New insights on electrochemical hydrogen storage in nanoporous carbons by in situ Raman spectroscopy

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ABSTRACT
In situ Raman spectroscopy was exploited to analyze the interaction between carbon and hydrogen during electrochemical hydrogen storage at cathodic conditions. Two different activated carbons were used and characterized by different electrochemical techniques in two electrolytes (6 M KOH and 0.5 M Na2SO4). The in situ Raman spectra collected showed that, in addition to the D and G bands associated to the graphitic carbons, two bands appear simultaneously at about 1110 and 1500 cm⁻¹ under cathodic conditions, and then they disappear when the potential increases to more positive values. This indicates that carbon–hydrogen bonds are formed reversibly in both electrolytes during cathodic conditions. Comparing the two activated carbons, it was confirmed that, in both electrolytes, the hydrogenation of carbon atoms is produced more easily for the sample with lower amount of surface oxygen groups. In KOH medium, for the two samples, the formation of carbon–hydrogen bonds proceeds at more positive potential with respect to the thermodynamic potential value for hydrogen evolution. Furthermore, changes in the shape of the D band (due to an intensity increase of the D1 band) during the formation of carbon–hydrogen bonds suggest that hydrogenation of the carbon atoms increases the number of edge planes.

1. Introduction
Carbon materials are widely studied as electrodes for energy storage devices (e.g. supercapacitors [1–5]), because of their high conductivity, low cost and versatility of structure/texture. A relevant electrochemical application of carbon materials is hydrogen storage by electro-reduction of water in alkaline and neutral media. This process entails storing electrical charge through water reduction and weak chemical bonding of hydrogen. Different carbon materials have been studied for this application, such as activated carbons [6–12], carbon nanotubes (CNTs) [13–17], and others [18,19].

The values of electrochemical hydrogen storage capacity published with CNTs show a large dispersion [13–15,17], what can be justified by the different purity degree of CNTs, which always contain some amorphous material and metal catalyst used in the synthesis [13,20]. Taking into account theoretical calculations and experimental results, storage of a relatively high amount of hydrogen in CNTs is quite unlikely [13,20]. Porous carbons have been studied for this application, giving more effective electrochemical hydrogen storage and greater reproducibility [7].

In the literature, several studies discussing the role of porosity and unsaturated carbon atoms in electrochemical...
hydrogen storage can be found. Generally, they all conclude that the higher the narrow micropore volume (i.e. pore size smaller than around 0.7 nm), the higher the electrochemical hydrogen storage capacity [6,21,22], and that the later decreases with decreasing the number of dangling carbon atoms [7,3]. The presence of surface oxygen groups in the activated carbon produces the saturation of the active sites(i.e. unsaturated carbon atoms), decreasing the amount of hydrogen electrochemically stored in alkaline solution [9]. The type of carbon–hydrogen bonds and the electrochemical hydrogen storage capacity depending on the electrolyte have been also studied. Hydrogen is weakly chemisorbed in alkaline medium [7], whereas electrochemical hydrogen storage efficiency is quite poor in acidic electrolyte [8].

Since carbon materials display characteristic vibrational modes by Raman spectroscopy [9,13,23,24], this technique has been used to in situ monitor the structural changes occurring during electrochemical conditions, and to characterize the type of carbon–hydrogen interaction under cathodic conditions [9,13,25].

The objective of the present work is to investigate the mechanism of electrochemical hydrogen storage, under cathodic conditions, comparing the behavior of two activated carbons, with different porosity and surface chemistry, in two different electrolytes (6 M KOH and 0.5 M Na2SO4). The activated carbons are electrochemically characterized by cyclic voltammetry and chronopotentiometric experiments, and in situ Raman spectroscopy is employed to analyze the surface structural changes of activated carbons at different potentials, in both electrolytes.

2. Experimental

The materials used for the study were: (a) an activated carbon (ANK-3) obtained by KOH activation of anthracite, following the procedure described elsewhere [26] and (b) a commercial activated charcoal (MWV-E510A from MeadWestvaco).

2.1. Porous texture characterization

The porosity of the two samples was determined by physical adsorption (N2 at −196 °C and CO2 at 0 °C) using an Autosorb-6 equipment (Quantrachrome) after samples outgassing at 250 °C under vacuum for 4 h. The total micropore volume (i.e. pore size smaller than 2 nm) was calculated from the application of the Dubinin–Radushkevich (DR) equation to the N2 adsorption data at −196 °C (0.005 < P/P0 < 0.17). The narrow micropore volume (i.e. pore size smaller than around 0.7 nm) was estimated from CO2 adsorption at 0 °C using the DR equation (P/P0 < 0.17) [27]. The apparent specific surface area was calculated by applying the BET theory to the N2 adsorption data (0.005 < P/P0 < 0.35) [27].

2.2. Surface chemistry characterization

Temperature programmed desorption (TPD) was performed in a DSC–TGA equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3), to characterize the surface chemistry of the samples. In these experiments, approximately 10 mg of the sample were heated up to 950 °C (heating rate 20 °C min−1) under a helium flow rate of 100 ml min−1.

2.3. Electrochemical characterization

Carbon electrodes were prepared by mixing the porous carbon powder, acetylene black and polytetrafluoroethylene as a binder (Polytetrafluoroethylene 60 wt.% dispersion in H2O, Sigma–Aldrich) in ratio 80:10:10, respectively. The mixture was dried under an infrared lamp and compressed (2 tons) during 10 min to prepare a monolith with a diameter of 13 mm. The total carbon electrode weight used for the measurements was about 50 mg. The monolith was introduced in a stainless steel mesh and compressed (2 tons) for 10 min. Lastly, the electrode was dried during 1.5 h (under vacuum and 80 °C). Before the experiments, the electrodes were soaked during 24 h in the electrolyte.

Cyclic voltammograms were obtained at 1 mV s−1 scan rate, and the specific capacitance (C in F g−1) of the activated carbon was calculated using Eq. (1):

$$ C = \frac{Q}{\Delta E} $$

where Q is the electrical charge obtained by integration of the voltammogram (C g−1) and ΔE is the potential window (V).

Hydrogen was electrochemically stored with a charge current of −500 mA g−1electrode during 1 h, and the amount stored was evaluated by applying a discharge current of 500 mA g−1electrode, until reaching the initial open circuit potential.

The total charge measured during the galvanostatic discharge (Qtotal discharge in C g−1) was calculated with Eq. (2):

$$ Q_{\text{total discharge}} = I \cdot t $$

where I is the current density referred to the mass of activated carbon (A g−1) and t is the discharge time (s).

As expressed by Eq. (3), Qtotal discharge includes a capacitive contribution, QEDL (specific capacitance of the activated carbon by the potential window of the discharge process), and the charge QH related with hydrogen electrochemically stored:

$$ Q_{\text{total discharge}} = Q_{\text{EDL}} + Q_H $$

Hence, the amount H (wt%) of hydrogen stored is calculated applying Eq. (4):

$$ \left( \frac{Q_H M}{F} \right) \times 100 = H $$

where M is the atomic mass of hydrogen (1 g mol−1) and F is the Faraday constant (96,485 C mol−1).

All the electrochemical measurements were performed in a three-electrode cell using a platinum wire as counter-electrode and a reversible hydrogen electrode (RHE) as reference electrode; all potentials were further referred to the normal hydrogen electrode (NHE). The temperature during all the electrochemical experiments was kept at 25 °C.

The electrochemical characterization was carried out with an Autolab FGSTAT30 potentiostat.
2.4. In situ Raman characterization

In situ Raman characterization was done using a three-electrode spectro-electrochemical cell made of polytetrafluoroethylene, as described elsewhere [9]. A platinum wire was used as counter-electrode, and Ag/AgCl (3 M KCl) (0.21 V vs NHE) was used as reference electrode; the potentials were further referred to the NHE. The working electrode was prepared by depositing a small amount of the electrode mixture (prepared as described earlier) on a glassy carbon bar (which acts as an electric contact). The Raman spectra were obtained with a LabRam spectrometer (Jobin–Yvon Horiba) coupled to an upright microscope Olympus BX30. The excitation line was provided by a 9 mW He–Ne laser at 632.8 nm. The calibration of the spectrometer was performed with a Si slice (521 ± 2 cm−1). The laser beam was focused through a 50× long-working objective (0.5 NA) into a 2 μm spot at the electrode surface. The sample viewing system consisted of a television camera attached to the microscope. The spectrometer resolution was better than 3 cm−1 and the detector was a Peltier cooled charge-couple device (CCD) (1064 × 256 pixels). It was used a 800 μm pinhole, a 200 μm slit and a 600 lines mm−1 diffraction grating. The electrochemical conditions were applied using a DropSens portable bipotentiostat/galvanostat MWV-E510A.

The spectra were acquired during 30 s at each potential, after a steady state current was reached. Since the He–Ne laser power may degrade the sample during the Raman measurements, each spectrum has been recorded in a different zone of the carbon electrode. Several spectra have been acquired with different electrodes in order to ensure that the results are reproducible and representative of the samples behavior under the given electrochemical conditions. Furthermore, in some experiments, consecutive spectra have been recorded at each potential in different zones of the carbon electrode. In all cases, the evolution of hydrogen bubbles has been avoided.

3. Results and discussion

3.1. Porous texture and surface chemistry characterization

Table 1 shows that both porous carbons have a highly developed porosity; ANK-3 has higher BET surface area and total micropore volume than the commercial activated carbon MWV-E510A.

Surface oxygen groups of activated carbons decompose upon heating producing CO and CO2 at different temperatures [28,29]. The evolution of CO occurs at high temperatures as a consequence of the decomposition of basic or neutral groups such as phenols, ethers, carbonyls and quinones. CO2 evolves generally at lower temperatures and it is mainly due to the decomposition of carboxylic groups and lactones. The decomposition of anhydride groups produces CO and CO2. Table 1 includes the amounts desorbed in the TPD experiments and it shows a much higher content of surface oxygen groups for ANK-3, which could be attributed, in part, to the activation method (KOH activation of anthracite) used for the preparation of this material. The lower oxygen content of the sample MWV-E510A, could be also explained considering that this is a commercial sample developed for supercapacitor application, which has been probably post-treated to eliminate functionalities.

### 3.2. Electrochemical characterization

The voltammograms of ANK-3 in 6 M KOH solution (Fig. 1) show a quasi-rectangular shape between −0.67 V and −0.27 V (dash line), typical of an essentially capacitive process associated with the formation of the electrical double-layer. If the potential window is broadened to more positive potential (i.e. anodic conditions) and more negative potentials (dot line), an oxidation current appears at high potential which corresponds to the oxidation of the sample. Upon broadening the potential window to more negative potentials (solid and dash dot lines) (i.e. cathodic conditions) a reduction current starts at −0.75 V which corresponds to incipient hydrogen evolution. During the positive scan from −1.27 V, a positive peak is clearly observed at −0.60 V (dash dot line) which can be associated to the oxidation of hydrogen weakly chemisorbed during the negative scan [7]. The voltammograms of MWV-E510A in 6 M KOH solution (Fig. 2) in the same potential range exhibit a similar behaviour.

Fig. 3 shows the voltammograms for the ANK-3 sample in 0.5 M Na2SO4 solution. When the potential window is maintained between −0.14 V and 0.26 V (dash line), the behavior corresponds mainly to a capacitive process. If the potential window is broadened to more positive and more negative values (dot line) an oxidation current starts above 0.90 V which corresponds to the oxidation of the sample. A small reduction peak that could be related to this oxidation process is observed at around 0.40 V during the negative scan. When the potential window is broadened to more negative potentials (solid line) the reduction current associated with hydrogen evolution is observed. The peak related to the oxidation of the stored hydrogen is observed approximately at 0.85 V during the positive scan. If the potential window is broadened to even more negative potentials (dash dot line), more hydrogen is chemisorbed as demonstrated by the increase in the oxidation peak at 0.85 V during the positive scan, but simultaneously hydrogen evolution takes place during the negative scan. The voltammograms for MWV-E510A in 0.5 M Na2SO4

<table>
<thead>
<tr>
<th>Table 1 – Porous texture and surface chemistry characterization results.</th>
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<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>ANK-3</td>
</tr>
<tr>
<td>MWV-E510A</td>
</tr>
</tbody>
</table>

*μmol O g⁻¹ = μmol CO g⁻¹ + 2μmol CO₂ g⁻¹.
solution (Fig. 4) show a similar behavior. It is important to emphasize that the over-potentials for hydrogen evolution and hydrogen oxidation are much higher in Na$_2$SO$_4$ than in KOH medium for the two samples.

Table 2 includes the specific capacitance values calculated from the quasi-rectangular voltammograms for the two samples in both media. For the two samples, the specific capacitance is higher in KOH than in Na$_2$SO$_4$ medium, as already reported [3]. The specific capacitance values are higher for ANK-3 in both electrolytes, in agreement with the higher development of porosity and the higher amount of surface oxygen groups of this sample (see Table 1) [1,2,22].

Figs. 5 and 6 present the galvanostatic charge–discharge curves for the two samples in KOH and in Na$_2$SO$_4$ medium, respectively. The samples are maintained during 1 h at open circuit potential and, after this time, a negative current $\left(-500 \, \text{mA g}^{-1}\right)$ is applied during 1 h. During the charge process a very negative potential close to $-1.30 \, \text{V}$ is reached for both samples and both electrolytes. As it has been previously seen in the voltammograms, at this potential value, electrochemical hydrogen storage takes place. The difference between the initial open circuit potential and the potential value reached during the charge process is higher in Na$_2$SO$_4$ medium for the two samples, and higher for the ANK-3 sample in both electrolytes. Interestingly, it can be observed that the galvanostatic curves are different depending on the electrolyte, but they are qualitatively comparable in a given electrolyte for the two activated carbons. The long discharge times are related to the oxidation of chemisorbed hydrogen [12]. In KOH medium (see Fig. 5), most of the charge is consumed approximately between $-1.00 \, \text{V}$ and $-0.50 \, \text{V}$ for the two samples, and it is related to the oxidation of weakly bonded hydrogen. By contrast, in Na$_2$SO$_4$ medium (see Fig. 6), the main consuming of charge occurs at high potentials (it starts at around 0.00 V for ANK-3 and at $-0.20 \, \text{V}$ for MWV-E510A), and it is linked to the oxidation of strongly bonded hydrogen. These results correlate with the cyclic voltammetry experiments where it has been seen that oxidation of adsorbed hydrogen occurs at higher potential in Na$_2$SO$_4$ than in KOH medium. This might explain the presence of two slopes in the discharge curves in Na$_2$SO$_4$ medium: the first part of the curves, where the potential is not high enough
to cause the oxidation of adsorbed hydrogen, would be mainly related to a capacitive process; and the second part, at higher potential, corresponds to the oxidation of strongly bonded hydrogen. These data correlate with the cyclic voltammetry experiments and they also are in agreement with previous observations that hydrogen may be stored in strongly and weakly bonded states, depending on the nature of electrolyte [7,8].

In the case of the two electrolytes herein investigated, one can conclude that weakly bonded hydrogen is the dominant form in KOH medium, whereas the strongly bonded one dominates in Na₂SO₄ medium.

The total charge involved in the discharge process \( (Q_{\text{total discharge}}) \) and the hydrogen storage capacity obtained after subtracting the double-layer charging contribution are collected in Table 3. It can be seen that the electrochemical hydrogen storage capacity is higher in KOH than in Na₂SO₄, mainly for ANK-3. The capacity is also higher for ANK-3 in both electrolytes, which is in agreement with the higher porosity development of this material [6,9,21,22], even though it has a higher amount of surface oxygen groups.

### 3.3. In situ Raman characterization

In order to better understand the mechanism of hydrogen storage, in situ Raman spectroscopy has been used. Figs. 7–10 contain the in situ Raman spectra recorded at different potentials in the two electrolytes with the two carbon materials. The selection of the potentials used to collect in situ Raman spectra was based on the previous cyclic voltammograms.

In general, the D (1350 cm⁻¹) and G (1585 cm⁻¹) bands, which are characteristic of graphene based carbons [30], are observed in all the experiments. The G band corresponds to the graphitic lattice vibration mode, and the D band is related to the presence of defects. It should be mentioned that all the spectra shown were normalized versus the D band. When decreasing the potential, two bands at around 1110 and 1500 cm⁻¹ are observed, which are related to electrochemical hydrogen storage [9] and have been assigned to Csp²-H and C=C stretching vibration, respectively, in amorphous carbon–hydrogen bonds [31,32]. These two bands appear simultaneously when the potential decreases, and disappear simultaneously when the potential goes to more positive values. This indicates that hydrogen chemisorption is reversible, which is in agreement with the results obtained by other authors [7,9].

In Figs. 7 and 8, showing the spectra of the two activated carbons in KOH medium, it can be observed that the bands associated to the carbon–hydrogen bonds appear at \(-0.69 \) and \(-0.59 \) V for ANK-3 and MWV-E510A, respectively, indicating that hydrogen storage proceeds more easily with MWV-E510A. These results suggest that the structural order of the carbon material and, especially, the surface functionality (both related with the raw material, the activation method and post-treatment) may have an influence on the rate of carbon atoms hydrogenation. As it can be seen in Table 1, the amount of surface oxygen groups in ANK-3 is much larger than in MWV-E510A, what makes that carbon–hydrogen bonds in the former will be essentially formed through the reduction of carbon–oxygen surface complexes under cathodic conditions [33]. Such reaction is slower than the direct formation of carbon–hydrogen bonds with the unsaturated carbon atoms of MWV-E510A.

The behavior obtained in Na₂SO₄ medium is similar (see Figs. 9 and 10), and carbon–hydrogen characteristic bands start to appear at \(-0.59 \) V for sample ANK-3 and at \(-0.39 \) V for sample MWV-E510A.

However, there are interesting differences among both electrolytes regarding the potential at which the bands
formation is observed compared to the thermodynamic potential values. Thus, in KOH medium, for the two samples, the formation of carbon–hydrogen bonds starts at more positive potential than the thermodynamic potential value for hydrogen evolution (≈0.87 V), whereas in Na$_2$SO$_4$ medium the hydrogenation of carbon atoms begins at similar value of potential for MWV-E510A and at more negative potential for ANK-3 than the thermodynamic potential value of hydrogen evolution (≈0.34 V). This indicates that carbon–hydrogen bond formation is easier in KOH, what is in agreement with the results obtained from the galvanostatic charge–discharge and cyclic voltammetry experiments that suggest that weakly bonded hydrogen is dominant form in KOH medium and the strongly bonded one dominates in Na$_2$SO$_4$ medium.

It should be noted that for the ANK-3 sample, in both electrolytes, the shape of the D band changes when the bands associated with carbon–hydrogen bonds appear. The shape of the D band depends on the intensities of the D1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution</th>
<th>$Q_{\text{total discharge}}$ (C g$^{-1}$)</th>
<th>H (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANK-3</td>
<td>6 M KOH</td>
<td>1060</td>
<td>0.78</td>
</tr>
<tr>
<td>MWV-E510A</td>
<td>6 M KOH</td>
<td>659</td>
<td>0.46</td>
</tr>
<tr>
<td>ANK-3</td>
<td>0.5 M Na$_2$SO$_4$</td>
<td>774</td>
<td>0.49</td>
</tr>
<tr>
<td>MWV-E510A</td>
<td>0.5 M Na$_2$SO$_4$</td>
<td>564</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Fig. 7** – Raman spectra for the sample ANK-3 at different potentials referred to NHE in 6 M KOH solution. Spectra normalized versus the D band.

**Fig. 8** – Raman spectra for the sample MWV-E510A at different potentials referred to NHE in 6 M KOH solution. Spectra normalized versus the D band.

**Fig. 9** – Raman spectra for sample ANK-3 at different potentials referred to NHE in 0.5 M Na$_2$SO$_4$ solution. Spectra normalized versus the D band.

**Fig. 10** – Raman spectra for sample MWV-E510A at different potentials referred to NHE in 0.5 M Na$_2$SO$_4$ solution. Spectra normalized versus the D band.
In situ Raman spectroscopy confirms that carbon–hydrogen bonds are formed during the charge process in both electrolytes. This hydrogen chemisorption is reversible, and the original Raman spectra of the samples are recovered after the discharge step. Comparing the two samples, it can be suggested that the surface functionality and porosity of the activated carbons have an important influence in the electrochemical hydrogen storage process. It is seen that hydrogen storage proceeds more easily for the sample with lower amount of surface oxygen groups. Moreover, the potential values corresponding to the starting of carbon–hydrogen bonds formation suggest that weakly bonded hydrogen is the dominant form in KOH medium, while strongly bonded hydrogen dominates in Na2SO4 medium. Furthermore, the hydrogenation of carbon atoms seems to produce edges, increasing the intensity of the D1 band of small crystalline domains based structure of ANK-3, as revealed by the intensity increase of the D1 band.

4. Conclusions

In situ Raman spectroscopy confirms that carbon–hydrogen bonds are formed during the charge process in both electrolytes. This hydrogen chemisorption is reversible, and the original Raman spectra of the samples are recovered after the discharge step. Comparing the two samples, it can be suggested that the surface functionality and porosity of the activated carbons have an important influence in the electrochemical hydrogen storage process. It is seen that hydrogen storage proceeds more easily for the sample with lower amount of surface oxygen groups. Moreover, the potential values corresponding to the starting of carbon–hydrogen bonds formation suggest that weakly bonded hydrogen is the dominant form in KOH medium, while strongly bonded hydrogen dominates in Na2SO4 medium. Furthermore, the hydrogenation of carbon atoms seems to produce edges, increasing the intensity of the D1 band of small crystalline domains based structure of ANK-3, as revealed by the intensity increase of the D1 band.

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