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Enhanced Electro-oxidation Resistance of Carbon Electrodes Induced by Phosphorus Surface Groups

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ABSTRACT: The electro-oxidation of carbon materials enormously degrades their performance and limits their wider utilization in multiple electrochemical applications. In this work, the positive influence of phosphorus functionalities on the overall electrochemical stability of carbon materials has been demonstrated under different conditions. We show that the extent and selectivity of electroxidation in P-containing carbons are completely different to those observed in conventional carbons without P. The electro-oxidation of P-containing carbons involves the active participation of phosphorus surface groups, which are gradually transformed at high potentials from less- to more-oxidized species to slow down the introduction of oxygen groups on the carbon surface (oxidation) and the subsequent generation of (C*OOH)-like unstable promoters of electro-gasification. The highest-oxidized P groups (-C-O-P-like species) seem to distribute the gained oxygen to neighboring carbon sites, which finally suffer oxidation and/or gasification. So it is thought that P-groups could act as mediators of carbon oxidation although including various steps and intermediates compared to electroxidation in P-free materials.

1. Introduction

Carbon materials are widely used and receive increasing interest as electrodes, electrocatalysts and/or electrocatalyst supports in different electrochemical applications, such as industrial synthesis (Al, Cl_2-NaOH, organics), electro-oxidation and -adsorption of pollutants, analysis and detection in (bio)sensors, medicine (neural communication, enzyme immunoassays, genetic mutation analysis, etc.), or their use for energy storage (supercapacitors, batteries) and conversion (fuel cells and solar cells) [1-7]. Nevertheless, their performance and durability in these applications generally decline as a consequence of electro-oxidation processes [8-15], so they usually have to be continuously replaced or substituted by other more stable but more expensive electrodes. Considering the enormous carbon consumption and, usually, the resultant loss of high-cost supported-electrocatalysts (Pt, Ru, etc.), together with the performance decay and/or the restricted utilization of carbon electrodes in these applications, any improvement of their electrochemical stability would suppose major consequences in savings and a wider and more sustainable use of these natural resources.

Various studies comparing the electro-oxidation behavior of different carbon materials have been published [16-20]. However, little is unambiguously known regarding the mechanism of electrochemical oxidation [21-25]. As a consequence, few strategies to improve the carbon electro-oxidation resistance have been proposed. Most approaches involve a decrease in the amount of active sites by controlling the carbon morphology and structure [15-20,26,27], and/or by reducing the surface area [19,28]. Nevertheless, other promising approaches have been also proposed [29].

On the other hand, the surface chemistry of carbons seems to play a key role on their electrochemical stability, so the attachment of stabilizing functionalities could entail a general strategy to improve the performance of all kind of carbons, independently of their surface area, morphology, etc. There again, real effects are not less controversial. Thus, whereas the presence of oxygen groups has been commonly found to be detrimental to the electrochemical stability [30], a beneficial influence of certain surface functionalities of nitrogen [31,32] or phosphorus [33,34] has been claimed. In spite of the promising perspectives for various applications, to the knowledge of the authors, there are few works proposing an enhanced electrochemical stability induced by P-functionalities and, in all cases, applied for widening the stability potential window of carbon-based supercapacitors [33,34]. Nevertheless, apart from the significance of the results, neither the electro-oxidation behavior nor the enhanced stability effect were

properly tackled and explained. Hulicova-Jurcakova et al. compared carbons prepared from completely different precursors, showing quite different surface areas and oxygen contents, and by using a two-electrode cell [33], where a control of the electrode potential, necessary for a meaningful comparison among oxidation currents of different materials, cannot be achieved. Moreover, they assigned the enhanced oxidation resistance to the physical blockage of active sites by phosphate groups [33], thus, using arguments employed in the thermal-oxidative gasification of carbons [35-40]. On the other hand, instead of an effect on the oxidation resistance, Huang et al. have recently objected that the P-groups, especially polyphosphates, play a critical role in stabilizing the surface of carbons during the reversible electrochemical hydrogen storage at low potentials [34].

Then, while the need for certain morphologies or a reduced surface area may restrict or decline the electro-chemical application of carbon materials, and the real effect of surface functionalities in the electrochemical stability is still unknown, more reliable studies and new approaches to enhance the electro-oxidation resistance of carbon materials are necessary and challenging. In this work, the positive influence of phosphorus surface groups in the electro-oxidation resistance has been unambiguously demonstrated in high-surface area activated carbons and analyzed in depth to gain a better understanding of the involved processes. We propose a new concept to minimize the electro-oxidation of carbon materials, in which phosphorus groups actively participate in the reaction by gaining oxygen preferentially among different surface sites. This delays the introduction of oxygen groups in the graphene layers (oxidation) and reduces the generation of (C*OOH)-like species, which have been previously suggested to be the unstable promoters of electro-gasification (term sometimes referred to as corrosion). The obtained results suggest that, once oxidized, phosphorus functionalities could act as mediators of carbon oxidation by distributing the gained oxygen to neighboring carbon sites, which finally would suffer gasification.

2. Experimental

2.1 Preparation of activated carbons (ACs)

Various ACs with or without P were prepared by either H_3PO_4-chemical activation or CO_2-physical activation of olive stones [41-44]. This precursor was provided by Sca Coop. And. Olivarera y Frutera San Isidro (Periana, Malaga). For the chemical activation, olive stones were impregnated with 85 wt% H_3PO_4 aqueous solution

(Aldrich) at room temperature and dried for 24 h at 60 ºC in a vacuum dryer. The impregnation ratio (H_3PO_4/precursor mass ratio) was 3. The impregnated materials were activated at 500ºC for 2 h under N_2 or air, using a gas flow to olive stone ratio of 150 mL min^{-1}/5g (samples denoted as HA3500 and HA3500-A, respectively). The activated samples were washed with distilled water at 60ºC, until neutral pH in the eluate, and dried at 110ºC overnight. In order to obtain carbons with different surface chemistry, these two samples were heat-treated up to 900ºC for 2 h under N_2 flow (samples referred to as HA3500-T and HA3500-A-T). For the physical activation, the olive stones were carbonized at 800 ºC for 2 h, followed by partial gasification with CO_2 at 800 ºC for 6 h (60% burn-off) (sample HAG800). All the activation and heat treatments were carried out in a tubular furnace, with 150 cm^3 STP/min gas flows, and by using heating rates of 10 ºC/min.

2.2 Physicochemical characterization of ACs

The textural properties were characterized by N_2 adsorption-desorption at -196 ºC and by CO_2 adsorption at 0 ºC in a Micromeritics ASAP2020, after outgassed for 8 h at 150 ºC under vacuum. From the N_2 adsorption/desorption isotherm, the apparent surface area (S_{BET}) was calculated by applying the BET equation, and the micropore volume ($V_t(N_2)$) by using the t-method. The mesopores volume ($V_{meso}(N_2)$) was determined as the difference between the adsorbed volume of N_2 at a relative pressure of 0.95 and the micropore volume ($V_t(N_2)$). The narrow micropore volume ($V_{DR}(CO_2)$) was estimated from the CO_2 adsorption isotherm using the expression of the Dubinin–Radushkevich adsorption isotherm.

X-Ray Diffraction (XRD) measurements of the powdery ACs were performed by using a Shimadzu XRD-6100 instrument with Cu-Kα radiation (λ=1.541 Å) generated at 30 kV and 20 mA. The temperature-programmed desorption (TPD) analyses were carried out up to 940 ºC (10 ºC/min) in helium flow (100 cm^3 STP/min) in a differential scanning calorimetry–thermogravimetric analysis (DSC–TGA) equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3). The amounts of CO and CO_2 desorbed from the samples were monitored following the 28 and 44 m/z lines, which were previously calibrated by non-isothermal decomposition of calcium oxalate monohydrate (99.999%). X-ray photoelectron spectroscopy (XPS) was performed in a 5700C model Physical Electronics apparatus, with Mg Kα radiation (1253.6 eV). The C1s peak position was set at 284.5 eV and used as reference to locate the other peaks. The fitting of the XPS

peaks was done by least squares using Gaussian–Lorentzian peak shapes and Shirley line as background. TPD and XPS measurements were carried out over the carbon electrodes (which are prepared by mixing the powder AC with 5% polytetrafluoroethylene (PTFE) and 5% acetylene black), and the effect of these additives in the measurements are described in the supplementary information.

2.3 Electro-oxidation treatments

The powder ACs were converted into electrode pastes, by mixing them with a small amount of PTFE, as binder, and acetylene black (Strem Chemicals), as conductivity promoter, in a ratio 90:5:5 wt%, and used as working electrodes. The total electrode weight was about 10 mg (dry basis), being conformed in circular shape (1.3 cm^2) and pressed for 5 minutes at 2 metric tons, for ensuring uniform thickness, against a macroporous graphite foil current collector. The electrodes were impregnated in 1M H$_2$SO$_4$ for 3 days prior to the electrochemical runs. A Pt wire and an Ag/AgCl/Cl$^-$(sat.) electrode were used as counter and reference electrodes, respectively. All the electrochemical measurements were carried out by using an Autolab PGSTAT302 potentiostat, 1.0 M H$_2$SO$_4$ aqueous solutions as electrolyte (prepared with ultrapure water (18 MΩ cm) and 98 wt% H$_2$SO$_4$), and a standard 3-electrode cell. This configuration allows a precise control of the electrode potential (referred against a reference electrode), which is of up most importance for comparison purposes.

Trying to generalize the study and results of this work, the electro-oxidation behavior of the carbons was studied by using non-particular potentiodynamic and potentiostatic conditions, which are intended to be representative of a wider range of more specific and real ones in different applications. For the potentiodynamic electro-oxidation conditions, the electrodes were cycled at 1 mV/s between -0.2 V to a gradually rising upper limit potential, from the open circuit potential (OCP) up to 1.1V, and by repeating 3 cycles at every upper limit potential (Fig. S1a). For the potentiostatic conditions, the potential was gradually increased from the OCP up to 1.1 or 1.4 V at 1 mV/s and hold at for 1-20 h (Fig. S1b). After the potentiostatic treatments, the electrode pastes were rinsed with abundant distilled water and dried at 60 ℃ overnight to be subjected to chemical characterization.

3. Results & Discussion

3.1 Physicochemical characterization of powder ACs

Figure 1 displays the porous texture and surface chemistry characterization of the powder ACs, whereas Table 1 resumes their main textural and chemical parameters. As it can be observed in Table 1, various ACs with a quite similar P content (2.5-3.3 wt% P) or without P, but with comparable specific surface areas (1300-1600 m^2/g) and low structural order have been prepared for this study. Significant differences exist in the porous texture of chemically- and physically-activated samples (Fig. 1a). The higher N_2 volume adsorbed at medium-high relative pressures and the large hysteresis loops observed for P-containing carbons (Fig. 1a) are characteristic of a wider microporosity, with a significant contribution of mesoporosity (Table 1). By contrast, the higher CO_2 adsorption volume ($V_{DR}(CO_2)$) obtained for HAG800 carbon, approaching that of N_2 ($V_t(N_2)$), points out that physical activation mainly generates narrow microporosity.

Table 1. Textural properties and oxygen and phosphorus surface contents of the powder ACs.

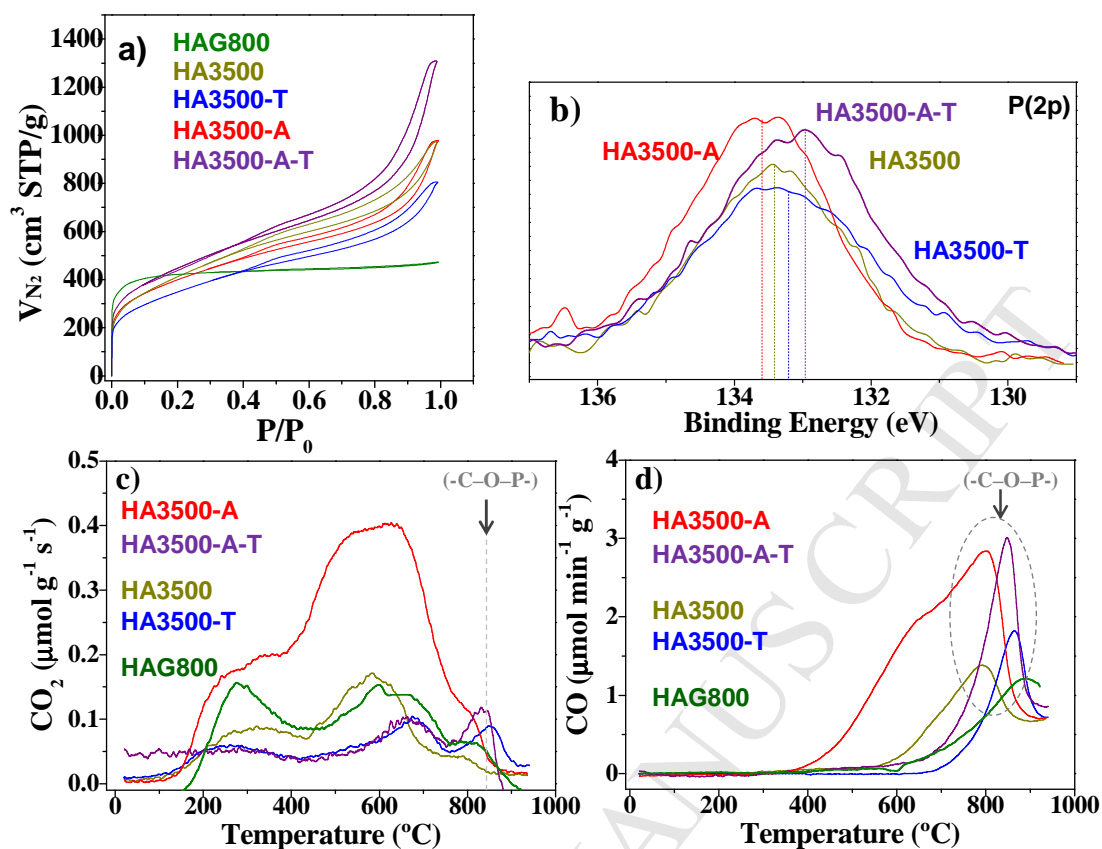| Sample	$S_{BET}(N_2)$ m^2/g	$V_{meso}(N_2)$ cm^3/g	$V_t(N_2)$ cm^3/g	$V_{DR}(CO_2)$ cm^3/g	O_{XPS} wt.%	P_{XPS} wt.%
HAG800	1465	0.086	0.613	0.447	4.8	---
HA3500	1495	0.642	0.525	0.247	11.2	2.5
HA3500-T	1265	0.771	0.433	0.177	5.2	2.8
HA3500-A	1440	0.755	0.518	0.277	16.8	2.7
HA3500-A-T	1610	1.258	0.548	0.292	5.4	3.3

Figure 1. (a) N_2 adsorption-desorption isotherms at -196 ºC, (b) XPS-P(2p) spectra and (c) CO_2- and (d) CO-evolution from TPD experiments for the different powdery carbons prepared by physical (HAG800) or chemical (HA3500-carbons) activation.

Furthermore, by the right choice of the chemical-activation atmosphere and thermal post-treatments, a variety of phosphorus functionalities (Fig. 1b) and a different concentration, between 5-17 wt% O (Table 1), and nature of oxygen surface groups (Fig. 1c and 1d) were introduced in the carbon materials. The activation in air at milder temperatures (HA3500-A) favors the introduction of a larger concentration of oxygen surface groups (Table 1) and a higher oxidation degree of phosphorus species, as deduced from the XPS spectrum centered at higher binding energies (Fig. 1b). Moreover, the significant CO_2 and CO evolutions over a broad range of temperature, mainly between 400-800 ºC (Fig. 1c and 1d), is indicative of the presence of different oxygen surface groups (mainly anhydride, phenols and quinones) [45]. On the other hand, inert atmosphere (HA3500) and, especially, treatments at higher temperatures (HA3500-T and HA3500-A-T) reduce the oxidation degree of P species (their XPS spectra are centered at lower binding energies) and remove the oxygen functionalities of P-containing ACs (see Table 1 and the low CO_2 and CO evolutions below 800 ºC in

Fig. 1c and 1d). As a result, these thermally-treated samples show similar oxygen contents to that without P (HAG800) (Table 1). Nevertheless, the oxygen of the P-free sample is in the form of carbon-bound oxygen groups of high thermal stability (evolving above 700 ºC), like carbonyl/ketone groups [45], whereas the CO_2 and, especially, the well-defined CO evolutions between 800 and 950 ºC of P-containing ACs have been assigned to the presence of -C-O-P- species that decompose in the form of CO at around 860 ºC [41,46-48].

3.2 Electro-oxidation behavior of ACs with and without P

As observed in Figure 2a, independently of the presence of P, the as-prepared samples with lower O wt% (HAG800 and HA3500-T) start to show anodic currents from ca. 0.65 V, which significantly and gradually increase with the upper limit potential (see CVs up to 1.1 V). As evidenced by the parallel development of pseudocapacitive contributions at around 0.4 V, the observed oxidation currents at high potentials can be mainly assigned to the oxygen gain (electro-oxidation) on the ACs. By contrast, the sample already-oxidized during its preparation (HA3500-A) registered no oxidation currents up to 1.25 V, probably concurring with the electrode corrosion and/or the electrolyte decomposition. Such a wide stability potential window of ca. 1.45 V is in agreement with those previously found for P-containing carbon based supercapacitors [33,34]. However, unlike these previous works, where the observed strong influence of the initial O wt% in the oxidation currents was not considered [33], when carbon materials with similar O wt% are compared (HA3500-T vs. HAG800 in Figure 2a), the delayed oxidation (towards higher potentials) and lower oxidation currents recorded for the P-containing one (Figure 2a) allow us to unambiguously conclude that the presence of P enhances their electro-oxidation resistance.
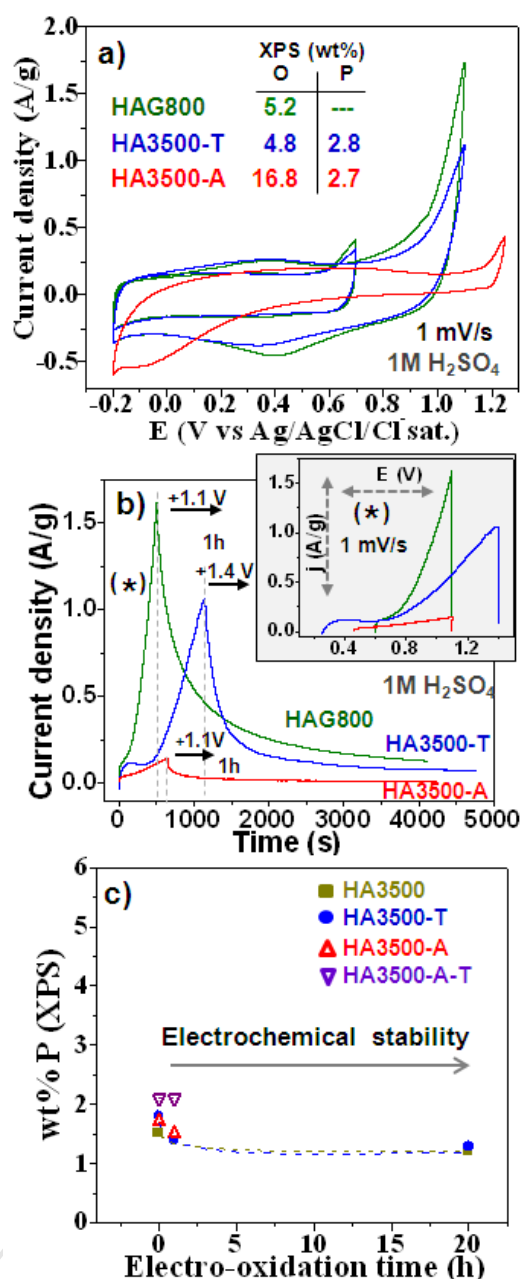
Figure 2. (a) Cyclic voltammograms (1st cycle in all samples) up to different upper limit potentials and (b) potentiostatic treatments of different samples comparing the influence of O and P contents. Inset: linear sweep voltammogram up to the different potentials; (c) Mass surface concentration of P in different samples before and after electro-oxidation treatments.

For the potentiostatic conditions, the electrode potential of the different ACs was raised up to 1.1 or 1.4 V and hold constant for 1 to 20 h. Compared to a cycling and gradual oxidation (Figure 2a), when a unique scan is performed directly to reach 1.1 V, even higher differences between both samples can be found (inset of Figure 2b). Particularly, the oxidation inhibition of P is so remarkable that the oxidation currents at

1.4 V for the sample with 3 wt% P are even lower than those at 1.1 V for the P-free one (Figure 2b). Upon holding the electrode potential at 1.1 V or 1.4 V, the oxidation currents start to decrease down to a stable value. These currents may be indicative of some electro-oxidation or electro-gasification (CO_2 evolution) processes under steady state conditions [21-27]. In addition, oxygen evolution reaction may also contribute to this current. The occurrence of these reactions was confirmed by comparing the quantified oxygen gain to the amount of electrons (charge) involved in the processes (see supplementary data), so that, the registered extra electrons may be related to reactions other than this oxygen gain. In this sense, the amount of extra electrons passed in the carbon without P is much higher than in the P-containing ones. Thus, these results point out that P functional groups may slow down also the electro-gasification currents of the studied carbon materials, enhancing their corrosion resistance. This effect was confirmed also by testing much longer potentiostatic treatments of 18-20 h.

Another important aspect from a practical point of view is the stability of phosphorus species under electrochemical conditions. This was evaluated by measuring the remaining P content after the electrochemical treatments (Figure 2c). Results point out that, more than 90 % of surface phosphorus from the chemically-stable P species detected in 3-days-impregnated carbon electrodes, remains after the electroxidation treatments under such harsh conditions (1.1 V) for 20 h. These results indicate that P complexes exhibit extraordinary electro-chemical stability.

The influence of phosphorus groups in the thermal oxidation inhibition of different carbon materials has been widely studied and discussed on the literature [35-40]. In most cases, the oxidation protection was achieved by impregnation of already-prepared carbon materials with H_3PO_4, phosphates and other kind of phosphorus-containing molecules, followed by a thermal treatment for their decomposition and P-anchoring on the carbon surface [35-40]. Some authors proposed that the phosphorus species enhance the oxidation resistance by blockage (poisoning) of the active sites that are prone to suffer from oxidation, formation of a protective glassy diffusion barrier, and/or neutralization of impurities that can catalyze the oxidation of carbon materials [35-40]. In the present study, however, P-containing carbons have been obtained with no additional impregnation step, and phosphorus is incorporated to the carbon surface during the activation process at temperatures of about 500 ºC [41-47]. These P-containing carbons presented very high gas-phase oxidation resistance (shown in previous works) [41-47], which coincides with the enhanced oxidation resistance under

electrochemical conditions observed in this work. Hence, the enhanced electro-oxidation resistance of these P-containing carbons could be explained in different terms to those postulated in the past [35-40]. In order to do so, the surface chemistry of electro-oxidized ACs has been analyzed to get some insights about the possible electro-oxidation mechanism of P-containing porous carbons.

3.3 Chemical characterization of electro-oxidized ACs

In order to explain the influence of P-surface groups on the electro-oxidation resistance, the surface chemistry of the different samples, before and after potentiostatic treatments, was analyzed by TPD and XPS. For this purpose, the properties of electroxidized samples were compared with those of the same electrodes immersed in the electrolyte for similar periods of time but in absence of imposed potential (see more details in supplementary data). Figure 3a points out that the electroxidation of the P-containing carbons (HA3500 series) selectively causes a higher increase in the most stable CO-evolving surface oxygen groups. Contrarily, the sample without P (HAG800) suffers from a marked non-selective electroxidation..
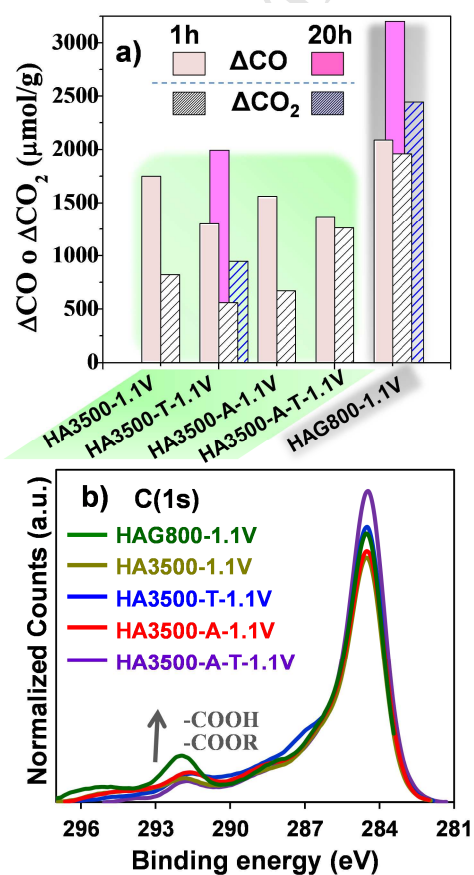
Figure 3. (a) Gain in CO_2- and CO-like oxygen evolving groups (from TPD) after electro-oxidation at 1.1 V; (b) C(1s) XPS-spectra of the electro-oxidized samples (1.1 V, 1 h).

Such a remarkable greater proportion of –COOH/-COOR surface species on the electro-oxidized P-free carbon was confirmed by XPS (Figure 3b). In addition, the electroxidation causes a much higher oxygen gain on the sample without P than on all those with P (in agreement with the higher oxidation currents for the P-free sample observed in Figure 2), and such a difference becomes more important with the time of treatment (Figure 3a).

Previous studies on the kinetics and mechanisms of carbon corrosion proposed that the corrosion rate is proportional to the concentration of highly oxygenated and unstable C*OOH-like species [21-25], as promoters and/or initiators of the electrochemical evolution of CO_2:

$$(C*OOH)_{surf.} \rightarrow (*)_{surf.} + CO_2 + H^+ + e^- \quad (1)$$
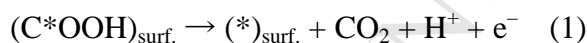
If we reasonably hypothesize that these electrochemically unstable C*OOH-like groups may correspond and/or be related to part of those electrochemically-introduced CO_2-evolving groups (ΔCO_2) determined by TPD and observed by XPS (Figure 3), our results indicate that the presence of phosphorus groups inhibits or delays, the generation of C*OOH-like gasification promoters, thus enhancing the electro-gasification (corrosion) resistance of the carbon materials.

A more detailed analysis of CO_2 and CO evolutions during TPD experiments shows remarkable differences in the selectivity of the electro-oxidation processes. In the absence of phosphorus species (Figure 4a and 4b), the increase in the whole temperature range of CO_2 and CO profiles points out that the electrochemical treatment augments all types of oxygen surface groups, stressing the lack of selectivity on the electro-oxidation of these P-free ACs. By contrast, the electroxidation of the P-containing carbons generally produces an outstanding higher increase in the CO profiles between 800-950 ºC (orange area in Figure 4d and 4f), just coinciding with the decomposition of -C-O-P-species, indicating that the electro-oxidation of P-containing ACs provokes a preferential formation of -C-O-P- species. In addition, the electro-oxidation concurs with a slight and selective increase in the CO_2-evolving groups between 200-500 ºC (grey area in Figures 4c and 4e), and in the CO-evolving groups between 600-800 ºC

(fuchsia area in Figures 4d and 4f), which can be mainly attributed to carboxylic- or phenol- and quinone-like groups on carbon, respectively [48].
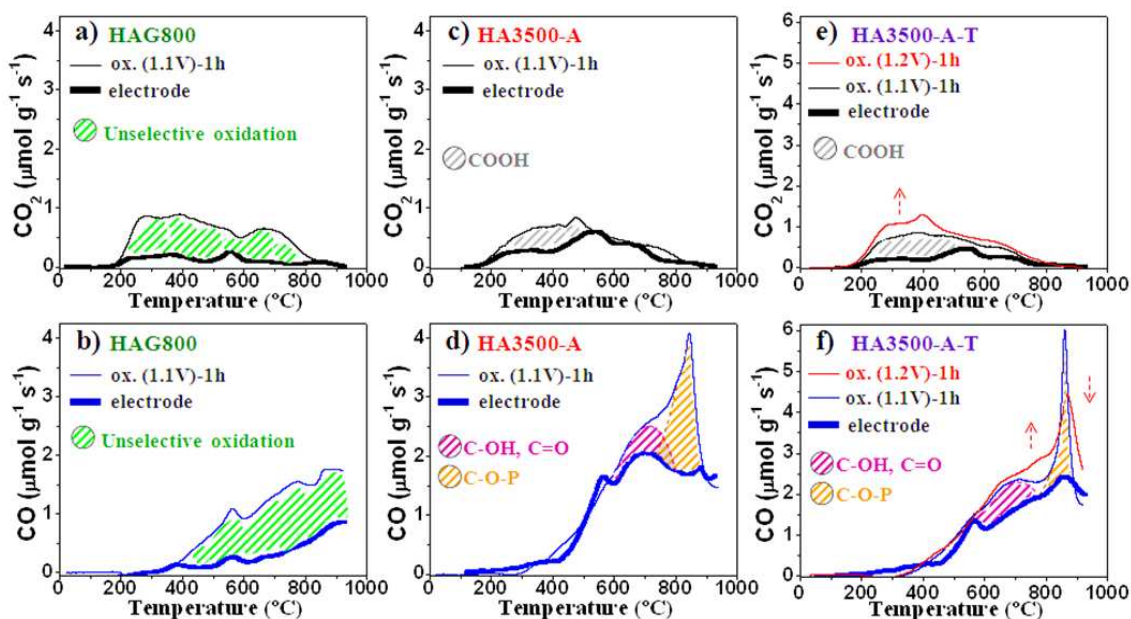

Figure 4. CO_2 and CO patterns from TPD experiments of the different carbons before (thick lines) and after (thin lines) potentiostatic electro-oxidation under different conditions.

The electrochemical oxidation of phosphorus groups was undoubtedly confirmed by the shift of P(2p) XPS-spectra towards higher binding energies (Figure 5a). Nevertheless, it must be noted that broad bands, reflecting a distribution of different P functionalities, were still found even in the most electro-oxidized samples. In this respect, the nature and relative contribution of the different phosphorus functionalities on P-containing carbons before and after the electrochemical treatments were estimated by deconvolution of their P(2p) spectra.

As shown in Figure 5b, these functionalities can be divided into four main contributions, namely, -C_3P, -C_3PO, -C-P-O- and -C-O-P-, from less to more oxidized species [41-47]. After 1h-electroxidation treatments (Figure 5c), thermally-treated samples (HA3500-T and HA3500-A-T), initially with a higher proportion of -C_3PO species, preferably gain in -C-P-O- species; whereas those prepared at 500 ºC, with a considerably higher O content and higher concentration of -C-P-O- ones, mainly gain in -C-O-P- species. This generation of new -C-O-P- species observed by XPS is in good agreement with the increase in TPD peak at 860 ºC (orange area in Figures 4d and 4f) for the electroxidized samples. In fact, the increase in this peak (orange area) would

represent the amount of oxygen (in absolute terms) introduced on the carbon surface by oxidation of -C_3PO and -C-P-O- groups to -C-O-P- ones, in agreement with the relative reduction of -C_3PO and -C-P-O- groups observed by XPS (Figure 5c).
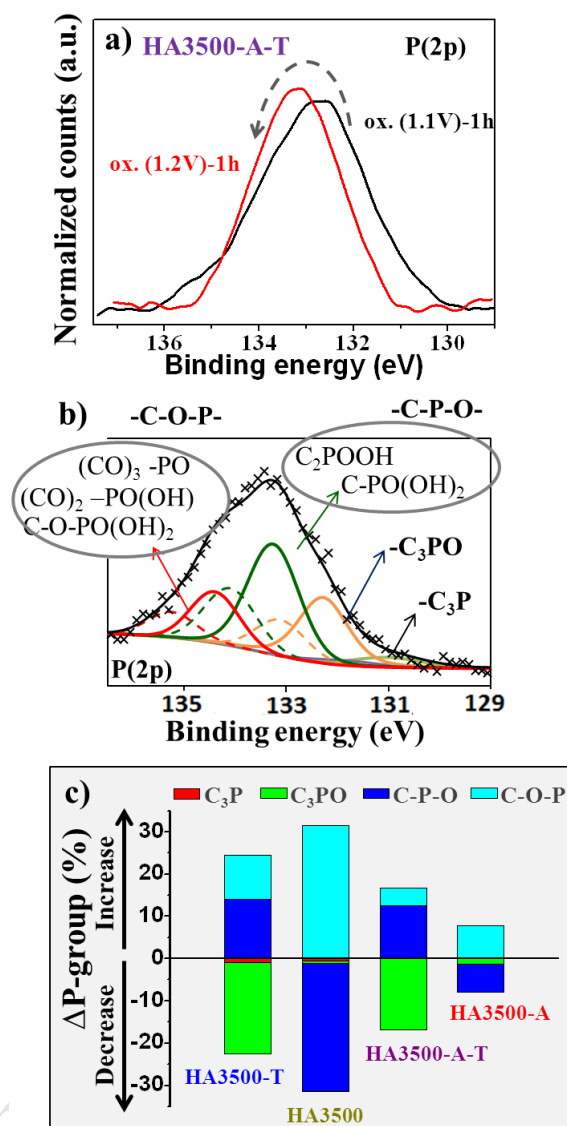

Figure 5. Examples of (a) P(2p) XPS-spectrum shift after potentiostatic electro-oxidation and (b) P(2p)-spectrum deconvolution; and (c) the relative change on P species (ΔP) after electroxidation at 1.1 V for 1 h.

These results indicate that in the case of P-containing carbons a remarkable proportion of the oxygen gain, caused by electroxidation, occurs on the phosphorus surface groups (orange area in Figures 4d and 4f). Hence, compared to the AC without P, in which the electro-oxidation only affects the carbon surface (see the green area from 200 ºC to 900 ºC, related to a wide variety of oxygen surface groups on carbons [48], in

Figures 4a and 4b), a considerably smaller oxidation corresponds to carbon sites in P-containing ACs (grey area in Figures 4c and 4e, and fuchsia area in Figures 4d and 4f).

TPD characterization further revealed crucial information on the electroxidation of P-containing carbons. When these samples are subjected to stronger potentiostatic conditions, for example, by increasing the applied potential (Figures 4e and 4f), the contribution of -C-O-P- groups (CO evolution at 860 ºC) does not further enlarge and an increase in phenol/quinone and carboxylic groups occurs (CO evolution at 600-800 ºC and CO_2 evolution at 200-480 ºC, respectively). Similar effects have been also observed by treating the samples for much longer times (see supplementary data). These findings highlight that, despite the harder conditions, the electro-oxidation of P-containing carbons is also very selective, suggesting that it could proceed through a different mechanism to that of conventional P-free ones.

3.4. Mechanistic aspects

The changes on the P surface functionalities observed by TPD (Figure 4) and XPS (Figure 5) clearly evidence a gradual transformation of phosphorus surface groups from less oxidized (-C_3P and -C_3PO) to more oxidized groups (-CPO_3 and –$COPO_3$ groups containing -C-P-O- and -C-O-P- species) caused by the electroxidation treatments. Only after P-surface groups are oxidized, selective oxidation of the carbon surface takes place. A possible reaction pathway for the initial transformations that take place in P groups is represented in the Figure 6. This electrochemical oxidation (oxygen uptake) may involve the nucleophilic attack of surface atoms by hydroxyl radicals, electrochemically generated from water at high potentials on the electrode surface [49,50], which must be favored on the positively polarized graphenic layers under the electroxidation conditions.

Based on the remarkable selectivity of electroxidation towards the P functionalities and the generation of -C-O-P- species found experimentally (Figures 4 and 5), and considering the low electron density that it may exist on -C-P- bonds (phosphorus atoms are surrounded of various oxygen atoms of higher electronegativity -electron-withdrawal character- and carbon atoms are subjected to positive potential), the electroxidation reaction may proceed with the participation of these P groups. In order to explain this preferential attack to -C-P- bonds, we propose that it could occur through the formation of epoxide-like intermediates $[-C-O^+-P-]^{\neq}$ (see Fig. 6). The formation of an epoxide ring is similar to the oxidation mechanism proposed for the gas-phase

thermal oxidation of carbon materials [53,54]. This epoxide intermediate can be opened following two general pathways: oxidation of the original -C-P- bond to form a -C-O-P- bond (*A routes* in Fig. 6) and scission of a second -C-P- bond to form a -P-OH bond (*B routes* in Fig. 6).
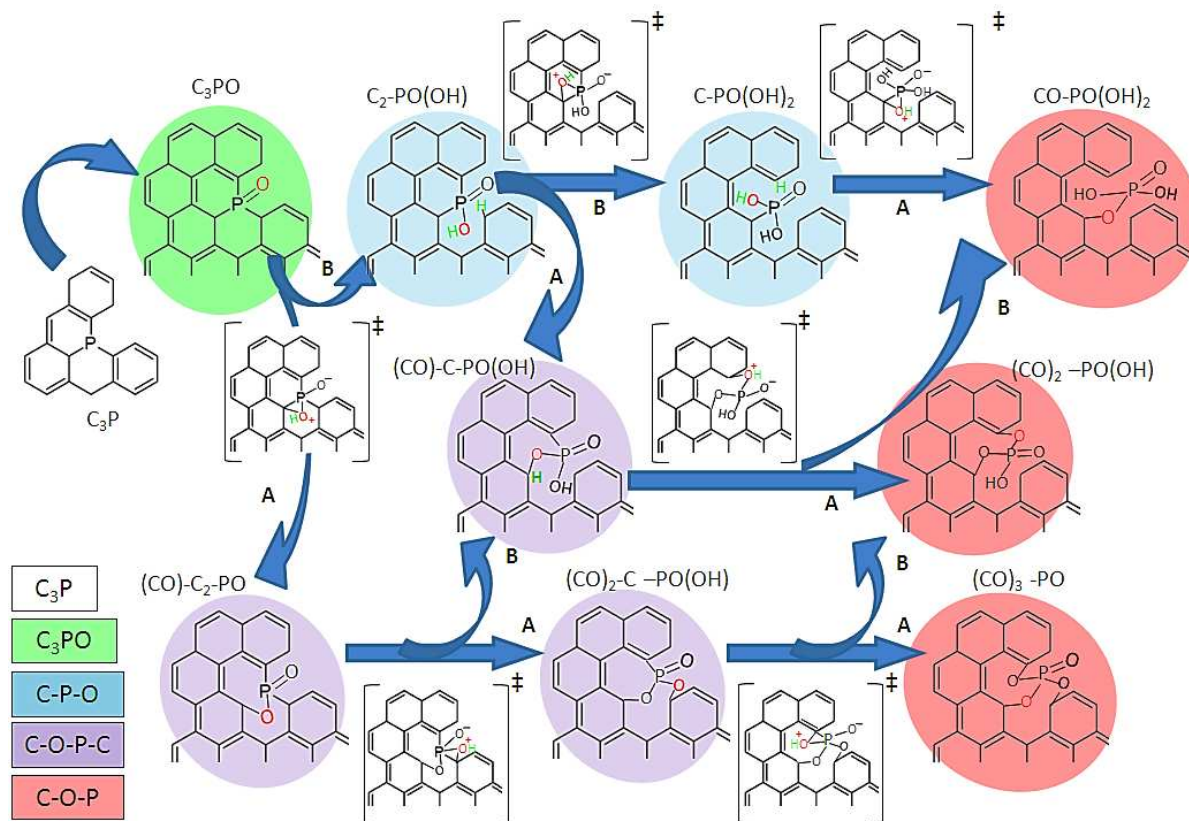

Figure 6. Proposed reactions for the electrochemical oxidation of phosphorus groups. Squared brackets display epoxide-like reaction intermediates. *A and B pathways* refer to the epoxide opening *routes a* and *b* (Fig. 7). The color code distinguishes the P-species, which are related to the oxidation state of P groups. These species are ordered from those found in the less oxidized (-C$_3$P) to those found in the more oxidized (-C-O-P-) P groups. Colored (red and green) atoms represent introduced atoms.

The existence of stable 3-membered rings with P is well documented [51,52]. A possible nucleophilic reaction for the formation of these intermediates based on the attack by HO$^\bullet$, is proposed in Fig. 7a. It involves a two-step electron donation from oxygen atoms to -C-P- bonds. Given the easier accessibility and/or less rigidity of phosphate tetragonal structure compared to that of carbon bonds in planar aromatic rings, the attack may be driven to the P atoms. Once formed, the opening of epoxide rings could proceed to generate a new -C-O-P-, -C-P-O- or C-OH species, depending on the broken bond: break of C-P bond (*route a*), break of C-O bond (*route b*) and break of

P-O bond (*route c*), respectively (see Fig. 7a). In agreement with experimental results (Figure 5c), the electroxidation of heat-treated samples (HA3500-T and HA3500-A-T), with a higher proportion of -C$_3$PO functionalities, to generate -C-P-O- and -C-O-P- species suggests that both *routes a* and *b* may be possible (*pathways A and B* in Fig. 6). By contrast, the generation of a new -C-OH bonding on a -C-P- one (*route c*) must be hindered and/or impeded by electronic reasons (the low electronic density on carbon atoms) and/or steric hindrance. Finally, the original or freshly-generated -C-P-O- species may further continue oxidation to form other more oxidized -C-P-O- species, with a higher number of -P-OH bonds or containing a mix of both -C-O-P- and -C-P-O- bond (referred to as -C-O-P-C- species), and -C-O-P- ones through the proposed *pathways A and B* (Fig. 6).
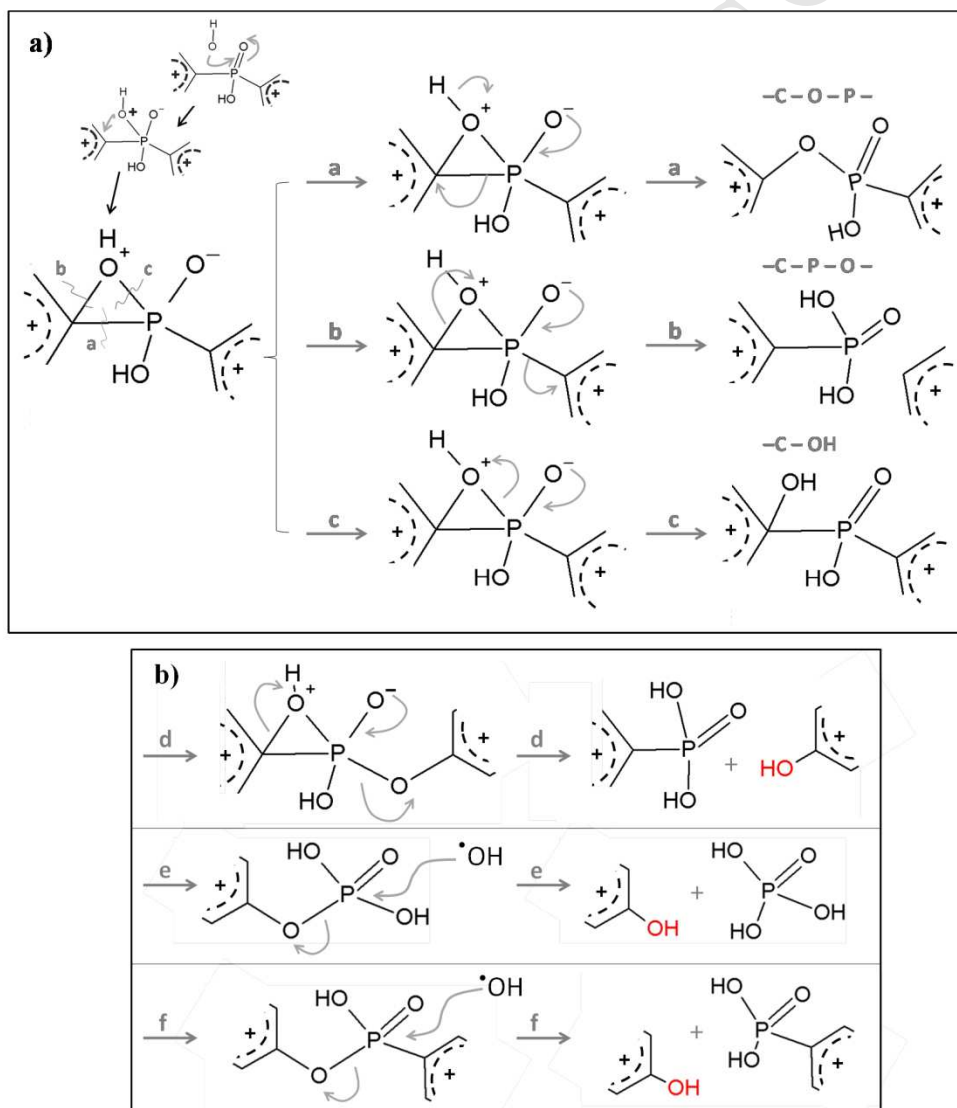

Figure 7. Proposed routes for the (a) formation & opening of epoxide-like intermediates and (b) P-mediated electroxidation of carbons.

After the electro-oxidation of P-groups, and in accordance with the experimental results previously shown, and although some carbon active sites could be directly electroxidized [49,50], we propose that during the electro-oxidation treatments, most of the oxidation proceeds through the initial and freshly-generated oxidized phosphorus species that transfer the gained oxygen to neighboring carbon atoms, acting as mediators of carbon electroxidation. In particular, among different phosphorus species, it is suggested that the mediated reaction may require of -C-O-P- connections, like in the case of mix -C-O-P-C- or -C-O-P- species. Given the lowest electro-oxidation currents observed for HA3500-A sample among the different P-containing ACs (Figure 2a and 2b), which initially contains a higher proportion of highly-oxidized -C-O-P- species, these species could show a high electrochemical stability, in agreement with the high temperature required for their decomposition, hindering the transfer of gained oxygen. Because they involve various steps and intermediates (Figures 6 and 7), all these reactions for oxygen fixation are expected to be slower than direct electroxidation processes, thus, justifying the lower oxidation currents observed for P-containing carbons (Figures 2a and 2b).

Previous calculations indicated that the -O-P- bonds are weaker than the -C-O- ones [40], so the introduction of oxygen groups (like -C-OH) may proceed through the break and generation of -O-P- bondings according to different possible routes (Figure 7b). In the case of mix -C-O-P-C- species, the reaction may progress with the epoxide formation followed by the breakdown of -O-P- bondings (*route d*). On the other hand, -C-O-P- species could suffer from a nucleophilic attack by HO• directly to the phosphorus atom and the subsequent break of -O-P- bondings with (*route e*) and/or without (*route f*) elimination of H_3PO_4. The occurrence of *route e* supposes an explanation of the observed loss of P upon electro-oxidation (Figure 2c), but it must be restricted considering the slight percentage lost. Therefore, *routes d* and *f* are proposed to be the prevailing ones. Since these routes lead to the regeneration of -C-P-O- species, the mediated electro-oxidation can continuously progress with successive cycles of -C-O-P- formation (*routes a* and *b*) and decomposition plus carbon oxidation (*routes d* and *f*). Furthermore, both routes result in the generation of CO-like oxygen groups, in agreement with the experimental results (Figure 3).

According to the proposed electro-oxidation mechanism, P-surface groups do not behave as physical barriers or poisoners, but instead, oxidation occurs through the phosphorus groups with higher reactivity compared to that of the free carbon sites. This

higher reactivity, however, is related to the HO$^\bullet$ nucleophilic attack; so that the subsequent transfer of gained oxygen, from highly stable phosphorus functionalities to carbon atoms, is hindered and slowed down to control the kinetics of the overall carbon electro-oxidation. Nevertheless, other possible stabilizing effects of phosphorus groups, by altering the chemical reactivity of the neighboring free or oxidized carbon sites and/or stabilizing the graphenic layers (like B or N) [38], should not be ruled out.

5. Conclusions

In this work, the enhanced electro-oxidation resistance induced by phosphorus surface groups in carbon materials has been clearly demonstrated in high-surface area ACs. Unlike previous approaches, involving the blockage or minimization of active sites, the introduction of stabilizing heteroatoms (B, N), or the introduction of a catalyst for water electroxidation, the proposed mediated mechanism is a completely new concept to explain the electro-oxidation of phosphorus-containing carbon materials. The mechanism involves the active participation of phosphorus surface groups, with preferential nucleophilic attack and oxygen uptake, which are gradually transformed from less- to more-oxidized highly stable species; and the slow and hindered transfer of gained oxygen from highly stable phosphorus species to neighboring carbon sites, to finally hamper the generation of (C*OOH)-like unstable promoters of electrogasification (corrosion).

Although this work has been focused on ACs, in principle, similar effects could be expected in other kind of carbon materials in which phosphorus species are effectively introduced during the chemical activation. Preliminary studies with other carbon materials confirm this idea. Hence, the electro-oxidation inhibition induced by phosphorus functionalities entails a general strategy to increase the electrochemical stability of carbons, offering promising perspectives for multiple electrochemical applications.

Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at

http://dx.doi.org/..."

REFERENCES

[1] Kinoshita K. Carbon: electrochemical and physicochemical properties. New York: Wiley; 1998.

[2] Steele BCH, Heinzel A. Materials for fuel-cell technologies. Nature 2001;414:345-52.

[3] Zhou XJ, Qiao JL, Yang L, Zhang JJ. A Review of Graphene-Based Nanostructural Materials for Both Catalyst Supports and Metal-Free Catalysts in PEM Fuel Cell Oxygen Reduction Reactions. Adv Energy Mater 2014;4;1301523-47.

[4] Turner APF. Biosensors: sense and sensibility. Chem Soc Rev 2013;42:3184-96.

[5] Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. Nature 2001;414:359-67.

[6] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat. Mater. 2008;7:845-54.

[7] Nishihara H, Kyotani T. Templated Nanocarbons for Energy Storage. Adv Mater 2012;24:4473-98.

[8] Kuhn AT. Industrial Electrochemical Processes. Elsevier: New York; 1971.

[9] Kuang JZ, Thonstad J, Sørlie M. Effects of additives on the electrolytic consumption of carbon anodes in aluminium electrolysis. Carbon 1995;33:1479-84.

[10] Trasatti S. Electrocatalysis: Understanding the success of DSA. Electrochim Acta 2000;45:2377-85.

[11] Gatrell M, Kirk DM. The electrochemical oxidation of aqueous phenol at a glassy carbon electrode. Canadian J Chem Eng 1990;68:997-1003.

[12] Ruiz V, Santamaría R, Granda M, Blanco C. Long-term cycling of carbon-based supercapacitors in aqueous media. Electrochim Acta 2009;54:4481-6.

[13] Cazorla-Amorós D, Lozano-Castelló D, Morallón E, Bleda-Martínez MJ, Linares-Solano A, Shiraishi S. Measuring cycle efficiency and capacitance of chemically activated carbons in propylene carbonate. Carbon 2010;48:1451-6.

[14] Wang JJ, Yin G, Shao YY, Zhang S, Wang Z, Gao Y. Effect of carbon black support corrosion on the durability of Pt/C catalyst. J Power Sources 2007;171:331-9.

[15] Antolini E. Carbon supports for low-temperature fuel cell catalysts. Appl Catal B Environ 2009;88:1-24.

[16] Antonucci PL, Pino L, Giordano N, Pinna G. A comparative analysis of structural and surface effects in the electrochemical corrosion of carbons. Mat Chem Phys 1989;21:495-506.

[17] Giordano N, Antonucci PL, Passalacqua E, Pino L, Arico AS, Kinoshita K. Relationship between physicochemical properties and electrooxidation behaviour of carbon materials. Electrochim Acta 1991;36:1931-5.

[18] Li L, Xing Y. Electrochemical durability of carbon nanotubes at 80 ºC. J Power Sources 2008;178:75-9.

[19] Gallagher KG, Yushin G, Fuller TF. The Role of Nanostructure in the Electrochemical Oxidation of Model-Carbon Materials in Acidic Environments. J Electrochem Soc 2010;157:B820-30.

[20] Tabti Z, Berenguer R, Ruiz-Rosas R, Quijada C, Morallón E, Cazorla-Amorós D. Electrooxidation methods to produce pseudocapacitance-containing porous carbons. Electrochemistry 2013;81:833-9.

[21] Choo H-S, Kinumoto T, Jeong S-K, Iriyama Y, Abe T, Ogumi Z. Mechanism for Electrochemical Oxidation of Highly Oriented Pyrolytic Graphite in Sulfuric Acid Solution. J Electrochem Soc 2007;154:B1017-23.

[22] Maass S, Finsterwalder F, Frank G, Hartmann R, Merten C. Carbon support oxidation in PEM fuel cell cathodes. J Power Sources 2008;176:444-51.

[23] Yu PT, Liu Z, Makharia R. Investigation of Carbon Corrosion Behavior and Kinetics in Proton Exchange Membrane Fuel Cell Cathode Electrodes. J Electrochem Soc 2013;160: F645-50.

[24] Pandy A, Yang Z, Gummalla M, Atrazhev VV, Kuzminyh NY, Sultanov VI, et al. A Carbon Corrosion Model to Evaluate the Effect of Steady State and Transient Operation of a Polymer Electrolyte Membrane Fuel Cell. J Electrochem Soc 2013;160:F972-9.

[25] Castanheira L, Dubau L, Mermoux M, Berthomé G, Caqué N, Rossinot E, et al. Carbon Corrosion in Proton-Exchange Membrane Fuel Cells: From Model Experiments to Real-Life Operation in Membrane Electrode Assemblies. ACS Catal 2014;4:2258-67.

[26] Shao Y, Yin G, Zhang J, Gao Y. Comparative investigation of the resistance to electrochemical oxidation of carbon black and carbon nanotubes in aqueous sulfuric acid solution. Electrochim Acta 2006;51:5853-7.

[27] Gallagher KG, Fuller TF. Kinetic model of the electrochemical oxidation of graphitic carbon in acidic environments. Phys Chem Chem Phys 2009;11:11557-67.

[28] Stevens DA, Hicks MT, Haugen GM, Dahn JR. Ex Situ and In Situ Stability Studies of PEMFC Catalysts. Effect of Carbon Type and Humidification on Degradation of the Carbon. J Electrochem Soc 2005;152:A2309-15.

[29] Jang SE, Kim H. Effect of water electrolysis catalysts on carbon corrosion in polymer electrolyte membrane fuel cells. J Am Chem Soc 2010;132:14700-1.

[30] Pyun S-I, Lee E-J, Kim T-Y, Lee S-J, Ryu Y-G, Kim C-S. Role of surface oxides in corrosion of carbon black in phosphoric acid solution at elevated temperature. Carbon 1994;32:155-9.

[31] Hulicova-Jurcakova D, Kodama M, Shiraishi S, Hatori H, Zhu ZH, Lu GQ. Nitrogen-Enriched Nonporous Carbon Electrodes with Extraordinary Supercapacitance. Adv Funct Mater 2009;19:1800-9.

[32] Shrestha S, Mustain WE. Properties of Nitrogen-Functionalized Ordered Mesoporous Carbon Prepared Using Polypyrrole Precursor. J Electrochem Soc 2010;157: B1665-72.

[33] Hulicova-Jurcakova D, Puziy AM, Poddubnaya OI, Suárez-García F, Tascón JMD, Lu GQ. Highly Stable Performance of Supercapacitors from Phosphorus-Enriched Carbons. J Am Chem Soc 2009;131:5026-7.

[34] Huang CC, Sun T, Hulicova-Jurcakova D. Wide electrochemical window of supercapacitors from coffee bean-derived phosphorus-rich carbons. ChemSusChem 2013;6:2330-9.

[35] McKee DW, Spiro CL, Lamby EJ. The Inhibition of Graphite Oxidation by Phosphorous Additives. Carbon 1984;22:285-90.

[36] Oh SG, Rodriguez NM. In situ electron microscopy studies of the inhibition of graphite oxidation by phosphorus. J Mater Res 1993;8:2879-88.

[37] Labruquère S, Pailler R, Naslain R, Desbat B. Oxidation inhibition of carbon fiber performs and C/C composites by H_3PO_4. J Eur Ceram Soc 1998;18:1953-60.

[38] Lee Y-J, Radovic LR. Oxidation inhibition effects of phosphorus and boron in different carbon fabrics. Carbon 2003;41:1987-97.

[39] Maier CR, Jones LE. The Influence of Aluminum Phosphates on Carbon-Carbon Oxidation. Carbon 2005;43:2272-6.

[40] Wu X, Radovic LR. Inhibition of catalytic oxidation of carbon/carbon composites by phosphorus. Carbon 2006;44:141-51.

[41] Bedia J, Rosas JM, Vera D, Rodríguez-Mirasol J, Cordero T. Isopropanol decomposition on carbon based acid and basic catalysts. Catal. Today 2010;158:89-96.

[42] Bedia J, Barrionuevo R, Rodríguez-Mirasol J, Cordero T. Ethanol dehydration to ethylene on acid carbon catalysts. Appl Catal B Env 2011;103: 302-10.

[43] Guerrero-Pérez MO, Valero-Romero MJ, Hernández S, López-Nieto JM, Rodríguez-Mirasol J, Cordero T. Lignocellulosic-derived mesoporous materials: An answer to manufacturing non-expensive catalysts useful for the biorefinery processes. Catal Today 2012;195:155-61.

[44] Rosas JM, Ruiz-Rosas R, Rodríguez-Mirasol J, Cordero T. Kinetic study of the oxidation resistance of phosphorus-containing activated carbons. Carbon 2012;50:1523-37.

[45] Bedia J, Rosas JM, Márquez J, Rodríguez-Mirasol J, Cordero T. Preparation and characterization of carbon based acid catalysts for the dehydration of 2-propanol. Carbon 2009;47:286-94.

[46] Rosas JM, Bedia J, Rodríguez-Mirasol J, Cordero T. HEMP-derived activated carbon fibers by chemical activation with phosphoric acid. Fuel 2009;88:19-26.

[47] Bedia J, Ruiz-Rosas R, Rodríguez-Mirasol J, Cordero T. A kinetic study of 2-propanol dehydration on carbon acid catalysts. J Catal 2010;271:33-42.

[48] Figueiredo J, Pereira M, Freitas M, Orfao J. Modification of the surface chemistry of activated carbons. Carbon 1999;37:1379-89.

[49] Berenguer R, Marco-Lozar JP, Quijada C, Cazorla-Amorós D, Morallón E. Effect of electrochemical treatments on the surface chemistry of activated carbón. Carbon 2009;47:1018-27.

[50] Berenguer R, Nishihara H, Itoi H, Ishii T, Morallón E, Cazorla-Amorós D et al. Electrochemical generation of oxygen containing groups in an ordered microporous zeolite templated carbon. Carbon 2013;54:94-104.

[51] Mathey F. Chemistry of 3-Membered Carbon-Phosphorus Heterocycles. Chem Rev 1990;90:997-1025.

[52] Huang CY, Doyle AG. The Chemistry of Transition Metals with Three-Membered Ring Heterocycles. Chem Rev 2014;114:8153-98.

[53] Radovic LR, Silva-Tapia AB, Vallejos-Burgos F. Oxygen migration on the graphene surface. 1. Origin of epoxide groups. Carbon 2011;49:4218-25.

[54] Radovic LR, Suarez A, Vallejos-Burgos F, Sofo JO. Oxygen migration on the graphene surface. 2. Thermochemistry of basal-plane diffusion (hopping). Carbon 2011;49:4226-38.

Supplementary Data

Enhanced Electro-oxidation Resistance of Carbon Electrodes Induced by Phosphorus Surface Groups

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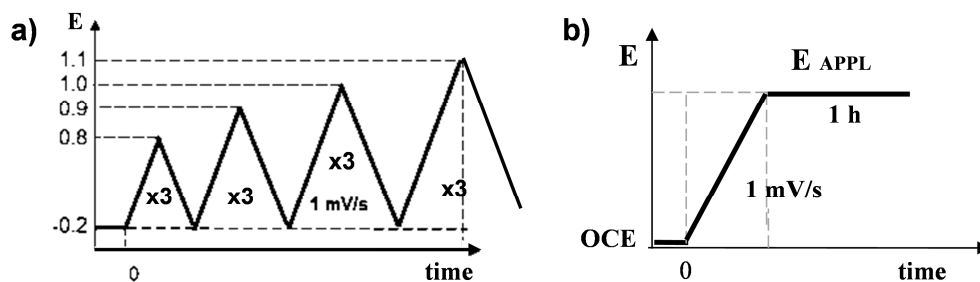*Corresponding author*

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Figure S1. Evolution upon time of the controlled electrode potential during the potentiodynamic (a) and potentiostatic (b) electro-oxidation treatments.
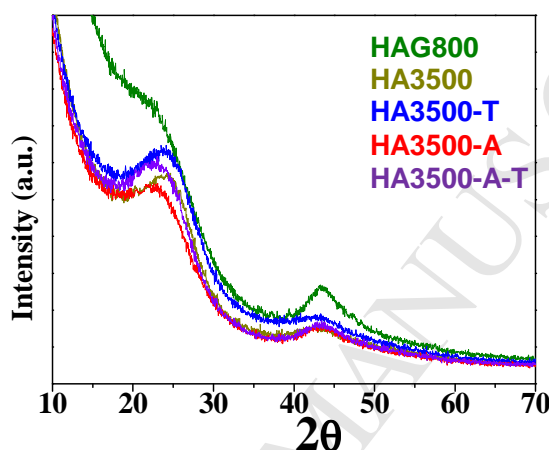

Figure S2. XRD patterns of the ACs prepared by physical (HAG800) or chemical (HA3500-samples) activation.
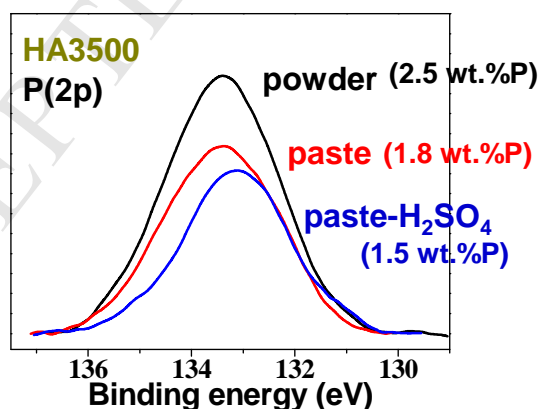

Figure S3. The influence of pasting (addition of PTFE and carbon black) (paste) and the 3-days H_2SO_4 impregnation (paste-H_2SO_4 = electrode) in the P(2p) XPS-spectrum of HA3500 sample (powder).

NOTES: the detected surface P content in the ACs decreases (around 25 %) as a consequence of blending with additives (for electrode preparation), and only about 15 % of P in pastes is washed out by contact with the 1 M H_2SO_4 electrolyte during the 3-days impregnation step, prior electroxidation treatments. This chemical leaching mainly affects the most oxidized P species (at higher binding energies).
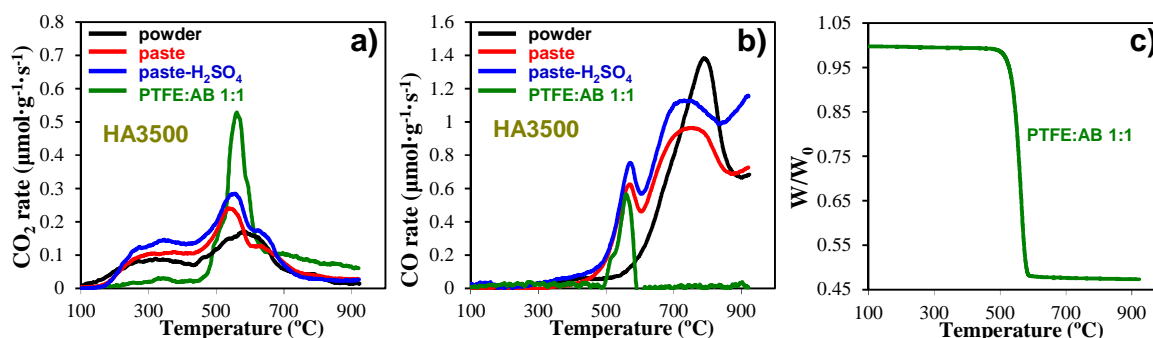
Figure S4. The influence of pasting (addition of PTFE and carbon black) (paste) and the 3-days H_2SO_4 impregnation (paste-H_2SO_4 = electrode) in the CO_2 (a) and CO (b) evolutions from TPD experiments of the HA3500 sample (powder), as well as the thermal behavior of the additives itself (PTFE:AB 1:1, where AB = acetylene black (carbon black)).

NOTES: The abrupt peak at ca. 560 ºC, which is absent on the profiles of powdery carbons (black line), is attributed to the thermal decomposition of PTFE binder, as deduced from the TPDs (green line) and the mass decay at the same temperature from a thermogravimetric measurement (Fig. S4c). Considering the low percentage of additives, that PTFE contains no oxygen atoms and that the oxygen content of carbon black can be neglected compared to that of ACs, the quantification of CO_2 and CO evolved groups is not affected by the presence of additives. Finally, the slight increase in both the CO_2 and CO TPD profiles after H_2SO_4 impregnation of carbon pastes (blue lines) suggests that carbons may be slightly oxidized during this step.
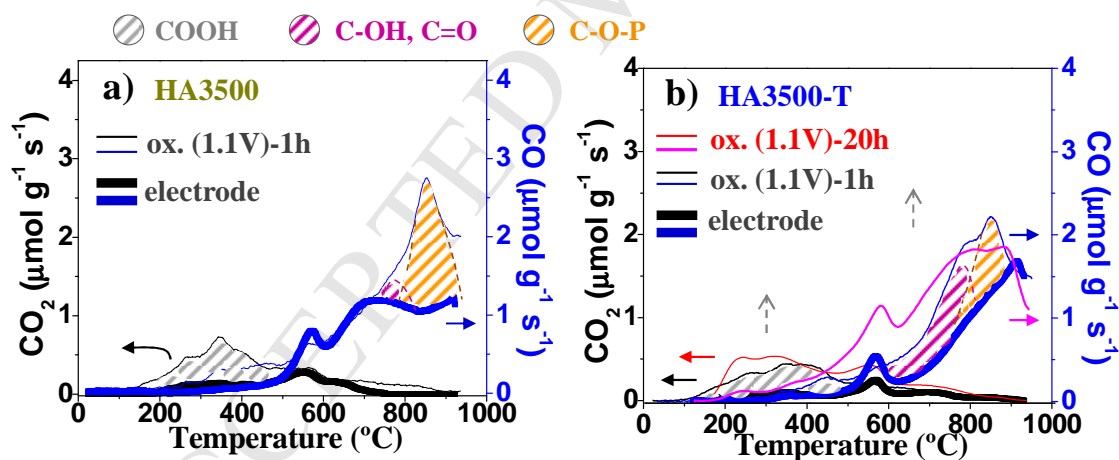

Figure S5. CO_2 and CO patterns from TPD experiments of the different carbons before (thick lines) and after (thin lines) potentiostatic electro-oxidation under different conditions. NOTE: data recorded from AC pastes.

Table S1. Total electric charge and electrons passed during the potentiostatic experiments and the change in oxygen content (ΔO), the electrons associated to the oxygen gain (ΔO-electrons) and the passed electrons (extra electrons) that may be related to reactions other than the oxygen gain, of the different ACs as determined after the treatments at 1.1V for 1 h (or other specified conditions).

Sample	Charge[a] (C/g_{AC})	Electrons[b] $(mmol\ e^-/g_{AC})$	ΔO[c] $(mmol\ O/g_{AC})$	ΔO-electrons[d] $(mmol\ e^-/g_{AC})$	Extra Electrons[e] $(mmol\ e^-/g_{AC})$
HAG800	1383	14.3	6.0	6.3	8.0
HA3500-T	481	5.0	2.9	2.9	2.1
HA3500	274	2.8	3.4	3.3	---
HA3500-A	244	2.5	2.9	3.6	---
HAG800 (18h)	3459	35.9	7.6	7.9	27.9
HA3500-T (20h)	2044	21.2	3.6	3.1	18.0

[a] The total electric charge (Q) was calculated by subtracting the charge of the double layer (DL) (estimated from the capacitance value on the 0.0-0.8V window) to the sum of the instant electric charges ($Q = (\Sigma\ Qt) - Q_{DL}$). On the other hand, the instant electric charges (Qt) were estimated from the current measured during the linear sweep scan up to 1.1V (Qt = it(A) * Et(V)/scan rate(V/s)), together with that measured during the course of the experiments at 1.1 V (Qt = it(A) * t(s)).

[b] The number of passed electrons was quantified by dividing the total electric charge by the Faraday constant ($F = 96485\ C/mol\ e^-$).

[c] The oxygen gain $(\Delta O) = O_{After} - O_{Before}$, calculated from TPD quantification: $O = CO + 2CO_2$, after and before the electroxidation treatments.

[d] The electrons consumed in the oxygen gain (ΔO-electrons) were calculated from deconvoluted TPD profiles (see below an example for HA3500-ox. (1.1V)-1h) and assuming that 1 electron per O atom may be involved in the generation/introduction of 1 phenol or -C-O-P- group; 1.5 electrons per O atom in the generation of 1 carboxylic group or any CO_2 and CO coming from anhydride groups; and that 2 electrons per O atom may participate in the generation of quinone and carbonyl groups.
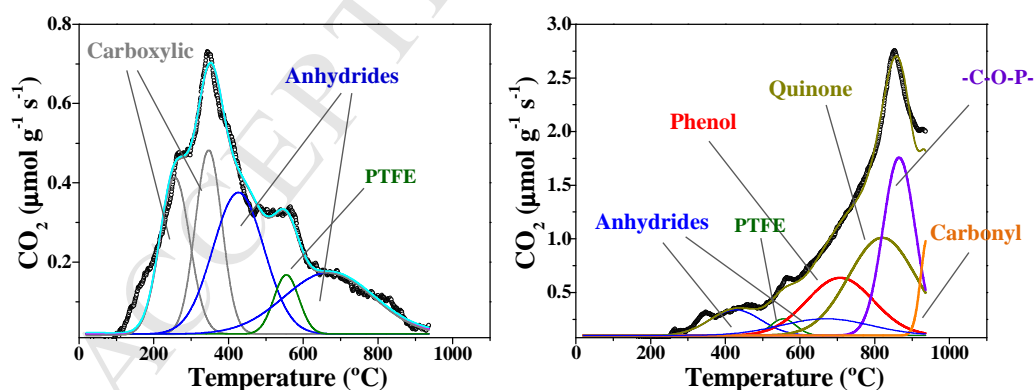
NOTES: the deconvolution considers that 1 anhydride group decomposes into 1 CO_2 and 1 CO; two types of anhydride groups have been identified in the studied ACs: those evolving CO_2 at lower temperatures may correspond to the common ones [(O=COH)-O-(HOC=O)], whereas the more stable ones could be associated to phosphorus species [like (O=COH)-O-(C-O-P-)]; nevertheless, the presence lactone and lactol groups should not be ruled out.

[e] Extra Electrons = Electrons - ΔO-electrons. Note: these extra electrons are expected to participate in the generation of oxygen groups that do not appear at the end of the potentiostatic experiments (although other side reactions could also occur) and, therefore, they may be somehow related to amount of oxygen evolved by electrochemical gasification.