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Tailoring the Surface Chemistry of Activated Carbon Cloth by Electrochemical Methods

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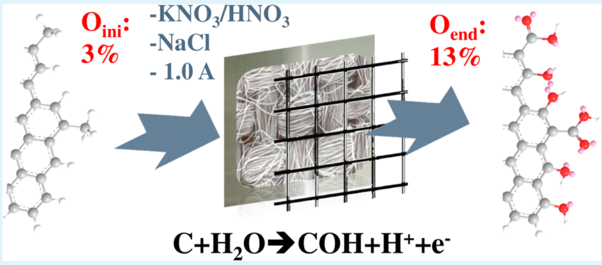
Supporting Information

ABSTRACT: This paper presents a systematic study of the effect of the electrochemical treatment (galvanostatic electrolysis in a filter-press electrochemical cell) on the surface chemistry and porous texture of commercial activated carbon cloth. The same treatments have been conducted over a granular activated carbon in order to clarify the effect of morphology. The influence of different electrochemical variables, such as the electrode polarity (anodic or cathodic), the applied current (between 0.2 and 1.0 A) and the type of electrolyte (HNO_3 and NaCl) have also been analyzed. The anodic treatment of both activated carbons causes an increase in the amount of surface oxygen groups, whereas the cathodic treatment does not produce any relevant modification of the surface chemistry. The HNO_3 electrolyte produced a lower generation of oxygen groups than the NaCl one, but differences in the achieved distribution of surface groups can be beneficial to selectively tune the surface chemistry. The porous texture seems to be unaltered after the electro-oxidation treatment. The validity of this method to introduce surface oxygen groups with a pseudocapacitive behavior has been corroborated by cyclic voltammetry. As a conclusion, the electrochemical treatment can be easily implemented to selectively and quantitatively modify the surface chemistry of activated carbons with different shapes and morphologies.



KEYWORDS: *electro-oxidation, porous carbon materials, activated carbon fiber, functionalization, surface chemistry, surface modification*

1. INTRODUCTION

The practical use and applications of activated carbons (ACs) in many industrial fields and technologies are based on their outstanding physicochemical properties, especially the surface area, the porous texture and the surface chemistry. In particular, the relevance of surface oxygen groups (SOGs) in the performance of carbon materials has been known for many years.[1−3] Activated carbon fibers are an interesting morphology for carbon materials for adsorption-related applications.[4−8] They are easily handled and used, show a reduced mass-transfer resistance due to the adequate arrangement of their microporosity and the shorter diffusion length when compared to granular activated carbons (GACs)[9,10] and have good hydrodynamic response with low pressure drops because of the empty spaces between fibers.[8,11] In addition, they can be woven or knitted into activated carbon cloths (ACCs), which is an advantage from an application point of view.

An appropriate modification of the surface chemistry can be useful to improve the performance of the carbon material and different methods are usually applied to modify the concentration and nature of surface functional groups. The most widely used methods are, essentially, chemical reactions in either gas or liquid phase with oxidizing or reducing agents and further heat treatments in an inert atmosphere. However, the electrochemical methods[12−20] are not so often applied to modify the surface chemistry of carbon materials and few studies focus on ACCs.[20,21] This method[15−21] has emerged as a promising technique for the modification of the surface chemistry of carbon materials in aqueous and organic solvents, because it presents several advantages when compared to conventional methods; mainly, (i) the treatment can be immediately interrupted; (ii) it can be run at room temperature and atmospheric pressure; (iii) the reaction conditions can be easily reproduced; (iv) oxidation and reduction processes are more selective and easily controlled by means of the proper setting of the applied current or electrode potential.

Received: April 23, 2014
Accepted: June 23, 2014
Published: June 23, 2014

The electrochemical modification of a commercially available GAC has been recently studied in our research group. The influence of the electrode polarity (anodic or cathodic), the applied current, the type of electrolyte and the electrode material were analyzed in detail.[17,19,20] In particular, it was observed that the anodic treatment in NaCl results in a high surface oxidation degree. This method was also applied to a powdered zeolite template carbon.[22]

This work is intended to find out the effect and efficiency of the electrochemical treatment in activated carbon cloths, because these are flexible materials with diameter in the 10–40 μm range with a low tortuosity porous structure and much faster mass-transfer rate compared to granular or powdered activated carbons.[5] In addition, other oxidizing electrolytes like HNO_3, whose utilization has been reported in the literature, will be studied.[23] Therefore, a systematic study of the electrochemical modification of a commercial activated carbon cloth is undertaken, in which the influence of different electrochemical variables, such as the electrode polarity (anodic or cathodic), the applied current and the type of electrolyte has been explored. A commercial granular activated carbon has also been modified in order to clarify any possible effect of the carbon morphology. The electrochemical treatments of these ACs have been carried out in a filter-press cell at constant current and the surface chemistry and porous texture of the electrochemically treated activated carbon samples have been characterized by gas adsorption, temperature-programmed desorption (TPD) and cyclic voltammetry.

2. EXPERIMENTAL SECTION

2.1. Materials. The commercial porous carbons selected for this study were a granular activated carbon provided by Waterlink Sutcliffe Carbons (pH at the point of zero charge, $pH_{PZC} = 9$), henceforth referred to as W, and a knitted, viscose-based activated carbon cloth, C-TEX20, supplied by MAST Carbon ($pH_{PZC} = 7.5$) and denoted henceforth as EX20. The samples were washed several times with distilled water and dried in an oven using very mild conditions (353 K for 3 h) before each electrochemical experiment.

2.2. Electrochemical Treatment of Porous Carbons. The electrochemical treatment of the carbon materials has been carried out in a filter-press electrochemical cell, with a plane electrode area of 20 cm^2. A detailed description of this experimental setup is reported elsewhere.[17] To study the influence of the electrode polarity, but minimizing the possible effects of the counter electrode, the filter-press cell is divided into two compartments by an appropriate ionic membrane. Each compartment is defined by the electrode, a flow distributor and the membrane. The experimental conditions for the electrochemical treatment were the following: 2 g of W or about 0.2 g of EX20, depending on the initial cut to fit into the measurement cell, was located in the electrochemical cell either in the anodic or cathodic compartment in close contact with the corresponding electrode. The electrolytic solutions (200 mL) were continuously stirred and forced to pass through both compartments by means of centrifugal pumps. The temperature was controlled at 298 K during the experiment. In the cathodic treatment, a platinized titanium (Pt/Ti) electrode was used as the anode whereas an antimony and platinum doped tin dioxide (SnO_2–Sb–Pt) DSA-like electrode was employed in the anodic treatment. In both processes, a stainless steel electrode was used as the cathode. The cell compartment separation was achieved using a cationic membrane in the case of the experiments performed in HNO_3/KNO_3 or an anionic membrane in that for NaCl. Electrochemical treatments were carried out at constant current conditions (galvanostatic) at 0.2, 0.5 and 1.0 A for 3 h. The electrolytes used were 0.5 M NaCl and 0.01 M HNO_3 + 0.5 M KNO_3 (pH = 2). Merck p.a. chemicals and distilled water were used for the preparation of the solutions. After the electrochemical experiments, and prior to their characterization, the samples were washed with successive portions of distilled water until constant pH. Next, they were dried at 383 K overnight.

The nomenclature of the electrochemically treated samples includes the name of the carbon material (i.e., W and EX20), the letters "c" or "a" to designate cathodic and anodic treatment, respectively, a number indicating the applied constant current (0.2, 0.5, or 1.0 A) and H^+ and Cl^- corresponding to the HNO_3/KNO_3 and NaCl electrolyte solutions, respectively.

2.3. Porous Texture Characterization. The porous texture of all samples was determined by physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6B, Quantrachrome Corporation) after outgassing them at 523 K under a vacuum for 4 h. Nitrogen adsorption at 77 K was used for determining the total volume of micropores ($V_{DR}(N_2)$) (pore sizes smaller than 2 nm) applying the Dubinin–Radushkevich (DR) equation (the range of relative pressures used for the DR analysis was $0.01 < P/P_0 < 0.1$) and for determining the apparent specific surface area by the Brunauer–Emmett–Teller (BET) equation (S_{BET}). The adsorption of CO_2 at 273 K was used to assess the narrowest micropores ($V_{DR}(CO_2)$) (pore sizes smaller than ~0.7 nm) also by application of the Dubinin–Radushkevich equation for relative pressures below 0.025.[24,25]

2.4. Surface Chemistry Characterization. The nature and amount of surface oxygen groups (SOGs) was assessed by temperature-programmed desorption (TPD) experiments, using a differential scanning calorimetry–thermal gravimetric analysis (DSC–TGA) instrument (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3). In these experiments, 10 mg of the sample was heated up to 950 °C (heating rate 20 °C/min) under a helium flow rate of 100 mL/min. In general, the TPD profiles show CO and CO_2 peaks which can be deconvoluted for a more detailed assessment of the surface chemistry. SOGs on carbon materials decompose upon heating by releasing CO and CO_2 at different temperatures. CO_2 results from decomposition of carboxylic acids at low temperatures, or lactones at higher temperatures; carboxylic anhydrides yield both a CO and a CO_2 molecules; phenols, ethers and carbonyls (and quinones) evolve as CO.[3] A multiple Gaussian function has been shown to fit the data adequately, allowing for the quantitative determination of the amount of each functional group on the surface.[26,27]

2.5. Electrochemical Characterization. The electrochemical characterization was performed with cyclic voltammetry (CV) in an electrochemical cell with three electrodes. Reversible hydrogen electrode (RHE) and platinum wire were used as the reference and counter electrode, respectively. A solution of 0.5 M H_2SO_4 was used as the electrolyte. The working electrodes made of treated W were prepared from powdered activated carbon, mixed with acetylene black and Teflon at 80:10:10 ratio, respectively. The total mass of the electrode was about 100 mg and the mixture was compressed to a pressure of 3 tons for 10 min, obtaining a monolith, which is placed on a current collector made of stainless steel. Prior to use, the electrode assembly was dried at 353 K for 3 h. The EX20 samples were also dried and placed directly on the current collector without any carbon black and binder. The cyclic voltammetry measurements were recorded on a Wenking potentiostat and EG&G generator at room temperature. Gravimetric capacitance (C) was determined from the average charge obtained from the positive and negative sweep of the CV and dividing the obtained value between the potential window (1 V) and the weight of the activated carbon.

3. RESULTS AND DISCUSSION

3.1. Porous Texture Characterization. Table 1 summarizes the main textural properties, such as the apparent surface area (S_{BET}), the total volume of micropores (V_{DR} (N_2)) and the volume of narrow micropores (V_{DR} (CO_2) for original EX20 and W materials, and the corresponding samples treated anodically or cathodically at different electrolysis currents in the different electrolytes. The N_2 adsorption isotherms are of type I

Table 1. Textural Characterization of the Original Activated Carbons and the Anodically- And Cathodically-Treated Activated Carbon Samples at Different Currents in Different Electrolytes

samples	S_{BET} (m^2/g)	VDR(N_2) (cm^3/g)	VDR(CO_2) (cm^3/g)
W	870	0.37	0.24
Wa 0.2 H^+	930	0.37	0.25
Wa 0.5 H^+	900	0.37	0.24
Wa 1.0 H^+	890	0.36	0.26
Wa 0.2 Cl^-	820	0.33	0.23
Wa 0.5 Cl^-	740	0.30	0.23
Wa 1.0 Cl^-	830	0.34	0.23
Wc 0.2 H+	920	0.37	0.25
Wc 0.5 H^+	860	0.36	0.25
Wc 1.0 H^+	860	0.34	0.24
Wc 0.2 Cl^-	920	0.37	0.22
Wc 0.5 Cl^-	900	0.37	0.25
Wc 1.0 Cl^-	940	0.37	0.24
EX20	890	0.41	0.35
EX20a0.2 H^+	820	0.39	0.35
EX20a0.5 H^+	840	0.40	0.32
EX20a1.0 H^+	860	0.41	0.36
EX20a0.2 Cl^-	800	0.39	0.30
EX20a0.5 Cl^-	740	0.35	0.29
EX20a1.0 Cl^-	740	0.35	0.30
EX20c0.2 H^+	860	0.41	0.34
EX20c0.5 H^+	880	0.41	0.32
EX20c1.0 H^+	870	0.41	0.35
EX20c0.2 Cl^-	870	0.41	0.33
EX20c0.5 Cl^-	850	0.41	0.33
EX20c1.0 Cl^-	860	0.41	0.37

according to the IUPAC classification, although that for W shows some mesoporosity contribution. The isotherm shape is unaltered as a result of the electrochemical treatments, but some of them cause a slightly lower nitrogen uptake. The micropore volumes measured by the DR method and the BET surface areas are fairly similar between EX20 and W samples, although the micropore volume measured by application of the DR method to CO_2 adsorption at 273 K is higher in EX20. W has some amount of supermicroporosity, as reflected by the larger value of the DR N_2 volume compared to the DR CO_2 volume, whereas EX20 porosity is more homogeneous, and also narrower than that of the granular carbon.[24,25]

As it can be observed in Table 1, neither the anodic nor cathodic treatments produce an important modification of the porous texture of the activated carbon under the studied conditions. The slight decrease in the porosity could be attributed to the increase in the concentration of surface oxygen groups, which could hinder or block the nitrogen adsorption. As it has been previously found,[26] this reduction in textural properties is lower than that observed when using chemical oxidation treatments.[19,28,29]

3.2. Surface Chemistry Characterization of Anodically Treated Porous Carbons. Figure 1 contains the CO_2 and CO TPD profiles obtained for the pristine EX20 sample, and those treated anodically at different currents in different electrolytes. TPDs for pristine and anodically treated W are presented in the Supporting Information. Table 2 summarizes the CO and the CO_2 amounts evolved in these TPD experiments. The reported total amount of oxygen (O) was calculated from the oxygen contained in the evolved CO and CO_2.

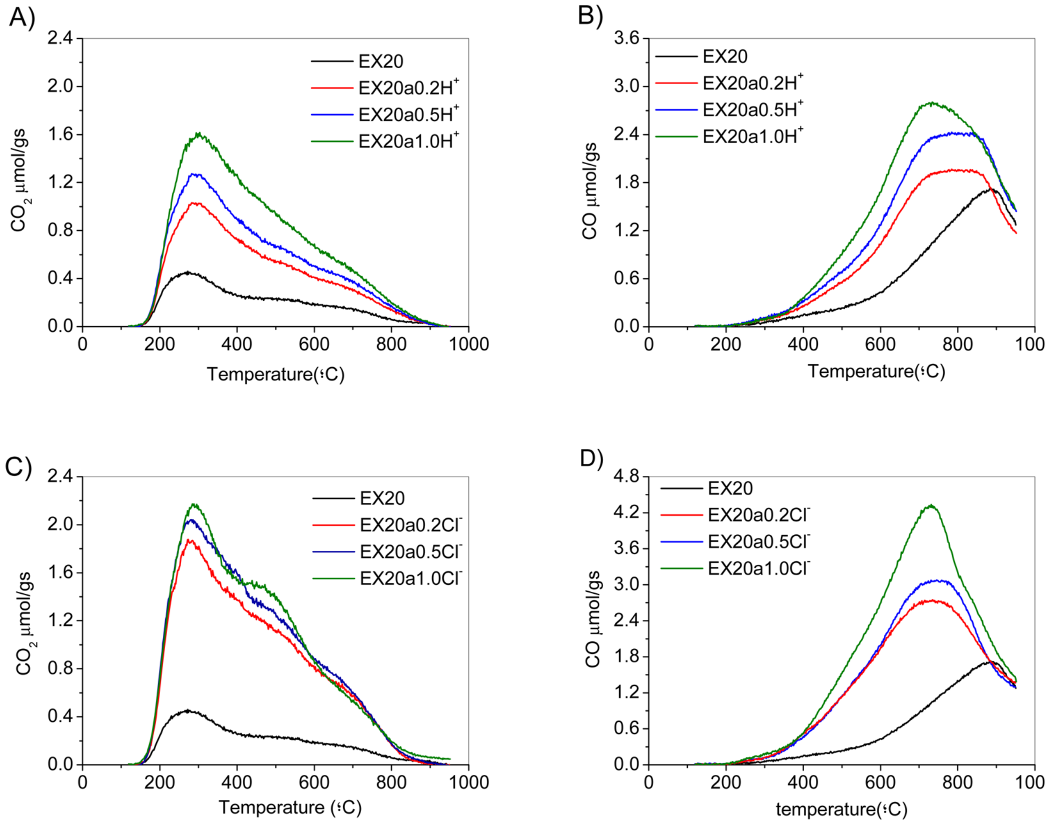


Figure 1. TPD profiles of untreated and anodically treated EX20 in 0.01 M HNO_3/0.5 M KNO_3 (a,b) or 0.5 M NaCl (c,d) at different currents.

Table 2. CO and CO_2 Evolved and the Total Amount of Oxygen (O) from TPD Experiments, CO/CO_2 ratio, Electrochemical Oxidation Efficiency (ε) and Specific Capacity of the Original and Anodically-Treated Activated Carbon Samples

sample	CO (μmol/g)	CO_2 (μmol/g)	O (μmol/g)	ΔO (μmol/g)	CO/CO_2	efficiency (μmol/g/C)	C (F/g)
W	620	260	1130		2.38		110
Wa 0.2 H^+	1380	570	2520	1320	2.42	0.61	118
Wa 0.5 H^+	1810	700	3210	2010	2.59	0.37	130
Wa 1.0 H^+	2870	1560	5990	4790	1.84	0.44	142
Wa 0.2 Cl^-	2570	1020	4610	3410	2.52	1.57	118
Wa 0.5 Cl^-	3230	1200	5630	4430	2.69	0.82	138
Wa 1.0 Cl^-	3340	1440	6220	5020	2.32	0.46	125
EX20	1420	540	2490		2.65		138
EX20a 0.2 H^+	2180	1120	4420	1930	1.95	0.89	149
EX20a 0.5 H^+	2700	1380	4520	2030	1.96	0.37	164
EX20a 1.0 H^+	3090	1760	6610	4120	1.75	0.38	178
EX20a 0.2 Cl^-	3140	2020	7180	4690	1.55	2.17	145
EX20a 0.5 Cl^-	3330	2270	7870	5380	1.47	0.99	165
EX20a 1.0 Cl^-	4280	2230	8740	6250	1.92	0.57	189

Both the untreated W and EX20 have a low amount of oxygen surface functionalities, being higher in the case of the activated carbon cloth. A severe modification of their surface chemistry is appreciated after the anodic electrochemical treatments. Moreover, there are significant differences in the surface chemistry of the samples obtained using either NaCl or HNO_3 as the electrolyte independently of the morphology of the carbon sample. Thus, the selection of the solution used as the electrolyte provides an experimental variable that allows tailoring the amount and nature of oxygen surface groups.

Nitric acid has been widely reported as an effective oxidizing agent for the modification of the surface chemistry of activated carbons. Nitric acid treatment by boiling to dryness a HNO_3 solution containing a porous carbon material introduces more oxygen surface groups than other oxidizing agents, as H_2O_2 or $(NH_4)_2S_2O_8$, at room temperature and it is particularly effective for introducing carboxylic acid groups.[28,30] The electrochemical modification in HNO_3 is able to generate large amounts of oxygen surface groups more efficiently using softer conditions than the conventional chemical treatment. The application of anodic current increases both the amount of CO_2 and CO-releasing surface complexes. In addition, an increase in current causes a higher degree of oxidation, i.e., higher oxygen content. For the sake of comparison, the chemical oxidation of the same GAC by boiling until dryness a solution of 23 wt % HNO_3 resulted in a total oxygen content of 2526 μmol/g,[19] which is lower than that reported in this work at higher currents (Table 2). The CO/CO_2 ratio slowly decreases with the extent of treatment, which seems to be commonplace to all wet oxidation methods, either chemical or electrochemical.[19,26,28]

In NaCl medium (Figure 1b,d and Table 2), the anodic treatment causes a higher amount of oxygen compared with the acid medium at the same applied current. Similarly, the amount of both CO- and CO_2-evolving groups also increases significantly. The greater oxidation degree obtained with the treatment in NaCl could be due to the electrogeneration of chlorine or chlorine radicals over the platinum and antimony doped tin dioxide DSA electrode surface[31] and other oxidant species that can be produced in an aqueous Cl_2 solution by disproportionation like hypochlorite/hypochlorous acid species.[32] Those species, which are strong oxidants, are able to diffuse into the porosity of the porous carbon materials and oxidize the inner surface in a process similar to that found in wet oxidation methods, which can be called indirect electro-oxidation.[22] It can be also accompanied by the electro-oxidation of the polarized carbon surface by water or by oxygen radicals formed over the carbon surface when the electrode is submitted to a positive potential, in a process called direct electro-oxidation.[22]

When the oxidation degree of EX20 is compared with that of W (Table 2), it can be observed that the former presents a higher oxidation degree and a lower CO/CO_2 ratio for all the tested oxidation conditions. The difference in oxidation degree is especially significant at low and medium currents. The lower CO/CO_2 ratio found in treated EX20 compared to as-received fabrics suggests that the formation of CO_2-releasing surface functionalities is favored. By contrast, treated W exhibits a CO/CO_2 ratio higher than that of the untreated material, and hence an enhancement in the formation of CO-like desorbing surface oxygen groups can be proposed. In the nitric acid electrolyte, considering the low concentration of oxidizing species and the low temperature used, the mechanism for modification of activated carbons should proceed preferentially through direct electrochemical surface oxidation, i.e., with the carbon materials behaving as electrodes. Then, the differences in the extent of oxidation degree are expected to be related to the distinct performance of W and EX20 as electrode materials.

The behavior of carbon materials as electrodes for electron transfer reactions in aqueous media is affected by several properties, namely, electrical conductivity, crystallinity, edge-to-basal sites ratio, wettability, surface area and porosity.[33] The two carbon materials investigated herein have a similar BET surface area and micropore volume (see Table 1), they possess a sufficiently high amount of surface oxygen groups (Table 2) to render their surfaces highly hydrophilic and readily available and also, as activated carbons, they have a low degree of crystallinity with small-size, randomly oriented basic structural units and an enhanced edge-to basal sites ratio. As a result of their structural disorder, activated carbons are relatively poor electrical conductors compared to other carbon materials. However, the practical ohmic resistance of a porous activated carbon electrode is a function of the intraparticle resistance and the contact or interparticle resistance. Depending on the physical conformation of the carbon material, contact resistance may give the major contribution to the total resistance. This is likely a key factor that may provide an explanation for the differences between W and EX20. The fibrous morphology and knitted structure of EX20 reduces the interparticle contact problems and provides a more intimate and effective contact between the fabric and the electrode, thus lowering the electrical resistance of the electrode−EX20 assembly. On the contrary, W is allocated inside the filter-press cell in a packed-bed-like configuration, with a looser contact among particles and with the electrode, which presumably causes a high contact resistance and a sharp (and probably uneven) potential drop across the bed. Then, electrochemical surface oxidation reactions are facilitated on EX20 and a higher oxidation degree is reached at the same applied current, especially at 0.2 and 0.5A, where the indirect oxidation is mostly neglected.

A second factor is the different weight of treated carbon (ten times lower in the case of carbon fabric). Then, the surface area exposed by EX20 to the electrolyte is much lower (see S_{BET} in Table 1) and the current density (current per unit surface area) is higher (by a factor of 11, if it is assumed that all the surface is accessible to the electrolyte). At the same input current, the larger charge passed per second and unit surface area in EX20 necessarily implies the formation of a higher surface concentration of oxygen groups and, provided that both type of carbon materials have nearly the same BET surface area, a higher amount of functional groups per gram of carbon than the granular carbon. In addition, a higher current density imposes a higher anodic overpotential to the carbon material and hence it raises the ability to reoxidize freshly generated CO-type groups to CO_2-type groups.

Activated carbon cloths electro-oxidized in NaCl medium also exhibit CO/CO_2 ratios lower than granular activated carbons (Table 2). In this chloride-containing electrolyte, electrogenerated chlorine-like species can be responsible for the oxidation of the carbon surface. Therefore, an enhancement in the production of CO_2-evolving groups should be related to a higher effective concentration of the oxidizing species within the carbon pores. A high effective concentration of oxidants can be much more easily achieved in carbon cloths because of (i) the smaller amount of carbon material exposed to the same amount of electrogenerated species (only dependent on the applied current), (ii) their aforementioned better performance as electrode, which favors efficient electrochemical generation of chlorine species within the pores and (iii) enhanced mass transfer of oxidizing species formed at the metal oxide mesh or on the carbon external surface to the inner pore network. Mass transfer inside the pore network of a carbon particle is a complex process that depends on several factors such as pore size distribution and tortuosity, particle size, temperature, bulk concentration of diffusing molecule and carbon surface chemistry, among others. The impact of these factors upon the concentration of the oxidizing species in our system can be summarized in the effective diffusivity coefficient and the particle radii, the mass transfer rate being proportional to the diffusivity coefficient, and inversely proportional to the square of the particle size.[34]

Diffusivity coefficients can be considered similar in both samples, because these porous carbons have a similar BET surface area, micropore volume and average pore size (1.7 vs 1.8 nm for W and EX20 when estimated as $4 \cdot V_{DR}/S_{BET}$). However, the diameter of the activated carbon fibers forming EX20 is around 7 μm, which is 200 times lesser than the particle size of W (∼1.5 mm). Consequently, the diffusional limitations that the oxidizing species have to overcome in W samples in order to reach the less-exposed carbon active sites located in the inner particle surface are much higher than in the case of EX20. Thus, concentration of oxidizing agents inside the micropores of EX20 is expected to be higher than for W carbon, producing a higher oxidation degree in the activated carbon cloth under mild current conditions.

The average oxidation efficiency (ε) for the electrochemical oxidation of the carbon material can be derived from the amount of oxygen (O) fixed for a given period of time according to the following equation:

$$\varepsilon = \frac{O_f - O_i}{It}$$

where O_f and O_i stand for the final and initial concentrations of oxygen in the carbon material after and before the electrochemical treatment, respectively; I is the applied current and t is the time of electrolysis. Average oxidation efficiency (ε) data are shown in Table 2.The oxidation efficiency in the HNO_3 electrolyte is found to be higher than that previously reported by Berenguer et al. upon electromodification of a GAC in a NaCl electrolyte.[19] The efficiency value is higher in the NaCl electrolyte for both conformations due to the much higher contribution of the indirect oxidation method in this medium. As a general rule, it can be concluded that the average oxidation efficiency is higher for activated carbon cloth, and it decreases with the applied current for the two studied porous carbons and in both electrolytes. The latter results can be explained considering the intensification of undesired side reactions (like molecular oxygen evolution from water oxidation and carbon corrosion reactions) when the current increases, whereas the former ones are connected to the aforementioned enhancement of the direct electroxidation for activated carbon cloth electrodes.

3.2.1. Selectivity of the Anodic Electrochemical Modification. The relative abundance of surface oxygen complexes estimated by TPD deconvolution is shown in Table 3 for all the W and EX20 samples. It should be noted that TPD deconvolution includes the formation of anhydrides (as it is usually found in wet oxidation processes). Probably, these groups were formed during the drying of the samples or during the TPD because electrooxidation was done in aqueous media.

Table 3. Relative Abundance (%) of Surface Oxygen Groups As Estimated by Deconvolution of CO_2 and CO TPD Profiles

	surface oxygen groups				
samples	carboxylic acid	anhydride	lactone	phenol	carbonyl/ quinone
W	15.0	3.3	14.5	24.6	42.6
Wa0.2H^+	11.3	8.2	7.6	29.4	43.5
Wa0.5H^+	12.4	8.5	7.1	28.2	43.8
Wa1.0H^+	15.7	15.4	6.4	33.4	29.2
Wa0.2Cl^-	15.7	9.8	5.5	43.8	25.2
Wa0.5Cl^-	13.4	10.0	5.4	49.3	21.9
Wa1.0Cl^-	14.9	10.4	5.7	48.3	20.7
EX20	14.6	5.4	6.3	29.2	44.5
EX20a 0.2 H^+	20.3	6.1	7.8	39.5	26.3
EX20a 0.5 H^+	19.3	8.1	7.3	40.4	24.9
EX20a 1.0 H^+	21.7	9.6	8.0	39.5	21.2
EX20a 0.2 Cl^-	23.4	9.8	9.4	42.7	14.7
EX20a 0.5 Cl^-	23.7	11.2	8.8	42.9	13.4
EX20a 1.0 Cl^-	21.8	10.1	6.5	49.9	11.7

Figure 2 presents the increase in the different types of surface oxygen groups, estimated from TPD deconvolution, as a

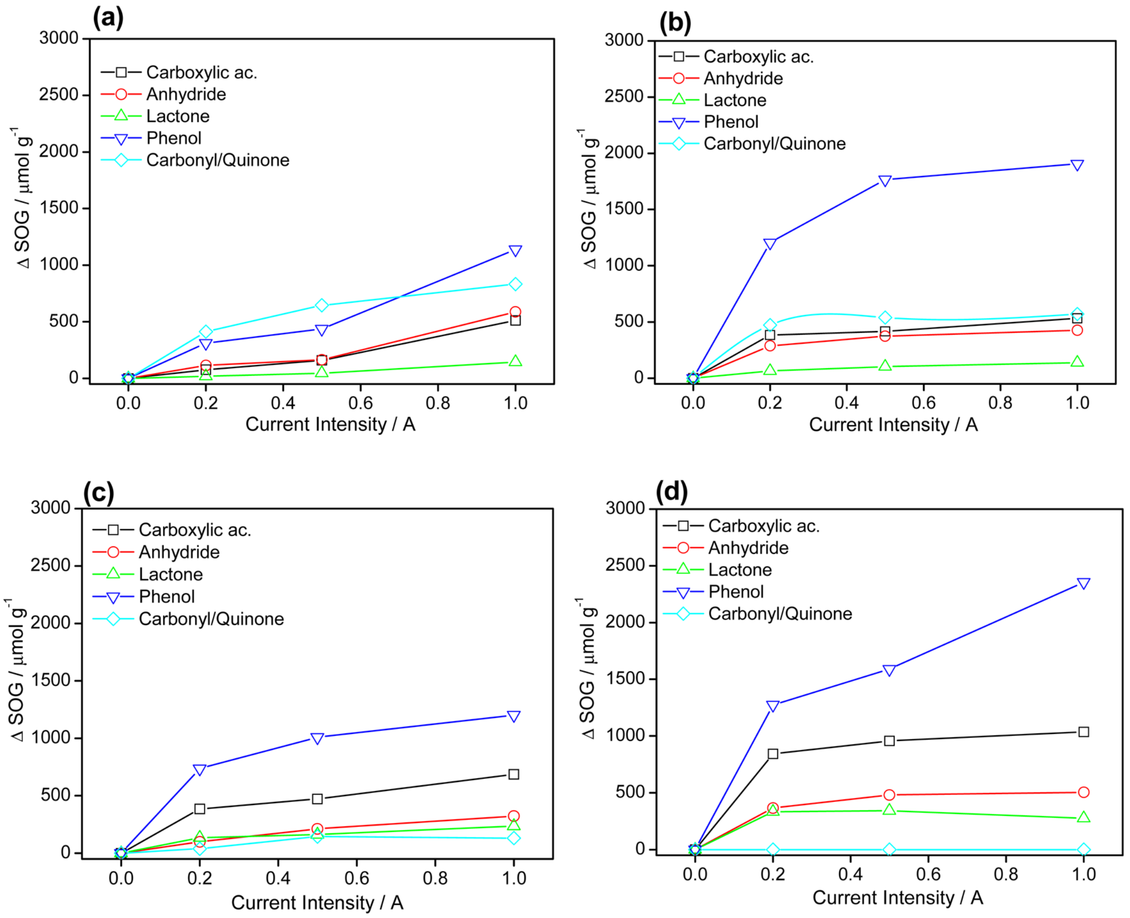


Figure 2. Increment in the concentration of surface oxygen groups estimated from deconvoluting TPD profiles of anodically treated W in (a) 0.01 M HNO_3/0.5 M KNO_3 and (b) 0.5 M NaCl and anodically treated EX20 in (c) 0.01 M HNO_3/0.5 M KNO_3 and (d) 0.5 M NaCl.

function of the current for the anodic treatment of both materials and under different conditions. In the case of the anodic treatment in acidic medium, a gradual increase in the content of all surface oxygen groups is observed on W as the applied current is raised (Figure 2a). This increase is especially significant in the case of groups that desorb as CO. Carbonyl/quinone groups show the highest increment at 0.2 and 0.5 A, but the highest increase is observed for phenolic functionalities at 1.0 A. On the contrary, lactone groups undergo the lowest increment. Carboxylic acid and anhydride groups show an intermediate and parallel increase with increasing the electrolysis current. About the relative amount, it can be seen in Table 3 that the NaCl electrolyte selectively introduce phenol groups, whereas in acid medium, carbonyls reach the highest amount up to 0.5A. The preferred generation of carboxylic and anhydrides functionalities at 1.0 A in this electrolyte shifts the surface oxygen group distribution to a more homogeneous one.

Different trends are observed for treated EX20 (Figure 2c). In acidic medium, the gain in carbonyl groups is negligible, and that of lactones remains rather low regardless of the applied current. The dependence of the amount of anhydride groups on the applied current resembles that described on W. However, the formation of carboxylic acid and phenols groups is largely favored with respect to that in W at low and medium currents. It has been long proposed in literature that electro-oxidation proceeds through the formation of phenol type groups, $C() + H_2O \rightarrow C(OH) + H^+ + e^-$, with carboxylic groups being subsequently formed through the oxidation of CO-type species: $C(O) + H_2O \rightarrow C(OOH) + H^+ + e^-$.[35,36] The preferred formation of carboxylic acids in EX20 seems to support that the electro-oxidation mechanism is more effective on EX20 for the reasons discussed in section 3.2.

The amount of surface oxygen complexes changes in EX20 as follows (Table 3). At a low current, the amount of carboxylic acids and phenolic groups increases, and that of carbonyl/quinone functionalities decreases in both electrolytes. At higher currents, the abundance of acid anhydrides keeps growing while the carbonyl content decreases. Phenol is the prevailing species at all tested currents, whereas the increasing abundance of carboxylic acid groups makes them even more frequent in relative terms than carbonyl/quinone functionalities at the highest current. These results suggest that the comparatively low CO/CO_2 found in anodically treated EX20 samples (Table 2) is due to reoxidation of freshly generated CO-desorbing groups to carboxylic acid functionalities rather than to the formation of carbonyl/quinone.

The anodic treatment of the porous carbons in NaCl (Figure 2b,d) produces a more pronounced increase in phenolic surface groups than in acidic medium. Phenolic groups become the most abundant surface oxygen complex at all the applied currents. On the other hand, formation of carboxylic acid groups seems to be favored in EX20. Acid anhydride groups also exhibit an increase, showing a dependence on the applied current similar to those described above. Another noteworthy feature is the huge loss in the relative amount of carbonyl/

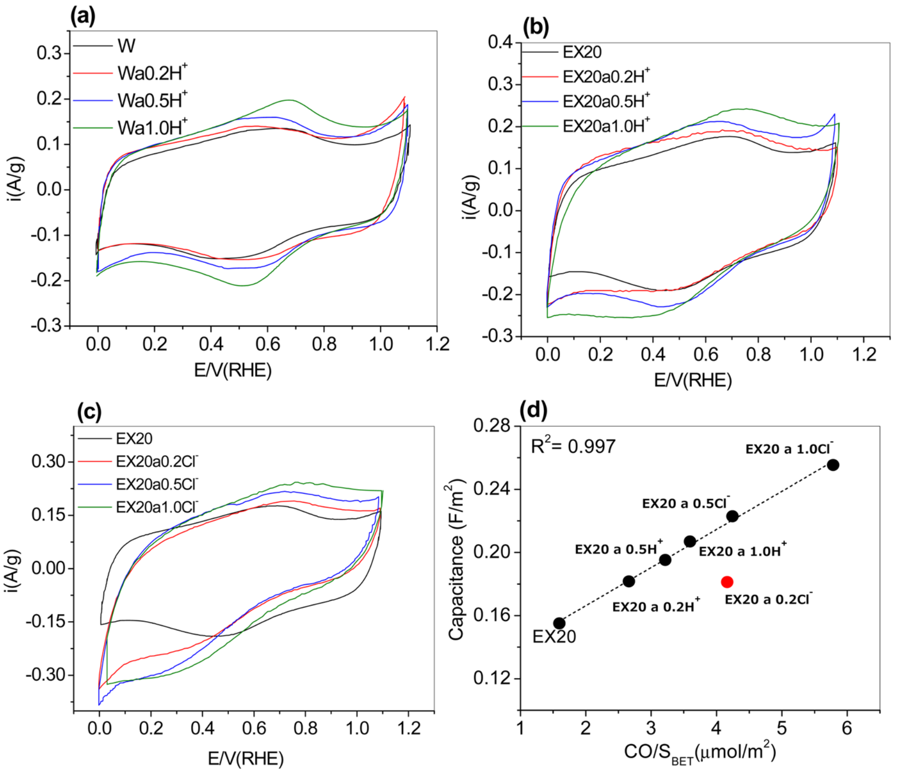


Figure 3. Cyclic voltammograms for anodically treated (a) W and (b) EX20 in 0.01 M HNO_3/0.5 M KNO_3, (c) EX20 in 0.5 M NaCl; sweep rate = 1 mV/s. (d) Specific capacitance of all the anodically treated samples versus CO amount evolved during TPD.

quinone groups for EX20. The relative amount of lactone groups also decreases at low currents, suffering from little changes at higher currents.

It is important to note that the oxygen functionalities have been modified, producing a different distribution than that found in other oxidation methods. For instance, techniques for selectively introducing phenolic groups are scarcely found in literature. A recent example in this sense is the work by Vivo-Vilches et al.,[28] where the authors proposed chemical oxidation followed by mild thermal treatment in activated carbons to reorganize the distribution of surface oxygen groups to a phenolic-prevailing one, but it comes at the cost of destroying the mesoporosity of the sample. This disadvantage is not found in electrochemical oxidation (Table 1).

3.2.2. Electrochemical Characterization. An interesting example of the relevance of surface oxygen groups in electrochemical processes is their contribution to the capacitance of porous carbons, when used as a component of supercapacitors. As it was shown in previous studies,[2,37−39] the faradic current can be significantly increased with the content in surface oxygen groups, while the increase in the electrical double layer as a result of improved wettability of the surface is not so important. It has been reported that the promotion of capacitance with the amount of oxygen surface complexes also takes place in a nonaqueous electrolyte, where wettability is not a limiting factor.[40] This remarks that the enhancement in capacitance is mainly based on pseudocapacitance or redox mechanisms. This idea had already been exposed by some authors.[38−44]

The participation of several oxygen-containing surface functionalities of carbon in electron transfer processes has been discussed by Leon y Leon and Radovic.[2] The authors reviewed and discussed the most likely mechanisms for the different surface groups to undergo electron transfer reactions, and evaluated the effect of the carbon surface nature on the redox behavior. Cheng and co-workers reported the relationship between the number of stable CO desorbing surface oxides titrated by temperature-programmed desorption and the charge storage capability of carbons.[41] They showed that oxidation enhanced the specific capacitance of the carbon electrodes, although a thermal treatment at mild temperatures after oxidation gave highest capacitances, thanks to the removal of CO_2-desorbing oxygen groups.

The capacitance of the pristine and anodically electro-oxidized samples has been measured by means of CV (Figure 3). The specific capacitance value of each sample, as obtained from the integration of its corresponding cyclic voltammogram, is tabulated in Table 2. From these data, it follows that the higher the amount of surface oxygen groups, the higher the specific capacitance. The CVs of the treated EX20 samples appear tilted compared to those of W samples, especially when NaCl was used as the modifying electrolyte (Figure 3c). Tilted voltammograms are usually associated with ohmic losses owing to poor wettability or decreased electrical conductivity. The surface wettability is expected to be promoted by acidic, ionizable surface groups attached to the surface by the electro-oxidation treatments. Therefore, we attribute CV tilting to a loss in the conductivity originated by strong charge localization on electron-withdrawing surface oxygen complexes.[38] However, we have to take into account that W electrodes were made up by mixing the powdered carbon with a conductivity promoter, whereas EX20 electrodes were used without powdering and mixing with the electrical conductivity promoter.

The observed capacitance enhancement is probably connected with the pseudocapacitance contribution, which is attributed to faradaic reactions involving electron transfer

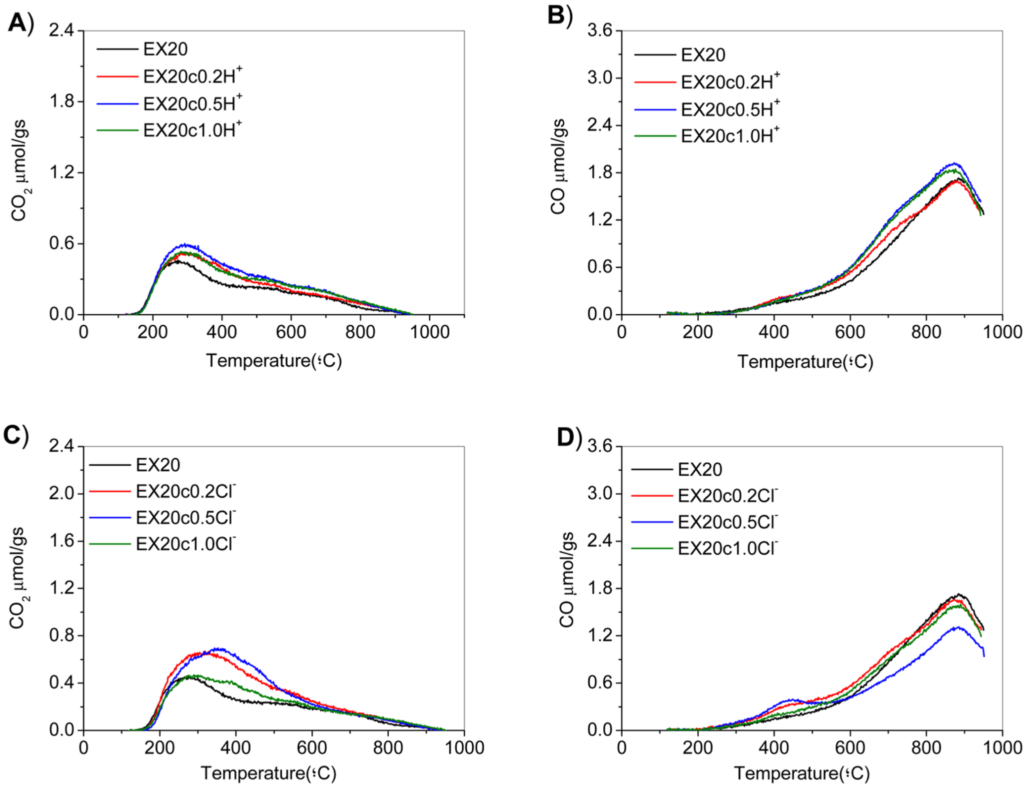


Figure 4. TPD profiles of untreated and cathodically treated EX20 in 0.01 M HNO_3/0.5 M KNO_3 (a,b) or 0.5 M NaCl (c,d) at different currents.

reactions of functional groups at the carbon surface. The electron transfer activity of the quinone/hydroquinone couple has been often described through radical reactions.[2] The carbonyl groups can stabilize the created radicals that may accept electrons and become anions, which can transfer one electron back and become radicals or can interact with cations in solution. In a protic medium, reversible proton transfer leads to phenolic hydroquinone sites. Further studies[30,39] have concluded that not only quinone but all CO-type desorbing groups are responsible for the enhancement in capacitance. This kind of redox processes can be observed in the voltammograms included in Figure 3 for all the anodically treated samples. In addition to a specific capacitance higher than that of the pristine porous carbons, these samples show a more intense peak between 0.55 and 0.85 V, which may be ascribed to the presence of surface quinone and other CO-desorbing groups.[42]

Different correlations between the specific capacitance and the oxygen-containing surface groups were attempted for EX20 samples, and the most accurate one was obtained when considering the amount of CO-evolving surface groups per surface area versus superficial capacitance (F/m^2), as shown in Figure 3d. Note that the correlation has been done dividing both capacitance and CO amount by the BET surface area (Table 1) of each sample. However, the correlation is similar to the absolute values because the surface area of all the materials is similar. These results are in agreement with those found by Bleda-Martínez et al., who reported a direct relationship between capacitance and total amount of CO evolved.[39] The excellent correlation seems to confirm the involvement of groups released as CO in surface electron transfer processes responsible for pseudocapacitance, and hence for the specific capacitance enhancement in anodically treated EX20.

3.3. Cathodically Treated Porous Carbons. Figure 4 shows the CO_2 and CO TPD profiles obtained for the as-received EX20 and for the cathodically treated samples at different currents in different electrolytes. Those for W samples can be found in the Supporting Information, Figure S2. The cathodic treatment of W in nitric acid medium results in a slight increase in surface oxygen groups, both the CO_2- and the CO-evolving surface groups, and in the total surface oxygen (O). This result is in agreement with those found by Berenguer et al.,[17] who studied the treatment of the granular activated carbon under cathodic conditions in different electrolytes (NaOH, H_2SO_4 and NaCl). Nevertheless, the same treatment over EX20 did not produce any relevant modification on the observed evolution of oxygen groups as CO_2 and CO, independently of the chosen electrolyte. Therefore, it can be concluded that the cathodic treatment is not suitable for electrochemical modification of this material at the experimental condition used in this work.

As suggested earlier,[17] the cathodic oxidation observed in this work can be due to peroxide oxidizing species electrogenerated during electroreduction of oxygen dissolved in the electrolyte in contact with air. It is well-known that carbon materials, in the form of graphite, reticulated vitreous carbon, carbon felt or foams, activated carbon fibers, or even carbon nanotubes, are good catalysts for the electrogeneration of H_2O_2.[45,46] Moreover, it is well established the capability of carbon materials to catalyze the heterogeneous decomposition of H_2O_2 to yield highly reactive free hydroxyl radicals.[47,48] In the absence of any organic substrate, this capability is most likely to result in the oxidation of the carbon surface itself. Brønsted basic sites like quinone/carbonyl, pyrone or chromene oxygen surface functionalities and Lewis basic sites assigned to delocalized π-electrons within graphene sheets have been identified as the active centers for the decomposition of H_2O_2 to $OH^•$.[47] Thus, there is a general consensus that basic carbons are the best catalysts for this process.[49] The different behavior exhibited by W and EX20 against oxidation by cathodic treatment could therefore be attributed to their different basicity. The granular activated carbon (pH_{PZC} 9) is a basic carbon whereas the carbon cloth is slightly alkaline (pH_{PZC} 7.5). It should then be expected that hydrogen peroxide is more easily converted to hydroxyl radicals on the surface of W rather than on the surface of EX20, and hence the former undergoes a small but noticeable oxidation.

4. CONCLUSIONS

The anodic electrochemical treatment of activated carbon cloths in filter press in nitric acid and NaCl electrolytes has been proved to be adequate to produce a controlled oxidation of the carbon fiber surface.

For the HNO_3 electrolyte, the anodic treatment in both granular activated carbon and activated carbon cloths causes an increase in the amount of surface oxygen groups, whereas the cathodic treatment does not produce any relevant modification on the surface chemistry of the activated carbon cloth, and minor changes in the granular activated carbon. The HNO_3 electrolyte produced a lower generation of oxygen groups than the NaCl one and a different distribution of the generated surface groups. The prevailing mechanism in the HNO_3 electrolyte is the direct oxidation of the carbon surface, whereas indirect oxidation becomes relevant for NaCl. The current can be used for tuning the amount of the oxygen functionalization of the carbon surface in both electrolytes. Moreover, the carbon morphology and particle size seem to influence the distribution of the generated oxygen surface groups. Probably, as a result of their small diameter, the surface of the activated carbon cloth is functionalized with carboxylic acid groups to a higher extent than the granular activated carbon, indicating that the oxidation of freshly formed C(O) groups is favored.

A very interesting result is found about porous texture of these samples. In contrast with the usual chemical oxidation treatments, where a high oxidation degree produces a decrease of the microporosity, the porous texture is mostly unaltered after the electro-oxidation treatment. The validity of this method to introduce oxygen surface groups with a pseudocapacitive behavior has also been corroborated by cyclic voltammetry studies. A clear relationship between CO-desorbing groups and capacitance has been established. The presence of high amounts of electron-acceptor carboxylic acid groups can be detrimental for the conductivity of ACCs, as pointed out by the tilting features observed in the voltammograms of the electrooxidized carbon cloths.

In summary, the electrochemical treatment can be implemented to selectively and quantitatively modify the surface chemistry of activated carbon cloths, preserving both their morphology and their textural properties, and without the need of adding any strong oxidizing agents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TPD profiles for the W samples before and after the electrochemical treatments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the MINECO and FEDER for financial support (MAT2010-15273 project). R.R.R. gratefully acknowledges funding from MINECO through "Juan de la Cierva" program (JCI-2012-12664)

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