Carbon xerogels electrochemical oxidation and correlation with their physico-chemical properties

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Abstract

The electrochemical oxidation of carbon represents a relevant limitation for the application of carbon-based materials at the electrodes of several electrochemical devices, like fuel cells, metal-air batteries, water electrolyzers or supercapacitors. Understanding the key influencing parameters is thus of paramount importance to prevent and avoid the degradation of carbon materials. In the present investigation, carbon xerogels (CXGs) as a model of synthetic amorphous carbon, were studied on the basis of different surface chemistry and structure. Electro-oxidation experiments consisted of potential holding (1.2 V vs. RHE) on electrodes prepared with CXGs. The results indicate that the presence of oxygen groups (-C-O) and a higher ordering degree hinder the carbon oxidation reaction. A sub-structural parameter considering both the amount of oxygen-free carbon atoms (C-C + C*-C-O) from X-ray photoelectron spectroscopy, and the disordering degree from Raman spectra (in terms of I_D/I_G) is here proposed as a new factor to evaluate the tendency of an amorphous carbon material, like xerogels, to be electrochemically oxidized.

Keywords: carbon xerogels, carbon electro-oxidation, oxygen groups, disorder, degradation, amorphous carbon.

1. Introduction

Advanced carbon-based materials are playing a key role nowadays in the development of low-cost and environmentally friendly electrochemical devices devoted to the conversion and storage of energy, such as fuel cells, water electrolyzers, advanced batteries, solar cells and supercapacitors [1–3]. Over the past decades, the rise of novel carbon materials (graphene, nanotubes, nanofibers, etc.) characterized by remarkable physico-chemical and surface properties, has been responsible for the success of more efficient electrodes, adding high value to the electrochemical conversion of energy [4]. In particular, the very low density of carbon gels and their easily tunable porous texture have attracted a great interest within the scientific community [5,6]. Since Pekala et al. first reported the synthesis of carbon gels [7], plenty of works have been aimed to optimize the porous structure of different types of gels to be fitted in specific applications [6,8–12]. Moreover, great efforts have been done to reduce the production cost of high quality carbon gels, as recently revised by Rojas-Cervantes [13].

Regardless the more or less graphitic nature of carbon materials, they are prone to electro-oxidation at highly positive potentials. The equilibrium potential of the carbon oxidation reaction (COR) to carbon dioxide is 0.207 V vs. NHE at 25 °C [14]. In the presence of electron acceptor species, like water (present in aqueous electrolytes and/or electrode environments) or oxygen (as in the case of the positive electrode of fuel cells, metal-air batteries, electrolyzers, etc.), the occurrence of relatively high positive potentials (> 1 V vs. RHE) unavoidably results in a certain degree of COR, and thus, the degradation and eventual modification of the electrode initial properties. At the positive electrode of an electrochemical cell, potentials more positive than the reversible potential for COR, may occur under normal operation (charge/discharge processes, current transients with time, etc.). Besides, some abnormal working conditions and/or situations,

such as sudden start-stop cycles or the starvation of reactant species, can be exceedingly damaging for carbon materials at the electrodes [15]. A typical example is the carbon corrosion at the cathode of polymer electrolyte fuel cells, which is a major concern towards the development of stable systems based on this technology [16–18].

Understanding the correlation between carbon features and oxidation kinetics is thus of high relevance to ameliorate electrode degradation [19]. The COR is a complex process involving several steps and the role of carbon matrix characteristics is not yet well understood. Up to date, the main known carbon features conditioning its electro-oxidation are correlated with high surface area, large graphitic interlayer spacing, high amount of oxygen species and low amount of graphitic domains [20–22]. The electrochemical oxidation of carbon has been investigated from different points of view [19,23–27], but the reaction mechanism is not yet clear. As a consequence, only a few strategies have been proposed to ameliorate the degradation of carbon. Most promising approaches consist of reducing the surface area [28], controlling the morphology or structure [29,30] or modifying the chemical composition at the surface [31,32]. Still, the individual contribution of each parameter is not well defined. Empirical investigations can lead to a general understanding based on a specific carbon morphology. For further details on kinetic models and interpretation, it is recommended to consult the work of Gallagher and Fuller [33].

Carbon xerogels (CXGs) are of great interest, from a quality-to-cost point of view, among the different carbon gels typologies (mainly comprising also aerogels and cryogels) [12]. CXGs, though possessing a certain ordering degree in the short-range, are not graphitic materials [34–36]. This fact, together with their relatively highly developed porosity, makes them more prone to oxidation processes than graphite-like carbons, such as carbon nanotubes or nanofibers [37]. The main scope of the present work is to examine

the electrochemical oxidation behavior of CXGs differing in porosity and surface chemistry. A cross-analysis between physico-chemical properties and electrochemical behavior is discussed, aimed to design strategies to minimize degradation phenomena on porous amorphous carbonaceous materials.

2. Experimental

2.1 Carbon xerogels synthesis

Carbon xerogels with different physico-chemical properties were synthesized according to the previous experience of the research group [38,39]. In order to significantly modify their properties, three synthesis variables were varied as shown in **Table 1**: the resorcinol to sodium carbonate molar ratio, the pyrolysis temperature and the solvent used during polymerization of the gel. The procedure was the same for all. Briefly, resorcinol (1,3-dihydroxybenzoic acid, Sigma-Aldrich), sodium carbonate (Panreac), formaldehyde (Sigma-Aldrich) and the solvent (water or acetone/water 1:9 w/w) were well mixed together in a closed vessel, and the pH was adjusted to 6.0 with diluted nitric acid. All carbon xerogels were synthesized with stoichiometric resorcinol to formaldehyde ratio (1:2) and a dilution ratio of 5.7 (i.e. moles of solid per mole of solvent).

Table 1. Description of the synthesis conditions of carbon xerogels

Carbon xerogel	Resorcinol to carbonate ratio	Pyrolysis temperature / °C	Polymerization solvent
CXG-8-8	8	800	H ₂ O (pure, > 15 MΩ cm)
CXG-8-9	8	900	H ₂ O (pure, > 15 MΩ cm)
CXG-10-8	10	800	H ₂ O (pure, > 15 MΩ cm)
CXG-8A-8	8	800	CH ₃ COCH ₃ (10%) in H ₂ O

The polymerization and curing processes took place in the closed vessels containing the mixture for one day at room temperature, one day at 50 °C and five days at 85 °C, as described in [10]. Afterwards, the so-obtained organic gels were submerged in acetone for 3 days, replacing the liquid with fresh acetone every day. The drying process was performed in sub-critical conditions: 5 h at 65°C and 5 h at 110°C. The resulting powder was milled and pyrolyzed at 800 °C or 900 °C (see Table 1) for 3 h under inert (N₂) atmosphere.

2.2 Physico-chemical characterization

The textural and morphological features of the carbon xerogels were determined by means of N₂ and CO₂ physisorption at –196 °C and 0 °C, respectively, in a Micromeritics ASAP 2020 instrument. The specific surface areas were calculated from adsorption-desorption isotherms applying the Brunauer-Emmet-Teller (BET) equation. Pore volume and average pore size were determined using the single-point and Barrett-Joyner-Halenda (BJH) methods, respectively. A further assessment of microporosity was obtained through CO₂ adsorption isotherms at 0 °C applying the Dubinin–Radushkevich equation. Mercury porosimetry was used to determine the total void volume, and the maximum pore size was deduced from Washburn’s equation. The measurements were performed in a Poremaster Quantachrome instrument. Hg measurements are limited to pores larger than 7.5 nm. All samples were grinded to sub-millimeter particles before characterization.

X-ray photoelectron spectroscopy (XPS) analyses were performed in a ESCA Plus Omicron spectrometer equipped with a Mg (1253.6 eV) anode, at 150 W (15 mA, 10 kV) power, over an area of sample of 1.75 × 2.75 mm. C1s (278-295 eV) and O1s (526-541 eV) signals were obtained at 0.1 eV step, 0.5 s dwell and 20 eV pass energy. Data analysis and quantification were performed using CasaXPS software. A Shirley background

subtraction was used for quantification of C1s, O1s spectra. A 70% Gaussian/30% Lorentzian line shape was utilized in the curve deconvolution of spectra.

Elemental analyses were performed with a Thermo Flash 1112 analyzer (ThermoFinnigan Waltham, MA, USA) for the determination of C, H, N, O and S, in the range 0.05%–99.95%, and upon stabilization of the samples at 120°C for 1 hour in order to remove adsorbed water.

Raman spectra of carbon xerogels were obtained with a Horiba Jobin Yvon HR800 UV, using the green line of an argon laser ($\lambda = 514.5$ nm) as excitation source. The carbon ordering degree was evaluated by means of the relative intensities of D (*ca.* 1350 cm^{-1}) and G (*ca.* 1590 cm^{-1}) peaks. Scanning electron microscope (SEM) images were recorded using a Hitachi S-3400 N.

2.3 Electrochemical experiments

Gas diffusion electrodes were prepared with a loading of 0.6 mg cm^{-2} of carbon and 33% wt. of Nafion® as binder and polymer ionomer, on a commercial hydrophobic diffusion layer (ELAT LT 1200W), according to a procedure described elsewhere [38]. Half-cell tests were carried out in a conventional thermostated three-electrode cell consisting of the gas diffusion electrode to be tested (working electrode), a mercury-mercurous sulfate reference electrode ($\text{Hg/Hg}_2\text{SO}_4$, K_2SO_4 sat.) and a high surface coiled platinum wire as counter electrode. The electrode geometric area was 0.2 cm^2 , and a 0.5 M H_2SO_4 aqueous solution was employed as electrolyte. Gas (nitrogen or oxygen) was fed to the electrode backing layer during the tests. A μ Autolab Metrohm potentiationstat/galvanostat was used to perform the measurements. Electrochemical carbon electro-oxidation experiments were conducted in the half-cell system by means of potential holding (1.2 V vs. RHE),

feeding nitrogen to the electrode. The evaluation of the decay process was carried out by in situ electrochemical tests: chronoamperometry and cyclic voltammetry.

3. Results and discussion

3.1 Physico-chemical properties of carbon xerogels

A detailed analysis of the physico-chemical properties of carbon xerogels is highly important to establish a correlation with their electrochemical behavior in the carbon oxidation reaction (COR). The porosity of CXGs was investigated by adsorption isotherms of N₂ and CO₂ as well as by Hg porosimetry (**Figure 1** and **Table 2**). They all present similar densities (**Table 2**), as determined by He picnometry, and similar morphology (see SEM images in **Figure S1**). **Figure 1a** shows the nitrogen adsorption-desorption isotherms of the CXGs at -196 °C. All the isotherms present a combination of types I and IV adsorption/desorption curves according to IUPAC classification [40], which corresponds to micro–mesoporous materials.

Textural properties are determined by the relative amount of basifying agent in the sol. Sodium carbonate acts as a buffer, regulating the sol pH. It is generally considered that low R/C molar ratios, i.e. R/C = 50, result in small polymer particles (about 3–5 nm size), which are highly interconnected by large necks giving the gel a fibrous appearance. In contrast, higher R/C molar ratios, R/C = 800, result in large polymer particles (16–200 nm diameter), yielding a carbon material of notably increased mesopore volume [5,7]. However, a further increase of R/C molar ratio from 800 to 1050 results in a CXG of substantially lower pore volume and much lower surface area in comparison to the materials synthesized at R/C 800 (CXG-8-8). CXG-10-8 (with R/C = 1050) gives rise to a low initial pH, that might not be sufficient to activate the resorcinol ring (by deprotonation), leading to un-reacted resorcinol molecules, that do not polymerize and

partially remain after pyrolysis, leading to a less developed porous structure. The partial substitution of water by acetone (in CXG-8A-8) leads to a carbon xerogel with a less developed textural structure, a fact that was also described by Fairén-Jimenez et al. for carbon aerogels [41]. Resorcinol-formaldehyde aggregates dissolve worse in acetone (an aprotic solvent), causing the system to be less time in the nucleation step, resulting in smaller primary particles, and therefore, leading to a gel with smaller pores [42].

The two CXGs prepared with a resorcinol-to-carbonate ratio of 800 in water (CXG-8-8 and CXG-8-9) show higher N₂ adsorption capacity than the other two CXGs, especially at partial pressures above 0.2. The difference between the two groups of CXGs is exacerbated at pressures approaching saturation (more than 5-fold difference). Such a different adsorption behavior reflects a relevant influence of the CXG gelation process conditions in the meso- and macro-porosity (pores larger than 2 nm) as well as a much lesser influence of the pyrolysis temperature. The shape and position of the hysteresis (0.75-0.95 partial pressure) do not change significantly with pyrolysis temperature (comparing CXG-8-8 and CXG-8-9), indicating that the mesopore structure is barely altered with the pyrolysis treatment.

Figure 1b shows the carbon dioxide adsorption isotherms for the various CXGs at 0 °C. The CXG-8-8 presents the lowest CO₂ adsorption capacity in the whole interval of relative pressures. Whereas, the other three CXGs show very similar adsorption curves, denoting a slightly larger content of micropores with respect to the xerogel obtained in the ‘reference’ conditions (gelation with R/C = 800 and pyrolysis at 800 °C). Globally, small differences are encountered in the CO₂ adsorption behavior, which indicates that the narrow microporosity is very similar among the whole set of CXGs herein investigated.

Figure 1. (a) N₂ adsorption-desorption isotherms; (b) CO₂ adsorption isotherms; (c) Hg porosimetry of carbon xerogels.

Quite different is the comparison resulting from the analysis of Hg porosimetry.

Figure 1c shows the Hg intrusion curves for the various CXGs. The xerogels pyrolyzed at 800 °C (CXG-8-8, CXG-10-8 and CXG-8A-8) present superimposed curves up to 0.3 MPa, due to the intrusion of Hg in the inter-particle space, and then develop an increase of the intruded Hg at different pressures with a similar shape achieving a plateau at high pressure. Both the pore volume at such a plateau, and the pressure at which most of the intrusion takes place, increase in the order CXG-8A-8 < CXG-10-8 < CXG-8-8. These results indicate that CXG-8-8 presents the largest intraparticle pore volume (1.71 cm³ g⁻¹) and, at the same time, the smallest macropores within the three mentioned samples (90 nm), evidenced by the Hg intrusion at pressure higher than 1 MPa. It is also remarkable that CXG-8-8 exhibits two intrusion slopes above 1 MPa, indicating a bimodal distribution of pore sizes. In particular, a small contribution of mesopores

centered at around 30 nm and a large contribution of interparticular macropores centered at around 90 nm. The xerogel characterized by the highest pyrolysis temperature, CXG-8-9, shows a completely different intrusion curve. It presents a higher intrusion slope at low pressure approaching volumes above $0.5 \text{ cm}^3 \text{ g}^{-1}$ at 0.2 MPa, followed by a mild pore volume increment up to 3 MPa ($0.7 \text{ cm}^3 \text{ g}^{-1}$) and then the main intrusion contribution, similar to the other xerogels, but at higher pressures. This porosimetry behavior indicates that two pore dimensions coexist: large pores from interparticle porosity, which depend on the grain size of particles, together with smaller pores, centered at 40 nm, as envisaged from the Hg intrusion curve at high pressure. In any case, CXG-8-9 presents the lowest intraparticular pore volume ($1.21 \text{ cm}^3 \text{ g}^{-1}$), as summarized in **Table 2**. CXG-10-8 and CXG-8A-8 exhibit a soft intrusion behavior at pressures over 0.9 and 0.55 MPa, indicating a wide pore size distribution, with most of the intruded Hg occurring in pores of over 200 nm size (**Table 2** indicates mean pore sizes) but with a tail at smaller pores.

Table 2. Textural properties of CXGs from N_2 and CO_2 adsorption isotherms and Hg porosimetry.

Sample	BET surface area / $\text{m}^2 \text{ g}^{-1}$	Pore volume (N_2) / $\text{cm}^3 \text{ g}^{-1}$	Pore volume (Hg) / $\text{cm}^3 \text{ g}^{-1}$	Pore volume (BJH_{des}) / $\text{cm}^3 \text{ g}^{-1}$	Pore volume ($\text{CO}_2\text{-DR}$) / $\text{cm}^3 \text{ g}^{-1}$	Mean pore size from BJH_{des} / nm	Mean pore size from Hg porosimetry / nm	Density (He picnometry) / g cm^{-3}
CXG-8-8	536	1.80	1.71	1.66	0.22	23	30 - 92	1.86
CXG-8-9	508	1.66	1.21	1.52	0.24	25	38	1.89
CXG-10-8	440	0.45	1.67	0.22	0.25	12	240	1.77
CXG-8A-8	425	0.39	1.48	0.16	0.24	11	380	1.80

Other than porosity, surface chemistry plays a fundamental role in determining the COR behavior. XPS and elemental analyses were carried out to investigate the composition of the CXGs. XPS is a surface-sensitive technique since the escape depth of the photoelectrons amounts to only a few atomic layers. From the survey spectra (**Figure S2**), the total content of carbon and oxygen (C1s and O1s peaks) were determined and are

reported in **Table 3**. No other elements were detected by XPS, as also confirmed by elemental analysis of the samples. The oxygen content is more than halved when increasing the pyrolysis temperature by 100°C, by comparing CXG-8-8 with CXG-8-9. At high temperature, strongly bonded oxygen functional groups desorb, reflecting that almost half of the oxygen groups created in the synthesis of CXG-8-8, being resistant to the treatment at 800°C, desorb at 900°C.

Figure 2. XPS spectra in the region of C1s of (a) CXG-8-8, (b) CXG-8-9, (c) CXG-10-8, and (d) CXG-8A-8.

CXG-10-8 presents higher oxygen content due to the incomplete polymerization because of unreacted resorcinol molecules, formed at acid pH, remaining after pyrolysis. The use of a mixture of water and acetone as solvent (CXG-8A-8) also results in higher oxygen content, due to partial polymerization of the organic gel, as previously established.

Figure 2 depicts the spectra for the C1s contribution of each carbonaceous material.

The C1s spectra have been resolved into five individual component peaks representing: (1) C-C non-functional structures (main peak at 284.6 ± 0.2 eV); (2) C*-C-O moieties attributed to carbon atoms located in defective regions (285.5 ± 0.4 eV) and providing asymmetry to the former peak; (3) C-O from carbon present in phenolic, alcoholic or ether groups (286.7 ± 0.3 eV); (4) C=O from carbon in the form of carbonyl, quinone groups (287.8 ± 0.2 eV); and finally (5) Π - Π^* transition interband or plasmon peak (290 ± 0.3 eV).

A high R/C molar ratio (acidic pH), leads to a material (CXG-8-8) with a high degree of polymerization, which favors the organization of the C-C bonds during pyrolysis. On the contrary, the content for C-oxidized is higher for xerogels CXG-10-8 and CXG-8A-8, due to the greater number of RF monomers that may have not completely reacted during synthesis and remain after pyrolysis.

By analyzing the results reported in **Figure 2**, it is evident that both the synthesis conditions (ratio of reactants, R/C) as well as the pyrolysis temperature greatly influence the chemistry of the carbon surface. First of all, the relative quantity of carbon related to oxygen groups, like C=O and especially C-O, notably decreases upon pyrolysis at 900 °C (CXG-8-9) compared to the sample treated at 800 °C (CXG-8-8). Indeed, the CXG-8-9 is the sample characterized by the highest percentage of C-C type moieties (62%), as reported in **Table 3**. On the other hand, the polymerization medium, and in particular the presence of a small amount of acetone in the solvent (CXG-8A-8), has a dramatic effect on the carbon chemistry as compared to the CXG-8-8. More specifically, there is a noticeable increase of the C-O contribution at 286.7 eV for the CXG-8A-8 sample. The deconvolution of the individual peaks (**Table 2**) indicates that about 43% of carbon is oxidized in the form of C-O, presumably coming from phenol, alcohols or ether groups,

and more than 50% of surface carbon atoms are present as oxidized moieties. Whereas, it appears that the effect of sodium carbonate concentration (by comparing CXG-10-8 with CXG-8-8), i.e. the initial pH in the polymerization process, has a minor effect on C1s profile. In the latter, it can be highlighted that the relative content of C=O coming presumably from carbonyl or quinone groups (287.8 eV) is slightly higher compared to the other CXGs.

Table 3. Chemical composition of CXGs: oxygen content from elemental analysis (wt%) subtracting the contribution of water; and carbon and oxygen content from XPS survey spectra (at %), carbon species from the deconvolution of C1s peak (%),

	O	C1s	O1s	C-C	C*-C-O	C-O	C=O	$\Pi-\Pi^*$
B.E.	wt%	at%	at%	284.6 eV	285.5 eV	286.7 eV	287.8 eV	290 eV
CXG-8-8	2.4	96.7	3.3	53.4	8.8	22.7	5.3	9.8
CXG-8-9	1.6	98.5	1.5	62.6	10.9	7.6	3.8	15.2
CXG-10-8	2.6	95.6	4.4	51.4	14.0	16.1	8.6	10.0
CXG-8A-8	3.5	94.3	5.7	42.4	0.2	43.4	7.3	6.7

The high-resolution spectra of the O1s as well as their deconvolution into several contributions are represented in **Figure 3** and summarized in **Table 3**. According to the bibliography [43], O1s spectra have been deconvoluted into five contributions: (1) O=C carbonyl oxygen from quinones (530.8 ± 0.2 eV); (2) O=C carbonyl oxygen in esters, anhydrides or lactones (532.4 ± 0.2 eV); (3) O-C from esters and anhydrides (533.4 ± 0.2 eV); O-C from carboxylic acids (534.5 ± 0.2 eV); and H₂O adsorbed on the surface of carbon (536.3 ± 0.2 eV). Some other authors consider the deconvolution into two peaks, one associated to O=C at 531.3 eV and one associated to O-C at 533.2 eV [44]. This assumption was not satisfactory when applied to B.E. higher than 534 eV of our CXG spectra, so we preferred using the first consideration.

Figure 3. XPS spectra in the region of O1s of (a) CXG-8-8, (b) CXG-8-9, (c) CXG-10-8, and (d) CXG-8A-8.

As seen in **Figure 3**, a significant difference in the O1s spectra is observed for the CXG-8-9 sample, which signal is mainly centered at approximately 532.8 eV whereas for the other three CXGs the maxima are centered at approximately 534.5 eV. The CXG-8-9 sample is indeed the one with the lowest oxygen content (1.5 at.%, **Table 3**) owing to the pyrolysis treatment at a higher temperature. Most of the oxygen is present as ester of anhydrides in the latter sample. In contrast, oxygen from carboxylic acids at 534.5 eV is the predominant specie for the CXGs pyrolyzed at 800°C.

Table 4. XPS analysis of CXGs: oxygen species from the deconvolution of O1s peak, atomic %. The relative atomic percentages with respect only to the O1s peak are indicated in brackets (total = 100%).

	O=C ^(a)	O=C ^(b)	O-C ^(c)	O-C ^(d)	H ₂ O
B.E.	530.8 eV	532.4 eV	533.4 eV	534.5 eV	536.3 eV
CXG-8-8	0.37	0.69	0.32	1.37	0.54

	(11.3)	(21.0)	(9.8)	(41.4)	(41.4)
CXG-8-9	0.30	0.34	0.57	0.19	0.09
	(20.3)	(22.5)	(38.0)	(12.9)	(6.3)
CXG-10-8	0.29	0.92	0.28	1.65	1.27
	(6.5)	(20.8)	(6.3)	(37.6)	(28.9)
CXG-8A-8	0.38	0.69	0.34	3.41	0.88
	(6.7)	(12.1)	(6.0)	(59.8)	(15.4)

^(a) carbonyls/quinones; ^(b) esters, anhydrides, lactones; ^(c) esters, anhydrides; ^(d) carboxylic acid

Raman spectra of CXGs were recorded to elucidate the degree of disorder in the carbonaceous matrix. **Figure 4** shows the spectra for the different xerogels. The disorder-induced band (D) appeared at about 1340 cm^{-1} , which is generally associated to the breathing modes of six-atom rings, requiring a defect for its activation [45]. Point defects, like vacancies or doping atoms, and crystallite borders in a multi-domain carbon sample contribute to the intensity of this D band [46]. Whereas, the band appearing at about 1590 cm^{-1} (G band) correlates the stretch vibration of sp^2 -bonded carbon atoms, generally associated to graphitic-like structure [47]. No other peaks, like D' or D'' that are commonly observed in other types of carbon like graphene [45], were advised in these carbon materials within the conditions of measurement.

Figure 4. Raman spectra of (a) CXG-8-8, (b) CXG-8-9, (c) CXG-10-8, and (d) CXG-8A-8.

The ratio between the D and G band intensities (I_D/I_G) is broadly used in the literature to quantify disorder in carbonaceous materials [46,48]. **Table 5** summarizes some of the important parameters extracted from Raman spectra deconvolution, including the position and full width at half maximum (FWHM) of D and G bands, the intensity ratio and the size of carbon domains in the direction of graphene layers (L_a) according to the Tuinstra and Koenig equation [49]. The CXG with the largest disordering degree is the CXG-8-8, followed by CXG-8A-8 and CXG-8-9, while CXG-10-8 presents the lowest disorder among all the investigated CXGs. It is thus deduced that a certain extent of ordering is achieved when either increasing the pyrolysis temperature, the resorcinol-to-carbonate ratio or adding acetone to the curing medium.

Table 5. Parameters from the deconvolution of D and G bands of Raman analysis of CXGs.

Sample	D-band position / cm^{-1}	D-band FWHM / cm^{-1}	G-band position / cm^{-1}	G-band FWHM / cm^{-1}	I_D/I_G ratio	L_a / nm
CXG-8-8	1336	153.6	1593	67.7	1.19	3.7
CXG-8-9	1340	133.1	1594	69.0	0.97	4.5
CXG-10-8	1360	206.0	1597	80.0	0.76	5.8
CXG-8A-8	1341	179.2	1591	69.4	1.0	4.4

Jorio and Filho [46] described that for $L_a < 30$ nm, the I_D/I_G ratio is not a well-defined figure of merit to quantify disorder, whereas the phonon line width is more appropriate, being related to phonon confinement. In our case, the FWHM of the G band is also a good descriptor of the disordering degree and follows the same trend than the I_D/I_G ratio, with the largest disorder for CXG-8-8 characterized by the narrowest G-band (67.7 cm^{-1}) and the lowest disorder for CXG-10-8 (80 cm^{-1}).

3.2 Electrochemical studies on carbon oxidation reaction (COR)

The main purpose of the present paper is to rationalize the COR behavior in carbon xerogels (CXGs) on the basis of their physico-chemical properties. To this purpose, this sub-section presents the electrochemical studies of carbon oxidation. In sub-section 3.3, a cross-analysis and discussion of the electrochemical and physico-chemical results will be presented. The COR was investigated by holding a constant potential of 1.2 V vs. RHE in acid electrolyte (0.5 M H_2SO_4) and monitoring the variation of current with time, according to the Kinoshita-Giordano methodology [20,50]. **Figure 5** shows the chronoamperograms obtained for the electrochemical oxidation of CXGs. According to Kinoshita-Giordano, current-time behavior obeys the **Equation 1**:

$$j = k t^{-n} \quad (\text{Equation 1})$$

with j being the current density (A g^{-1}), t being time (s) and k and n being constants (> 0). A double-logarithmic plot of current vs. time (**Figure 5a**) results in a linear representation with $-n$ as slope and $\log k$ as intercept with the y-axis. The linear scale representation of current density vs. time is shown in **Figure 5b**.

Figure 5. Chronoamperometric curves obtained at 1.2 V vs. RHE in aqueous 0.5 M H₂SO₄ electrolyte, room temperature, 0.6 mg cm⁻² carbon. (a) Double logarithmic scale of the whole test (90 min), (b) Detail of the first 600 s in linear scale (inset: initial 20 s).

The CXG-8-8 xerogel presents the highest oxidation current, followed by the CXG-8A-8, whereas CXG-8-9 and CXG-10-8 show similar current-time curves. The three samples prepared at 800°C exhibit higher current density at the very beginning compared to CXG-8-9. The fitting of the chronoamperometric curves to **Equation 1** is represented by the straight lines in **Figure 5a**, while the main kinetic parameters are summarized in **Table 6**.

Table 6. Carbon electrochemical oxidation parameters of CXGs.

	k / A s ⁿ g ⁻¹	k' ^(a) / μmol s ⁿ⁻¹ g ⁻¹	n	Q_{COR} (90 min) / C g ⁻¹	Oxidized carbon (90 min) ^(a) / %
CXG-8-8	12.8	33.2	0.74	424	1.32
CXG-8-9	2.5	6.5	0.68	134	0.42
CXG-10-8	1.9	4.9	0.63	132	0.41
CXG-8A-8	4.2	10.9	0.65	299	0.93

^(a) Assuming a 4-electron process in the oxidation of carbon.

The kinetic constant, expressed either in terms of current, k , or in molar basis, k' , indicates how fast carbon oxidizes with time [14]. The kinetic constant varies from 1.9 A sⁿ g⁻¹ for the CXG-10-8, to 12.8 A sⁿ g⁻¹ for the CXG-8-8. Previous works resulted in k values in the interval from 0.4 to 11 A sⁿ g⁻¹ for graphitized ordered mesoporous carbon [51], from 1 to 3 A sⁿ g⁻¹ for carbon nanofibers [18] and up to 33 A sⁿ g⁻¹ in the case of non-graphitic mesoporous carbon [51]. It has to be noted here that a direct comparison of kinetic constants is not precise since they are not dimensionally identical: the units depend on the value of the n factor. This is applicable to the discussion along this paper. However, as values in the same order of n (average 0.67) were obtained, significant differences of k parameter are valuable to analyze the COR rate as an indicator of the oxidation current. Taking into account that the slope in the double-logarithmic plots is similar among CXGs, it appears that changes in the carbon substrate properties influence the oxidation rate in a larger extent than the oxidation/passivation mechanisms.

CXGs present small differences in their exponential constant (ranging 0.63-0.74), indicating that the oxidation mechanism does not dramatically change with the carbon characteristics. Comparatively, a higher n value indicates a larger passivation of carbon surface with time, *i.e.* the formation of oxygen groups that no longer oxidize upon the application of highly positive potentials. In the case of carbon nanofibers, the exponential

constant ranges 0.71-0.78 [18], while in the case of ordered mesoporous carbon it was 0.77-0.89 [51].

Another good indicator of the extent of carbon oxidation is the charge associated to the chronoamperometric curve. **Table 6** summarizes the charges obtained during 90 min at 1.2 V vs. RHE (Q_{COR}). The higher the kinetic constant and the lower the exponential factor, the higher the oxidation charge. CXG-8-8 results about 1.4 times more oxidized than the second xerogel, CXG-8A-8 and much more than the two xerogels more resistant to electro-oxidation (CXG-8-9 and CXG-10-8). The extent of carbon oxidation can be derived by assuming a 4-electron mechanism (**Equation 2**) of the overall reaction from carbon to carbon dioxide:

Up to 0.4%-1.3% of the carbonaceous material is estimated to be lost in our tests by electrochemical oxidation depending on the xerogel characteristics. In the subsequent section (3.3), the correlation between the oxidation rate parameters and the CXG physico-chemical features will be discussed in detail.

Cyclic voltammetries (CVs) were carried out in the deaerated 0.5 M H_2SO_4 aqueous electrolyte before and after the chronoamperometry tests. The values of capacitance extracted from CVs (**Figure S3**) are summarized in **Table 7**. The gravimetric capacitance (F g^{-1}) was obtained from CVs using **Equation 3** [9]:

$$C = \frac{\left| \int_{E_1}^{E_2} i dE \right| + \left| \int_{E_2}^{E_1} i dE \right|}{2\nu(E_2 - E_1)} \quad (\text{Equation 3})$$

where i is the current density (mA cm^{-2}), E_1 and E_2 are the lower and the upper potential values of the cyclic voltammetry (V), respectively, m is the carbon mass loading on the electrode (mg cm^{-2}), and v is the scan rate (V s^{-1}). The small contribution of pseudo capacitance, most probably arising from the oxidation/reduction of hydroquinone groups [52,53], is included.

Bleda-Martínez et al. found a linear correlation between the CO-like oxygen groups in carbon and the gravimetric capacitance [54] due to the improved wettability of the carbon material, allowing the ions in the electrolyte to reach the microporosity, or to the contribution of pseudocapacitance coming from such oxygen functionalities. This is also the case of CXGs as depicted in **Figure 6a**, where the higher the content of oxidized carbon from C1s spectrum (as a sum of C-O and C=O), the larger the initial capacitance normalized by the surface area ($\text{mF m}^{-2}_{\text{BET}}$).

Table 7. Gravimetric and specific capacitances from cyclic voltammetry at 10 mV s^{-1} in deaerated $0.5\text{M H}_2\text{SO}_4$.

	Gravimetric capacitance before COR $/ \text{F g}^{-1}$	Gravimetric capacitance after COR $/ \text{F g}^{-1}$	Specific capacitance before COR $/ \text{mF m}^{-2}_{\text{BET}}$	Specific capacitance after COR $/ \text{mF m}^{-2}_{\text{BET}}$	Gravimetric capacitance increase $/ \%$
CXG-8-8	37	74	69	138	100
CXG-8-9	10	28	20	55	180
CXG-10-8	16	29	36	66	81
CXG-8A-8	39	64	92	151	64

All CXGs experience an increase of the capacitance after the oxidation test at $1.2 \text{ V vs. RHE (COR)}$. An increase in the interfacial double-layer capacitance points toward a more hydrophilic carbon surface or to an increase of the roughness. Kangasniemi et al. reported an increase of the carbon hydrophilicity upon electrochemical oxidation (aging) [55]. In the present work, there is a clear correlation between the initial oxygen content

(Table 3) and the relative increase in capacitance (Table 7), where the higher the initial oxygen content, the lower the increase of capacitance, as depicted in Figure 6b. Oxygen functional groups in the surface of carbon are well known to aid in increasing the hydrophilicity. The COR thus leads to the formation of oxygen groups which, in turn, improves hydrophilicity and capacitance as a consequence.

Figure 6. (a) Dependence of the initial capacitance normalized by BET surface area with the content of oxidized carbon (C-O + C=O) from XPS; (b) correlation between the variation of capacitance after COR and the *ex-situ* initial oxygen content.

3.3 Discussion on the correlation of COR and physico-chemical properties of CXGs

Elucidating the causes of the electrochemical oxidation of a carbon material is of paramount importance towards the development of highly durable and stable electrodes for long-term application devices. COR has been proposed to proceed via the sequence of chemical and electrochemical steps. Namely, the adsorption of water on the carbonaceous surface which can be accompanied (or not) by an electron transfer process from carbon surface sites resulting in oxidized species.

A kinetic model for the COR in aqueous environment has been recently proposed by Gallagher and Fuller [33]. They assumed a two-site model for carbon atoms on the surface to allow for the formation of an oxide species that does not consume sites involved

in the rate determining step. An interpretation of the Gallagher-Fuller mechanism is schematized in **Figure 7**. From an excellent correlation between this kinetic model and electrochemical experiments, they concluded that the rate determining step (*rds* in the figure) is the oxidation of a phenol-based intermediate to carboxyl group (*i.e.* the cleavage of C-C bond).

Figure 7. Scheme of carbon electro-oxidation mechanism as interpreted from the kinetic study of Gallagher and Fuller [33].

The oxidation of carbon is thus a complex process involving several parallel and series reactions. The complete and irreversible oxidation to CO₂ is preceded by the formation of carboxylic groups, which are more labile than other oxygen functionalities. These carboxylic groups arise from the oxidation of phenol-like groups aided by adsorbed water in neighboring carbon atoms. According to a recent study from Radovic et al., carboxyl groups are formed by virtue of sequential hydroxyl attack at the carbon active

sites which weakens and cleaves the contiguous aromatic C-C bonds [56]. Besides, water is involved in the formation of oxygen groups like carbonyls/quinones (C=O), which can be reversibly reduced to the hydroquinone-like species (C-OH), or irreversibly form anhydrides.

Carbon xerogels are composed by the random aggregation of primary carbon spherules, with sizes in the interval of 10-20 nm. These spherules contain small carbon domains of about 4-6 nm size according to Raman spectrometric analyses (see L_a in **Table 5**). Edge carbon atoms exposed to the aqueous electrolyte are more prone to electrochemical oxidation with water than basal atoms, the former representing less than ~15% of total atoms. In the very first microseconds of potential transient (from open circuit to 1.2 V vs. RHE), the fastest electron charge events take place, such as the oxidation of carboxyl acid to CO₂ or the formation of metastable quinone/hydroquinone species, contributing to a high initial current density (**Figure 5b**). Indeed, the prevalence of carboxylic groups in the samples treated at 800°C (1.37-3.41 at%, **Table 4**) gives place to higher initial current density if compared to sample CXG-8-9 (**Figure 5b**, inset), with much lower carboxylic acid concentration (0.19 at%).

Afterwards, the quasi-steady state oxidation of carbon proceeds with good agreement to the mechanism proposed by Gallagher and Fuller. Clearly, the higher the average number of carbon species interacting with the aqueous electrolyte, the greater the extent of carbon oxidation. In this context, Cherstiouk et al. found that the current associated to the electrochemical oxidation of a certain type of carbon (Sibunit) follows a linear trend with the specific surface area (S_{BET}), indicating that the specific oxidation rate barely changes in this kind of carbon material [57]. This is not the case of CXGs in this work; it appears instead that there is not a simple correlation between these two parameters. Surface area, as determined by nitrogen physisorption (S_{BET}), might not be

indicative of the area exposed to the electrolyte for CXGs due to differences in hydrophilicity. An indirect way of measuring the extent of carbon-electrolyte interface is by considering the capacitance (i.e. the higher the capacitance, the higher the number of exposed carbon atoms). Capacitance is much more representative because it takes into account also differences in surface chemistry. Nevertheless, no correlation was either found between carbon oxidation rate and capacitance in our work. This indicates that not only the exposed area but also the surface nanostructure and/or chemistry of CXGs are greatly influencing the oxidation rate.

To better understand the individual contribution of surface chemistry and nanostructure on the carbon oxidation rate, the most relevant oxidation parameters have been normalized by the surface area taking into consideration the electrochemical capacitance. **Table 8** summarizes the kinetic constant, k , and the oxidation charge, Q_{COR} from chronoamperometric curves at 1.2 V vs. RHE, normalized by the electrochemical capacitance at the beginning (C_i) and at the end (C_f) of the oxidation test.

Table 8. Specific carbon oxidation parameters normalized by the capacitance.

	k/C_i ratio / $\mu\text{A s}^n \text{F}^{-1}$	k/C_f ratio / $\mu\text{A s}^n \text{F}^{-1}$	Q_{COR}/C_i / C F^{-1}	Q_{COR}/C_f / C F^{-1}
CXG-8-8	349	175	11.5	5.7
CXG-8-9	253	90	13.4	4.8
CXG-10-8	121	67	8.3	4.6
CXG-8A-8	108	66	7.7	4.7

Giordano et al. found a correlation between the oxygen content and the specific oxidation rate at 170 °C in H_3PO_4 for carbon blacks [50]. In this work, the specific oxidation rate (k/C) follows the increasing order CXG-8A-8 < CXG-10-8 < CXG-8-9 < CXG-8-8. The lowest normalized oxidation rate corresponds to the carbon xerogel CXG-8A-8 ($k/C_i = 108 \mu\text{A s}^n \text{F}^{-1}$), which presents the largest content of carbon bonded to oxygen as C-O (43%, **Figure 2, Table 3**) as the most differing feature compared to the

other CXGs. Some carbon-oxygen surface species may act as inert carbon sites towards oxidation, thus reducing the density of available carbon atoms for COR, as proposed by Giordano et al. [50]. Upon oxidation, these C-O-like groups (*e.g.* phenols) become more stable as carbonyl groups (C=O) which do not further oxidize to CO₂ in agreement to the Fuller-Gallagher mechanism (**Figure 7**), therefore decreasing the normalized faradaic current. On the other hand, CXG-8A-8 is characterized by a higher capacitance compared to CXG-8-9 and CXG-10-8, owing to its higher oxygen content and wider pores (according to Hg porosimetry), where the electrolyte can penetrate and ions can interact with the surface. This fact evidences that the presence of oxygen groups on the surface limits the electro-oxidation of carbon atoms by creating stable oxygen species and diminishing the availability of labile carbon sites.

On the other hand, the carbon sample with the lowest content of oxygen (CXG-8-9) and thus, a higher density of carbon atoms, does not exhibit the largest normalized electro-oxidation current density. This fact indicates that not only the oxygen content influences the COR of CXGs. In this sense, Cherstiouk et al. found a direct correlation between the electro-oxidation rate and a generalized substructural parameter defined as $(I_{002}/I_{10}) \cdot (d_{002}/L_c)$ [57], accounting for the size of graphitic three-dimensional domains, and being thus valid for graphite-like carbon materials. This generalization is not applicable to amorphous-like carbon materials such as CXGs, activated carbons, carbon blacks, etc., where no crystalline structure is advised in X-ray diffraction analyses. A novel approach would be therefore useful to correlate carbon features and oxidation rate. In the present work, a statistical parametric study was carried out to elucidate the best correlation between the normalized kinetic constant and physico-chemical factors.

Figure 8. Correlation of the capacitance-normalized kinetic constant ($k \text{ C}^{-1}$) against the substructural parameter $I_D/I_G \cdot (C-C + C^*-C-O)/C$ at the beginning of test (full dots and dashed line) and after oxidation (empty dots and dash-dot line).

Here, the main differing parameter is the carbon structure, as evidenced by Raman spectra. The larger disordering degree of CXG-8-8 ($I_D/I_G = 1.19$) make this carbon substrate more prone to corrosion than the sample treated at larger temperature (CXG-8-9). As a conclusion of this discussion, a combination of one feature indicative of the density of active sites (percentage of C-C and C*-C-O sites) and one characteristic revealing the disordering degree (I_D/I_G) can be considered as a good parameter to determine the electro-oxidizing character of carbon xerogels. The normalized current density (k/C) as a function of this substructural parameter ($I_D/I_G \cdot [(C-C) + (C^*-C-O)]/C$) is represented in **Figure 8** with a good correlation as indicated by the discontinuous lines.

The normalization of the charge associated to carbon oxidation reaction (Q_{COR}) considering the initial and final capacitances (C_i , C_f) is also summarized in **Table 8**. These normalized values of charge (Q/C) take into consideration the influence of both the kinetic constant (k) and the exponential parameter (n), being representative of the whole oxidation process occurring during the first 90 min of COR. **Figure 9** shows the relationship between the $Q_{\text{COR}} \text{ C}^{-1}$ and the initial O-C content as determined by XPS,

considering both the capacitance at the beginning (full symbols) and at the end (empty symbols) of the test. Interestingly, when considering the initial capacitance, the normalized charge associated to electro-oxidation decreases from 13 C F⁻¹ to 8 C F⁻¹ when increasing O-C content up to 4 at%. If one considers the capacitance after the test, the normalized charge presents values in the order of 5 C F⁻¹ regardless the initial phenol-like oxygen content. This indicates that the oxidation reaches a steady-state behaviour with an associated charge of about 5 C F⁻¹.

Figure 9. Correlation of the capacitance-normalized oxidation charge ($Q_{COR} C^{-1}$) against the initial content of oxygen as O-C. Capacitance is considered at the beginning of test (full dots and dashed line) and after oxidation (empty dots and dash-dot line).

4. Conclusions

The resistance towards electrochemical oxidation of carbon xerogels with different physico-chemical features was assessed. CXGs characterized by different oxygen content and ordering degree were synthesized and investigated to establish a correlation of physico-chemical parameters and the rate of carbon electro-oxidation. Solid state techniques including XPS, nitrogen and carbon dioxide physisorption, mercury porosimetry, Raman spectroscopy and elemental analysis were used to identify the main properties of the carbon materials. CXGs were subjected to potential holding at 1.2 V vs

RHE for 90 minutes. The presence of oxygen functionalities on the surface, and in particular of phenolic groups, hinders the electro-oxidation of carbon by creating stable oxygen groups (carbonyl/quinone) that no longer oxidize to CO₂. Another important parameter regards the exposed area to the electrolyte, which relies in both porosity and hydrophilicity. Wider pores and carboxylic groups contribute to the carbon-electrolyte interface, thus favouring the electro-oxidation by water. The surface nanostructure and chemistry of CXGs greatly influence also the oxidation rate. In this work, a sub-structural parameter including the content of carbon as determined by X-ray photoelectron spectroscopy (C-C + C*-C-O)/C and the disordering degree as determined by Raman spectrometry (I_D/I_G) is proposed as revealing factor to estimate the specific rate of carbon oxidation. These results will help to rationalize strategies to ameliorate carbon degradation in electrodes based on amorphous structures.

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