Electrooxidation Methods to Produce Pseudocapacitance-containing Porous Carbons

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ABSTRACT

Surface oxygen groups play a key role on the performance of porous carbon electrodes for electrochemical capacitors in aqueous media. The electrooxidation method in NaCl electrolyte using a filter press cell and dimensionally stable anodes is proposed as a viable process for the generation of oxygen groups on porous carbon materials. The experimental set-up is so flexible that allows the easy modification of carbon materials with different configurations, i.e. cloths and granular, obtaining different degrees of oxidation for both conformations without the requirement of binders and conductivity promoters. After the electrooxidation method, the attained porosity is maintained between 90 and 75% of the initial values. The surface oxygen groups generated can increase the capacitance up to a 30% when compared to the pristine material. However, a severe oxidation is detrimental since it may decrease the conductivity and increase the resistance for ion mobility.

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1. Introduction

Due to their unique physico-chemical properties, together with their harmless character, light weight, electrical conductivity and a combination of high availability and well-known and simple synthesis methods, that make them comparatively cheap, carbon materials are currently considered the best choice as electrodes for electrochemical energy storage in supercapacitor devices. 1 The capacitance performance of these materials is mainly based on their high specific surface area, high micropore volume and versatile pore size distributions and conformations. These parameters essentially contribute to the electrochemical double-layer capacitance. They can also show an additional pseudocapacitive contribution coming from certain electrochemically-active functionalities, mainly surface oxygen groups, 2−4 that are usually loaded on the carbon material by oxidative post-treatments after the synthesis procedure. The surface oxygen groups play also a relevant role in the wettability and stability of the porous carbon.

In this sense, the development of processes for tailoring both the porous structure and surface chemistry of carbon materials to optimize both the double-layer and pseudocapacitive contributions has received a great interest. Oxygen functional groups, which are readily found on porous carbon materials and can be incorporated into them by a variety of methods, play an important role in this context. 5−7 Consequently, there have also been a strong interest in the development of processes for tailoring the surface oxygen functionalities of porous carbons. The selection of oxygen-rich precursors can help in this task, but the most straightforward method to obtain different amounts of surface oxygen groups are the oxidation post-treatments.

The electrochemical modification techniques have been demonstrated to show much better controllability than conventional chemical oxidations in liquid phase. 7−9 Essentially, by the right choice of some parameters, the electrochemically-addressed process allows a higher control of the oxidation kinetics as well as of the electro-oxidation mechanism to attain a more efficient and selective introduction of oxygen functionalities than the fast and unselective chemical treatments, what is of upmost importance to increase the pseudocapacitance of carbon materials. Moreover, it has been recently proved the much softer effects of the electro-oxidation technique, compared to conventional chemical treatments, on preserving the structural properties of designed architectures, like that of a zeolite templated carbon (ZTC), which may find potential application in supercapacitors. 9,10

In spite of all these advantages, the practical use and feasibility of the electrochemical methods to optimize carbon materials for supercapacitor applications will require simple, versatile and easily scalable technologies capable to treat not only large amounts of carbon but also to deal with a wide range of conformations.

In previous works, we have systematically studied the electrochemical modification of a granular activated carbon in a filter-press cell. 4−5 However, the suitability of this system towards the electrochemical modification of different types of carbon materials as well as the effect of such electrochemical treatments on their electrochemical performance have not been reported yet. In this sense, the use of activated carbon cloths are of great interest since it permits the possibility of preparing flexible electrodes for capacitors.

In this work two commercial activated carbons (ACs), i.e. a granular activated carbon (GAC) and an activated carbon cloth (ACC), as representative of a discontinuous particle-shaped and a continuous fibrous-shaped carbon material, respectively, have been subjected to galvanostatic treatments in a filter-press electrochemical cell to show its capability and adequacy to address the electrochemical oxidation of carbon materials with completely different...
morphologies and conformations. For this purpose, the textural and chemical properties of the pristine and electrochemically-treated materials have been analyzed and correlated with their electrochemical response. As a consequence, the electro-oxidation of carbon materials in a filter-press is shown as a promising method for the optimization of their surface chemistry.

2. Experimental

2.1 Carbon materials

The commercial activated carbons used along this work as the parent materials were a granular activated carbon provided by Waterlink Sutcliffe Carbons, which is referred as WS, and an activated carbon cloth supplied by MAST Carbon, termed as ExT27. These samples were washed several times with distilled water and dried in an oven using very mild conditions (80°C for 3 h) before each experiment.

2.2 Electrochemical modification of the activated carbons

The electrochemical modification of the aforementioned porous carbons has been carried out in a filter-press electrochemical cell, with a geometrical electrode area of 20 cm². A detailed description of this experimental setup is detailed elsewhere.7,8 To study the influence of the each electrode polarity, the filter-press cell is divided into two compartments by an ionic membrane. Each compartment is defined by the electrode, a flow distributor and the ionic membrane.

The experimental conditions for a typical electrochemical treatment are the following: 2 g of granular activated carbon (W) and about 0.2 g of activated carbon cloth are placed in the anodic compartment of the electrochemical cell. 200 mL of electrolytic solution was continuously recirculated through both compartments by means of centrifugal pumps. The temperature was fixed at 25°C during the experiment. For the proposed anodic modification, an antimony and platinum doped tin dioxide (Ti/SnO₂-Sb-Pt) dimensionally stable anode (DSA) was employed, whereas a stainless steel electrode was used as cathode. In the case of cathodic treatment, the electrode was a platinized titanium (Ti/Pt). An anionic membrane was used as the separator. Electrochemical treatments were carried out at constant current conditions (galvanostatic modification) at 0.2, 0.5, and 1.0 A for 3 h and an Ag/AgCl/Cl⁻ (3 M) electrode was used as a reference electrode. The electrolyte used was 0.5 M NaCl. Merek p.a. chemicals and distilled water were used for the preparation of the solutions (including the 0.5 M H₂SO₄ electrolyte for electrochemical characterization). The cut-off voltages of the working electrode at the end of each anodic experiment were measured using an Ag/AgCl/3 M KCl reference electrode.

The nomenclature of the electrochemically-treated samples includes the name of the parent activated carbon (i.e., W and ExT27); the letters “c” or “a” are used to designate cathodic and anodic treatment, respectively, and a number indicating the applied constant current (0.2, 0.5, or 1.0 A) is included.

2.3 Characterization of the activated carbons

After the galvanostatic experiments, and prior to their characterization, the AC samples were washed with successive portions of distilled water until constant pH. Next, AC samples were dried at 110°C overnight.

Porosity texture of all samples was determined by physical adsorption (N₂ at −196°C and CO₂ at 0°C) using an automatic adsorption system (Autosorb-6, Quantrachrome) after samples out-gassing at 250°C under vacuum for 4 h. The apparent specific surface area (S₆₇₅) was calculated by the BET (Brunauer-Emmett-Teller) method in the relative pressure range of 0.04–0.16 and by NLDFT (Non Local Density Functional Theory). The total micropore volume (pore size below 2 nm, V₆₇₅) was calculated from the application of the Dubinin-Radushkevich equation to the N₂ adsorption at −196°C (range of relative pressures used for the DR analysis was: 0.005 < P/Pₒ < 0.10). The narrow micropore volume (pore size smaller than around 0.7 nm) has been assessed from CO₂ adsorption isotherms at 0°C using the DR equation and for relative pressures below 0.025.11,12 The densities of the adsorbed phases used for the calculations, were 0.808 and 1.023 g/ml for N₂ and CO₂, respectively. The narrow microporosity pore size distribution (PSD) has been obtained from application of NLDFT to the CO₂ adsorption isotherms.

Temperature programmed desorption (TPD) experiments were carried out 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. In these experiments, approx. 10 mg of sample were analyzed. The thermo-balance chamber was purged for 2 hours under a helium flow rate of 100 ml/min⁻¹ and then heated up to 950°C (heating rate 20°C min⁻¹).

For the cyclic voltammetry characterization, composite electrodes were prepared from each powdered porous carbon material, acetylene black (Strem Chemicals) and binder (PTFE, aqueous dispersion (55% solids), Sutcliffe Speakman), in a ratio 80:10:10 wt%, respectively. The materials were mixed and pressed up to 10 Tons for 5 min. The resulting sample was dried for 3 hours at 80°C. Total dry electrode weight used for the measurements was about 100 mg. After that, the composite electrode was placed in a stainless steel mesh as a current collector. In the case of the activated carbon cloths, the sample was placed directly in the stainless steel mesh without binder and acetylene black. The standard three electrode cell configuration was employed for obtaining the cyclic voltammograms. Reversible hydrogen electrode (RHE) was used as reference electrode, a platinum wire was utilized as a counter-electrode. 0.5 M H₂SO₄ was used as aqueous electrolyte in ultrapure water (Purelab ELGA) and a scan rate of 1 mV/s. The capacitance values have been calculated from the integration of the area enclosed by the voltammogram, dividing by two, thus obtaining the average value between charge and discharge processes. The result is then divided by the weight of porous carbon that is, in the case of powdered activated carbon, about 80% of the total composite. All electrochemical measurements were carried out with a standard set-up (Wenkeng potentiostat and a EG&G generator).

3. Results and Discussion

3.1 Textural characterization: N₂ and CO₂ adsorption isotherms

The textural properties, i.e. specific surface area and pore volume, of activated carbons constitute one of their most valued features. In the particular case of enhancement of the electric double layer capacitance on porous carbons, it is broadly accepted that capacitance increases proportionally with surface area, at least up to values higher than 2000 m²·g⁻¹, and that the average pore size of the material must be similar or slightly higher than that of the electrolyte ions, which corresponds with micropores in many cases.13-15 Therefore, any modification of the surface chemistry must be achieved without compromising the structural integrity of the carbon. Table 1 compiles the textural properties for the activated carbon cloth and granular activated carbon series. All the obtained isotherms are of type I according to the IUPAC classification, what is characteristic of microporous solids. In consequence, the reported nitrogen micropore volume accounts for most of the pore volume of the sample. The activated carbon cloth shows a higher surface area, whereas a rough estimation of the mean pore size supposing spherical shape, 3 · V₆₇₅/S₆₇₅ gives similar values for both materials. The comparison between the total micropore volume, V₆₇₅(N₂), and the narrow micropore volume, V₆₇₅(CO₂), provides information about the micropore size distribution.14,15 Micropores
with sizes smaller than 0.7 nm are represented by $V_{\text{DR(CO}_2)}$, while those smaller than 2 nm and bigger than 0.7 nm can be roughly estimated as the difference between $V_{\text{DR(N}_2)}$ and $V_{\text{DR(CO}_2)}$. Figure 1 depicts the pore size distribution obtained from application of NLDFT to CO$_2$ adsorption isotherm at 273 K. The two pristine materials have a similar narrow-micropore size distribution, being most of the pores of a size below 0.7 nm. From the ratio of $V_{\text{DR(CO}_2}$ and $V_{\text{DR(N}_2)}$, we can deduce that both materials have a similar content of narrow microporosity which accounts for about 80% of the total micropore volume.

Some small changes were observed on the textural parameters after the electrochemical treatment. Cathodic treatment did not significantly modify the textural properties for both porous carbon conformations. However, the anodic electrooxidation produces a decrease between 10 and 25% of both the surface area and the micropore volume. CO$_2$-PSDs obtained from ExT27 after the most aggressive treatment, Fig. 1, and the data in Table 1, show a small decrease in porosity contribution of both wide and narrow microporosity, indicating that the phenomena behind the changes in porosity seem to take part in all the porosity range; however, these changes for W samples are not so remarkable. It can also be seen that the higher the current used in the electrochemical treatment, the higher the reduction of the surface area, Table 1. Therefore, this decrease in the porosity can be ascribed to the increase in the amount of surface oxygen groups (as discussed later), which could reduce the mean pore size and therefore hinder or block gas adsorption. This change in textural properties is a feature also frequently observed after the oxidation treatment of microporous activated carbons with acid agents. For instance, Shim et al. obtained a porosity blockage of more than 35% on activated carbon fibers after treating them with 1 M HNO$_3$ at boiling point for 2 hours. Furthermore, under the most drastic conditions (concentrated acid, heating until complete evaporation) necessary to achieve similar oxidation degrees as those obtained by the electrochemical treatment in this work, a greater decrease in surface area and pore volume has been observed, while the average micropore width increases due to the collapse of the pore walls. The milder oxidation conditions obtained by the electrooxidation method seems to favor a homogeneous oxidation of the activated carbon, minimizing the pore mouth blockage produced by more aggressive chemical treatments. In this sense, the benefits of using the electrooxidation treatments are straightforward.

### Table 1. Textural characterization of the activated carbon cloth (ExT27) and granular activated carbon (W) before and after the anodic and cathodic electrochemical treatments.

<table>
<thead>
<tr>
<th>Samples/Current intensity</th>
<th>Anodic treatment</th>
<th>Catholic treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cut-off voltage</td>
<td>$S_{\text{BET}}$</td>
</tr>
<tr>
<td>ExT27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 A</td>
<td>1.36 V</td>
<td>1130</td>
</tr>
<tr>
<td>0.5 A</td>
<td>1.45 V</td>
<td>920</td>
</tr>
<tr>
<td>1.0 A</td>
<td>1.95 V</td>
<td>890</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>870</td>
</tr>
<tr>
<td>0.2 A</td>
<td>1.17 V</td>
<td>850</td>
</tr>
<tr>
<td>0.5 A</td>
<td>1.56 V</td>
<td>770</td>
</tr>
<tr>
<td>1.0 A</td>
<td>2.58 V</td>
<td>770</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>870</td>
</tr>
<tr>
<td>0.2 A</td>
<td>1.17 V</td>
<td>850</td>
</tr>
<tr>
<td>0.5 A</td>
<td>1.56 V</td>
<td>770</td>
</tr>
<tr>
<td>1.0 A</td>
<td>2.58 V</td>
<td>770</td>
</tr>
</tbody>
</table>

Figure 1. (Color online) PSD of the original and anodically electrooxidized carbon samples obtained from DFT analysis of CO$_2$ isotherms.

3.2 Surface chemistry evaluation: TPD experiments

Elemental analyses revealed an important increase on the oxygen amount of the anodically electrodemodified samples. The same conclusion was ensured by XPS, as well as the absence of other elements, such as chlorine or sulfur, apart from carbon, oxygen and nitrogen. As the changes in the surface chemistry rely mostly on the nature and amount of surface oxygen functionalities, they were studied by temperature programmed desorption. TPD remains as one of the most used techniques that can, qualitatively and quantitatively, provide the broad outline of the distribution of oxygen functional groups throughout the surface of carbon materials. Past studies have reported that upon heat treatment in inert environment, oxygen functional groups such as carboxyls, anhydrides, and lactones desorb as CO$_2$ while hydroxyl, carbonyl, and quinone groups desorb as CO. The literature reports that carboxylic acid and anhydrides surface groups decompose at low temperatures, while lactones are more stable and evolve at higher temperatures. On the other hand, thermal stability of the functional groups causes that the CO decomposing-groups follow the anhydrides, phenols and quinones/carboxyls order. Figure 2 represents the CO and CO$_2$ profiles for the anodically electrooxidized ExT27 and W carbon materials. ExT27 is richer in the amount and variety of surface oxygen groups than the granular activated carbon. The proposed galvanostatic treatment causes a high increase in both desorption profiles, even at the lowest current employed. Interestingly, the TPD profile for the samples obtained at the highest current is very similar for both activated carbons. The underlying mechanism for this oxidation has been described as the combination of two processes, that is, the direct anodic oxidation of the carbon surface caused by the applied positive potential and the indirect oxidation process, which is attributed to the formation of...
concentration than the granular one at all the applied currents. Even after such calculation, the ACC shows a higher surface oxygen total amount is divided by the surface area of the sample. be electrooxidized. To rule out the effect of the textural properties, higher surface area could have more active sites which are prone to argued that, considering a similar structural order, the ACC having a obtained results, as well as the total oxygen content. It could be the estimation of total CO and CO2 amounts. Table 2 details the closer to that of the chemical oxidation treatment. The chloride ions are able to form free chlorine, hypochlorite ions oxidizing species coming from chloride oxidation over the electrode. The chloride ions are able to form free chlorine, hypochlorite ions and hypochlorous acid in solution,20,21 which are strong oxidizing agents that will be available for diffusion into the pore network of the carbons producing the oxidation of the surface on a mechanism closer to that of the chemical oxidation treatment.
The areas under the TPD profiles have been integrated, allowing the estimation of total CO and CO2 amounts. Table 2 details the obtained results, as well as the total oxygen content. It could be argued that, considering a similar structural order, the ACC having a higher surface area could have more active sites which are prone to be electrooxidized. To rule out the effect of the textural properties, total oxygen amount is divided by the surface area of the sample. Even after such calculation, the ACC shows a higher surface oxygen concentration than the granular one at all the applied currents (Table 2).

Moreover, regarding the increase in current, the electrooxidation treatment appears to behave differently for each carbon conformation. The W activated carbon seems to be current sensitive for the tested values, whereas the ACC reaches almost the highest amounts of surface oxygen groups at the lowest current used (0.2 A). Such a different behavior can be explained by the higher specific charge, i.e. charge divided by sample weight, which was used on the electrooxidation of the activated carbon cloth. This number is for ExT27 roughly ten times higher than that of W carbon, so the concentration of oxidizing species with respect to the amount of carbon material is higher in this case. It cannot be discarded that it may also be caused by the better contact between the cloths and the electrode. The ACC can be easily deployed dressing the electrode, so the cloth is directly in contact with the electrode, and the surface of the ACC may be more polarized than in the case of the granular porous carbon, rendering a more efficient electrooxidation treatment.

In order to clarify these aspects, Fig. 3 plots the increase in the amount of CO- and CO2-type surface oxygen groups and the increase in the total amount of oxygen loaded on the carbon surface, with respect to the specific charge applied in the anodic treatment, for electrooxidized materials coming from both W and ExT27. The ΔCO/ΔCO2 ratio is also included in the figure. There seems to be a good agreement between the data points of all the samples considering the very different morphology of W and ExT27 pristine activated carbons. As these points seem to fit in the same curve, it further supports that the most likely argument regarding the high oxidation extent attained in ACC sample is that it is a consequence of the excess on the employed specific charge. It can be seen that the increments in the total oxygen amount grow logarithmically with the specific charge. This is similar for the increase in both CO- and CO2-type oxygen groups. The slope of these curves reaches a nearly zero value when the anodic specific charge is higher than 10000 C·g⁻¹. Moreover, Fig. 3 also shows that high ΔCO/ΔCO2 ratios are formed at low oxidation levels and they diminish until levelling off from the same specific charge of 10000 C·g⁻¹.

**Table 2.** CO and CO2 evolved from TPD experiments and specific capacitance obtained from CV analyses for the anodically electrooxidized carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO  µmol·g⁻¹</th>
<th>CO2 µmol·g⁻¹</th>
<th>O µmol·g⁻¹</th>
<th>ΔCO/ΔCO2</th>
<th>O/SBET</th>
<th>C F·g⁻¹</th>
<th>ExT27</th>
<th>ExT27a0.2</th>
<th>ExT27a0.5</th>
<th>ExT27a1.0</th>
<th>W</th>
<th>Wa0.2</th>
<th>Wa0.5</th>
<th>Wa1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>ExT27</td>
<td>1370</td>
<td>665</td>
<td>2700</td>
<td>—</td>
<td>2.38</td>
<td>137</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ExT27a0.2</td>
<td>4110</td>
<td>2230</td>
<td>8570</td>
<td>1.75</td>
<td>8.08</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ExT27a0.5</td>
<td>4220</td>
<td>2290</td>
<td>8800</td>
<td>1.75</td>
<td>9.56</td>
<td>143</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ExT27a1.0</td>
<td>4560</td>
<td>2630</td>
<td>9820</td>
<td>1.62</td>
<td>11.03</td>
<td>47</td>
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<tr>
<td>W</td>
<td>420</td>
<td>390</td>
<td>1200</td>
<td>—</td>
<td>1.37</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Wa0.2</td>
<td>1320</td>
<td>640</td>
<td>2600</td>
<td>3.60</td>
<td>3.06</td>
<td>119</td>
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<td></td>
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<tr>
<td>Wa0.5</td>
<td>2370</td>
<td>1340</td>
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<td>2.06</td>
<td>6.56</td>
<td>143</td>
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<tr>
<td>Wa1.0</td>
<td>2800</td>
<td>1570</td>
<td>5950</td>
<td>2.02</td>
<td>7.72</td>
<td>124</td>
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</table>

**Figure 2.** (Color online) TPD profiles for the original and anodically electrooxidized carbon samples. Heating rate: 20 K·min⁻¹.
The above results suggest that for the preferential CO-type group generation on the carbon surface in the 0.5 M NaCl electrolyte, the specific capacitance behavior of an electrode material would result in a rectangular shape of the cyclic voltammogram. Materials with pseudocapacitance show redox peaks coming from electron transfer reactions. Figure 4 displays the CVs obtained for the W activated carbon before and after the electrochemical treatment on both anodic and cathodic conditions.

The pristine activated carbon presents a CV more similar to the rectangular shape, with the presence of a small reversible redox process at around 0.53 V. Formally, the reduction potential of the quinone/hydroquinone peak is reported to be around 0.7 V vs. NHE, although this potential value is lowered when the number of aromatic rings bonded to the oxygen group, i.e. the case of quinone groups on edge sites of graphene layers of activated carbons, is increased. These carbonyl/quinone type groups can be assessed on the W sample as those of high thermal stability that evolved as CO during the negative scan at around 0.55 V.

The specific capacitance values of parent and electrooxidized samples obtained from the voltammograms are reported on Tables 2 and the capacitance values of parent and electrooxidized samples obtained from the voltammograms are reported on Tables 2 and 3.
and 3. For the voltammograms in Fig. 4(a) for the W sample, a clear increase in capacitance is attained after the electrooxidation treatment. Moreover, if surface capacitance is estimated from the W capacitance and BET area results (similar results are obtained using the DFT surface area), it is possible to draw an estimation of the expected capacitance on Wa0.5 sample assuming a linear relationship between capacitance and surface area. W specific capacitance is 0.126 F·m⁻², rendering an expected capacitance of 97 F·g⁻¹ for Wa0.5. This result points out that the contribution of the presence of surface oxygen groups, probably by pseudocapacitance development, can be stated to be around 46 F·g⁻¹, accounting for 33% of the total capacitance.

The voltammograms of cathodically electrotreated granular activated carbon samples are plotted in Fig. 4(b). The obtained voltammograms are almost identical to that of the parent carbon. One should note that this result is somewhat expected. As previously discussed, cathodic electrotreatment of porous carbons did not produce any substantial increase of CO-desorbing groups. This result further confirms that cathodic treatment in NaCl electrolyte is not suited for capacitance enhancement of porous carbons in aqueous media.

Another interesting feature of the voltammograms is the slope of the curve on the edges of the CV, where the polarity of the sweep rate is reversed at the end of a positive or negative scan. This slope is inversely proportional to the electrical series resistance of the sample. Nian and Teng suggested that the presence of CO₂ desorbing complexes would retard the double layer mechanism.²² If carboxylic acids are introduced in high amounts [sample Wa1.0 in Fig. 4(a)] in the pore mouth, their ability to strongly attach water molecules can block the access to the pore and consequently hinder the mobility of ions into the porous structure, producing a decrease in the slope.²³ As has been discussed before, the electrooxidation seems to produce the oxidation along all the available carbon surface,²⁴ so the sieving effect by the presence of carboxylic acids may be avoided using mild electrooxidation instead of classical oxidation methods.

Figure 5 shows the cyclic voltammograms obtained from pristine and anodically electrooxidized ACC. Similarly to the case of the granular activated carbon, the original ACC presents a small and wide redox peak corresponding to the CO-evolving surface oxygen groups on the carbon surface. The resulting capacitance is higher for the ACC than for the W activated carbon (see Table 2), in agreement with the higher surface area and amount of surface oxygen groups in the pristine carbon cloth. However, the electrooxidation of ExT27 produced a tilt distortion of the voltammogram, even at the lowest current employed. This feature manifests the problems of charge propagation on the oxidized samples, even at such a low sweep rate. We have previously discussed that the use of a lower weight of ACC rendered higher oxidation extent on this sample, probably due to an excess on the specific charge. As seen in Table 2, gravimetric capacitance is only slightly increased for the oxidized samples, prepared at low and medium oxidation currents, but when it is expressed with respect to the surface area, the capacitance moves from the initial 0.118 F·m⁻² to 0.139 and 0.155 F·m⁻² for low and medium current, respectively. This shows that the introduced surface oxygen groups contribute to the capacitance. The contribution of these surface complexes can be seen in the positive scan of the voltammogram of ExT27a0.5 sample, Fig. 5. Again, a broad peak with a maximum on the vicinity of 0.7 V is observed. On the negative scan, the peak maximum is shifted to 0.3 V, indicating the irreversibility of the redox processes involved. In the case of ExT27a1.0 sample, the voltammogram appears with a high ohmic drop as consequence of the loss of electrical conductivity after a severe electrooxidation treatment (we have to take into account that in these samples no promoter of conductivity has been used for cyclic voltammetry characterization). Moreover, problems of ions diffusivity into porosity have to be considered.

The results on the electrochemical characterization of the electrooxidized samples confirms that it is possible to selectively generate surface oxygen groups that promote pseudocapacitance by electrooxidation, although a severe oxidation is detrimental since it may decrease the conductivity and increase the resistance for ion mobility.

4. Conclusions

Electrochemical treatment of two porous carbon materials, one granular activated carbon and an activated carbon cloth, has been carried out in a filter press system using DSA electrode and 0.5 M NaCl electrolyte and without using neither binder nor conductivity promoter. Anodic and cathodic configurations using currents of 0.2, 0.5 and 1.0 A were applied for achieving high oxidation degrees. The textural parameters derived from N₂ and CO₂ adsorption isotherms demonstrated a porosity decrease between 10 and 25% after the anodic treatments, being higher with increasing the specific charge. The TPD analyses demonstrate that electrooxidation permits to control the amount of surface oxygen groups in the samples and mild oxidation treatments are beneficial in terms of pseudocapacitance contribution. However, at high specific charges, as those employed on the treatment of the activated carbon cloth, oxidation degree is very important and a saturation effect upon the insertion of oxygen groups is observed. The electrochemical characterization by cyclic voltammetry of anodically modified porous carbons points out a clear capacitance enhancement by the contribution of redox processes attributed to surface oxygen groups. However, if the oxidation degree is very important, then a decrease of the electrical conductivity of the porous carbon and a significant pore blockage may occur, what is not beneficial for a material in supercapacitors. The cathodic treatment does not modify significantly the porous texture and surface oxygen groups.

The results reported in this work point out the versatility of this technique for the modification of the surface chemistry of activated carbons, although the electrooxidation conditions have to be carefully chosen to get an improvement in the electrochemical capacitors application.

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