Fig. 9 (that is, to take
477 into account that one anhydride contributes with two elec-
478 trons in the redox process), we will have to change the plot
479 for samples treated under 450 °C. Each carboxylic anhy-
480 dride contributes to capacitance with two electrons, so
481 the amount of anhydrides should be taken into account
482 twice when the plot is done vs. CO. The amount of CO
483 desorbing groups in the corrected plot, corresponds to
484 the CO desorbed in TPD experiments plus the part corre-
485 sponding to anhydrides (obtained from the deconvolution).
486 Then Fig. 10 is obtained in which all the samples fit much
487 better to the linear trend.

488 This result could indicate that anhydrides play a special
489 role in the redox contribution of the surface oxygen com-
490 plexes in the capacitance. In our previous work [8], we
491 did not observe this contribution as we used the activated
492 carbons without any treatment after activation. Because
493 the activation temperature is usually higher than 700 °C,
494 anhydrides groups will not remain in the carbon material.
495 Then, to observe this effect it is necessary the selection of
496 samples with appropriate surface chemistry as we did in
497 this study.

498 On the other hand, CA series evidences that surface
499 chemistry has also a key role in improving carbon wettabil-
500 ity. As it can be observed, sample CAH, the most hydro-
501 phobic one, presents a negligible value of capacitance
502 (Table 2) in agreement with results obtained with graphite
503 fibers [43]. When this sample is reoxidized in air flow, it
504 practically recovers the capacitance value of the original
505 sample (Table 2). The capacitance value of CAHO_x sample
506 is smaller than that of sample CA, but this can be under-
507 stood taking into account that this sample has lost some
508 surface area and some structural order due to the aggres-

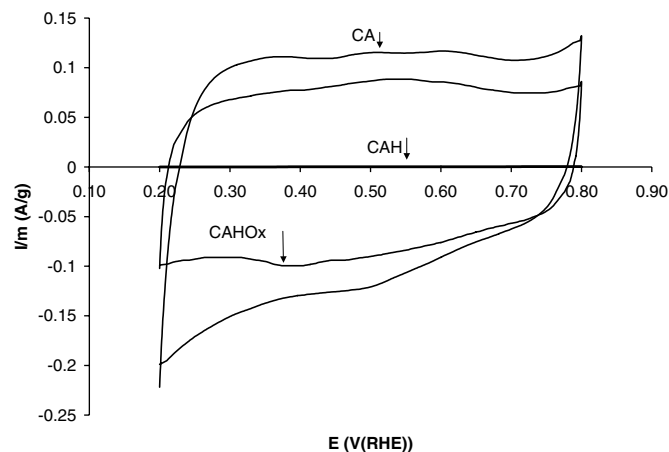


Fig. 11. Steady cyclic voltammograms of CA series. 1 M H₂SO₄, V = 0.5 mV/s.

509 sive procedure carried out before H₂ thermal treatment.
510 Fig. 11 contains the cyclic voltammograms for samples
511 CA, CAH and CAHO_x.

512 Interestingly, we can deduce that only the heat treat-
513 ment in hydrogen produces such a decrease in wettability,
514 because the surface oxygen-containing samples and those
515 heat-treated in inert atmosphere (i.e., AKN-900 and
516 ANaN-900 samples), still have enough wettability to create
517 most of the double layer, showing the role of dangling
518 bonds in this property.

519 It can be observed that in CA sample a broad peak
520 appears as it happened in the AKN and ANaN samples.
521 However, the intensity of the peak at 0.63 V is lower
522 because the content in carboxylic anhydrides is smaller
523 than in the samples oxidized by HNO₃. In the voltammo-
524 gram of sample CAHO_x, the redox process below 0.6 V,
525 related to quinone/hydroquinone redox pair, has the high-
526 est intensity. It is important to note that this sample has
527 a low content in carboxylic anhydrides as it can be seen in the
528 TPD spectra (Figs. 5 and 6).

529 Finally, it should be noted that the presence of surface
530 oxides also has an influence in the formation and structure
531 of the double layer, as a consequence of the ion–ion inter-
532 actions between surface oxygen groups and electrolyte ions
533 (H⁺ and HSO₄⁻ in this case). This type of interactions might
534 have an influence on the kinetics of the charge–discharge
535 process and on the effective pore dimensions. These ques-
536 tions need to be studied in future work.

4. Conclusions

537 Activated carbons with similar porosity but different
538 surface chemistry have been studied by chemical and elec-
539 trochemical methods to characterize their surface chemis-
540 try. The combination of both techniques has allowed us
541 to deepen into the surface electrochemical properties of
542 porous carbon materials. Thus, the features observed in
543 the steady cyclic voltammograms have been tentatively
544 assigned to redox processes associated to CO-type groups
545

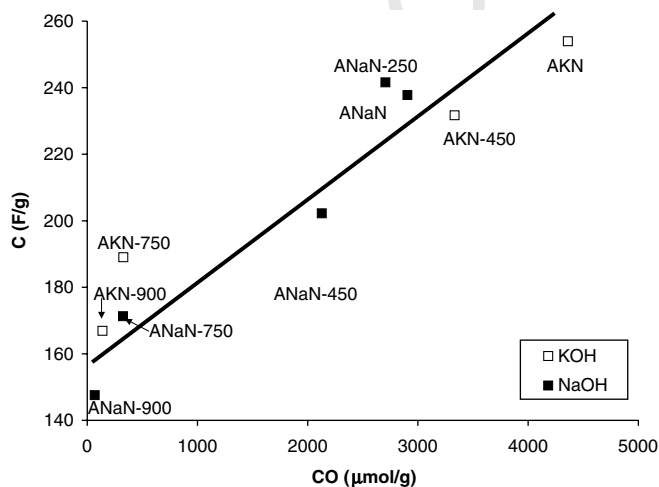


Fig. 10. Capacitance vs. CO content. Corrected values to take into account the contribution of anhydrides.

546 (broad peak below 0.6 V RHE) and carboxylic anhydrides
 547 (peak at about 0.63 V RHE). The surface oxygen groups
 548 have, at least, a twofold relevant contribution to the total
 549 capacitance of porous carbons. On one hand, the surface
 550 oxygen groups have an important contribution to the
 551 capacitance through faradic processes which involve one
 552 or two electron transfer reactions. On the other hand, the
 553 surface oxygen groups (or the dangling bonds created after
 554 decomposition in inert atmosphere), determine the wetta-
 555 bility of aqueous electrolyte; thus, their presence on the
 556 carbon surface is essential to take profit of the large double
 557 layer contribution to the capacitance of the porous carbons
 558 which is associated to their high porosity. Further studies
 559 in organic medium will be done to understand the role of
 560 these functionalities in the capacitance.

561 Acknowledgements

562 The authors thank MEC for financial support (Project
 563 PPQ2003-03884) and I.M.J. Vilella for thermal treatment
 564 in H₂ carried out with sample CA. M.J.B.-M. thanks
 565 MEC for the thesis grant.

566 Appendix A. Supplementary data

567 N₂ and CO₂ adsorption isotherms and their DR plots
 568 are available as supplementary material on the web. Sup-
 569plementary data associated with this article can be found,
 570 in the online version, at doi:10.1016/j.carbon.2006.04.017.

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