Title: [Insights on the Electrochemical Oxidation of Ordered Mesoporous Carbons]

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Abstract Text

Ordered mesoporous carbon materials (OMC) present a developed porosity, making them promising candidates for electrochemical energy-conversion devices. However, OMC undergo electrochemical oxidation causing the degradation of electrodes and exhibit low electrical conductivities due to their amorphous carbon structure. To address these issues, OMC can be graphitized by thermal treatments. Herein, the electrooxidation behaviour of different OMC, prior and upon graphitization, is studied by chronoamperometry in a highly acidic electrolyte (0.5 M H₂SO₄). Several oxidation potentials and temperatures are used to gain insights on the electrooxidation mechanism. Potential holding tests evidenced differences in the oxidation behaviour of as-synthesized and graphitized materials. Graphitization results in a strong decrease of the oxidation charge from 93 to 7% depending on the carbon properties, applied potential and temperature. Temperature plays an important role on carbon degradation of not-graphitized OMC, with a strong electrochemical capacitance loss (90-93%) after tests at 40 and 60 °C. Conversely, graphitized materials present a raise of the capacitance by the creation of oxygen-functionalities as confirmed by post-mortem X-ray photoelectron spectra analysis. Additionally, graphitized materials show an increase of the apparent activation energy associated to electrooxidation (7 times higher), indicative of their improved resistance.

Introduction

Low temperature fuel cells, such as proton exchange membrane fuel cells (PEMFC) and direct alcohol fuel cells (DAFC), are alternative technologies for green energy production.^{1,2} In these electrochemical devices, a fuel (such as hydrogen, methanol or ethanol) is oxidized at the anode side, whereas oxygen is reduced to water at the cathode. In both electrodes (anode and cathode), an electrocatalyst is used, which usually consists on nanoparticles of a Pt-group metal deposited on a carbon material. These supported catalysts provide a large electrochemically active surface area aimed to decrease the cost of the catalyst.³⁻⁷

Carbon blacks have been extensively used as electrocatalyst support.⁸⁻¹¹ In spite of the low cost and high availability of these materials, they generally present a high content of micropores, which hinders the access of the reagents to active sites and worsens the anchoring of nanoparticles.^{12,13} On the other hand, carbon blacks undergo electrooxidation at highly enough positive potentials in aqueous environment,¹⁴⁻¹⁹ following the equation 1;

Although the mechanism of the irreversible carbon oxidation reaction (COR) to CO₂ is not yet exactly understood, it is a complex process which involves the formation of several surface oxides. COR is thermodynamically favourable under PEMFC and DAFC operation conditions. Indeed, COR is the main cause of degradation of PEMFC cathodes,

which usually operate in a range of potential within 0.6-1.0 V.^{20,21} The scenario is even worse under start/stop operation or fuel starvation conditions, where the cathode potential may reach 1.4 V.^{20,22} The anode is also susceptible to carbon loss under fuel starvation conditions.²³ COR conducts to a severe reduction of the lifetime and performance of fuel cells due to the depletion of the active sites, resulting in an aggregation and dissolution of metal nanoparticles.^{15,23-25} Additionally, COR may result in a severe modification of the porous structure of the electrode leading to mass transport limitations.^{15,26} The irreversible carbon oxidation can also cause an important increase of the electrode hydrophobicity by the creation of a passivation oxide coating, contributing to the flooding of the catalyst layer.²⁷

In order to improve PEMFC and DAFC performances, different carbons obtained by sophisticated routes have been developed in the last decades, such as carbon nanotubes, graphene, carbon nanofibers, xerogels, ordered mesoporous carbons (OMC), etc.^{4-6,8,28,29} Among them, OMC obtained from silica templates (hard-templating or sacrificial methodology) have attracted special attention due to their large surface area and open ordered porous structure.³⁰⁻³² Additionally, OMC can be subjected to different graphitization methodologies to increase their electrical conductivity and electrooxidation resistance, including heat treatments at high temperature,³³⁻³⁵ catalytic approaches³⁶ or doping with different heteroatoms, such as N, P and B.^{37,38}

Several authors have found an improved resistance to COR in graphitized carbons, suggesting that minimizing the density of defects represents an efficient strategy to increase durability.^{21,39,40} However, the electrokinetics are not yet established to understand the correlation between oxidation current and overpotential or temperature. It is well known that, as any electrochemical process, the electrochemical oxidation rate of carbon exponentially depends on the overpotential and temperature according to the Butler-Volmer equation, being key parameters conditioning the degradation of electrodes.⁴¹⁻⁴³ Thus, the study of graphitized and bare OMC electrooxidation under different potentials and temperatures could help to clear up the carbon oxidation mechanism and kinetics.

Herein, OMC with different properties have been obtained from SBA-15 silica (template) and posteriorly graphitized at 1500 °C. The oxidation behaviour of as-synthesized and graphitized OMC was studied by accelerated stress tests involving current transients at 1.2, 1.4 and 1.6 V vs. RHE in 0.5 M H₂SO₄. Different temperatures were also evaluated: 25 °C, 40 °C and 60 °C. Additionally, cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) analysis of fresh (before electrochemical oxidation) and oxidized electrodes (post-mortem) were performed to gain insights of the electrochemical oxidation pathway of OMC.

Experimental

Synthesis of ordered mesoporous carbons. OMC were synthesized using SBA-15 silica as template and a furan resin/acetone mixture as carbon precursor by the sacrificial methodology.⁴⁴ A mass ratio (R) of the silica precursor (Tetraethyl Orthosilicate, TEOS, 98 wt. %, Aldrich) and the surfactant (P123) of 2 and 5 were used. Accordingly, two different OMC were prepared: OMC-R2 and OMC-R5.⁴⁰ Graphitized carbons (gOMC-R2 and gOMC-R5) were obtained by heat treatment at 1500 °C of the as-synthesized OMC for 1 h under Ar flow.^{34,40} These graphitization conditions enhance the formation of a crystalline carbon framework without a significant impact on the mesoporous structure of OMC.^{33,34}

Electrooxidation tests. Electrochemical experiments were performed in a thermostated three-electrode electrochemical cell using gas diffusion electrodes as working electrodes (area = 0.2 cm²). The working electrodes were obtained depositing a carbon layer (1 mg cm⁻²) of the corresponding material on a carbon paper with a gas diffusion layer (Sigracet[®] GDL 39BC).⁴⁰ Following this procedure, composite electrodes containing 67 wt.% carbon and 33 wt. % Nafion[®] ionomer (10 wt.%, Aldrich) were obtained. A large surface area carbon rod as counter electrode and a reversible hydrogen electrode (RHE) as reference complete the cell. All potentials in the text are referred to this reference electrode. Electrochemical experiments were recorded by an Autolab PGSTAT302 (Metrohm) potentiostat-galvanostat. The jacket of the cell was connected to a thermostatic bath to keep a constant temperature.

The resistance to electrooxidation of OMC was studied by chronoamperometric (CA) experiments at a known potential and temperature for 30 min in the base electrolyte (0.5 M H₂SO₄) saturated with N₂. Two different set of experiments were performed: i) different potentials (0.2, 0.4 and 0.6 V vs. RHE) at 25 °C to study the effect of the oxidation potential and ii) different temperatures (25, 40 and 60°C) applying 1.4 V to evaluate the temperature impact on the carbon electrooxidation. Fresh electrodes were employed for each electrochemical measurement.

After these electrochemical accelerated tests, cyclic voltammograms (CV) from 0.4 to 1.6 V vs. RHE at 50 mV s⁻¹ were performed in the base electrolyte to determine the capacitance. The capacitance was calculated from the integration of the area enclosed by the current vs. potential curve from 0.5 to 1.0 V vs. RHE (a potential window where no faradaic reaction takes place). The averaged value from positive and negative going scans was considered. Then, EIS measurements were recorded at 1.4 V vs. RHE from 100 kHz to 1 Hz with an amplitude of the sinusoidal excitation signal of 0.01 V r.m.s. A Frequency Response Analyzer (FRA) was used for these experiments. CV and EIS of fresh electrodes (before electrochemical oxidation) were also carried out. During the measurements, nitrogen was fed to the base electrolyte and the backing layer of the working electrode.

XPS analyses. XPS analyses of the carbon electrodes were obtained using an ESCAPlus OMICRON system with a MgK α X-ray source (h ν = 1253.6 eV) operating at 225 W. Survey spectra were recorded at 0.5 eV step, 0.2 s dwell and 50 eV pass energy from 0 to 1000 eV. C1s and O1s high-resolution spectra were carried out at 0.1 eV step, 0.5 s dwell and 20 eV pass energy. The C1s binding energy (BE) of the graphitic peak was referenced at 284.5 eV for calibration. CasaXPS data processing software was used for Shirley background, peak fitting and quantification. C1s spectra was deconvoluted in five components: i) sp² graphitic carbon (C=C) contribution (at 284.5 eV $\pm$ 0.01), ii) C-O bonds in hydroxyls, phenols (C-OH) or epoxides (C-O-C) (at 286.7 $\pm$ 0.3), iii) C=O bonds (at 289.1 $\pm$ 0.1) in carbonyls (C=O) or carboxyl (O=C-OH), iv) CF₂ at 291.8 $\pm$ 0.1 eV and v) CF₃ at 293 $\pm$ 0.3 eV. The last two contributions are related to groups in the Nafion[®] structure. A Gaussian (40%)/Lorentzian (60%) fitting was used for all the contributions, with the exception of the Csp², where an asymmetric peak shape was employed.^{40,45,46}

Results and discussion

Physicochemical characterization of ordered mesoporous carbons. The physicochemical features of the carbon materials have been already studied in previous works.^{34,47} Transmission electron microscopy (TEM) images showed that OMC present an ordered honeycomb structure, which consists of carbon nanorods with uniform mesopores. Crystalline structure of OMC was studied by X-ray diffraction (XRD). Main outcomes indicate the following: i) bare OMC (prior graphitization) do not show

diffraction between $2\theta = 10 - 80^\circ$ due to their amorphous character; ii) g-OMC present the graphite characteristic peak at $2\theta \approx 25^\circ$ indicating that heat treatment at 1500°C resulted in a graphitized carbon; iii) materials exhibit diffraction at low Bragg angles associated to the formation of a highly ordered 2D hexagonal mesostructure (p6mm).⁴⁸ Regarding the textural properties, ordered carbons presented a developed porosity, and the specific surface area and the total pore volume increase as follows: gOMC-R5 ($417\text{ m}^2\text{g}^{-1}$, $0.33\text{ cm}^3\text{g}^{-1}$) < gOMC-R2 ($576\text{ m}^2\text{g}^{-1}$, $0.41\text{ cm}^3\text{g}^{-1}$) < OMC-R5 ($812\text{ m}^2\text{g}^{-1}$, $0.55\text{ cm}^3\text{g}^{-1}$) < OMC-R2 ($884\text{ m}^2\text{g}^{-1}$, $0.59\text{ cm}^3\text{g}^{-1}$).

Electrooxidation studies: influence of the applied potential. At highly positive potentials, the irreversible carbon oxidation occurs following the equation 1.¹⁴ Although the exact mechanism is not completely clear, previous works have determined that carbon degradation may take place by the direct oxidation to CO_2 (COR) or by the formation of different surface oxides, which may evolve the formation of CO_2 .⁴⁹

Carbon electrooxidation was studied by CA tests at different potentials (1.2, 1.4 and 1.6 V vs. RHE) and 25°C in 0.5 M H_2SO_4 aqueous solution. The current-time curves (double logarithmic scale) at 1.2, 1.4 and 1.6 V are displayed in Figure 1. A decay of the oxidation rate with time was observed for the carbon materials. This decrease are related to the formation of surface oxides progressively accumulated on the carbon, behaving as a passive layer, or to a decrease in the number of available sites by carbon loss. The material synthesized using a ratio TEOS/P123 of 2 (OMC-R2) presented a higher oxidation current than that obtained for OMC-R5. This fact can be explained by the larger specific surface area of the former material, which induces a better wettability of the carbon by the electrolyte, and thus a higher capacitance (see Figure S1 and Table 1). Regarding the effect of graphitization on the carbon degradation, thermal treatments at 1500°C led to a significantly slower carbon oxidation rate, as can be seen in the lower oxidation currents exhibited by g-OMC compared to their OMC counterparts. The latter may be explained by the graphitization of carbon during the thermal treatment, creating a more ordered carbon structure, but also by the decrease of the surface area and the removal of oxygen groups, which enhances the hydrophobicity.⁴⁰ On the other hand, a higher oxidation current was obtained as the applied potential increases. This effect is more noticeable for graphitized carbons. Indeed, the oxidation current density after 30 minutes of electrooxidation increases around 3 times when the potential is shifted from 1.2 to 1.6 V vs. RHE for OMC-R5, whereas its graphitic analogue (gOMC-R5) exhibits a value 74 times higher at 1.6 V than that obtained at 1.2 V.

A deeper inspection of the double-logarithmic representation of current vs. time evidences different behaviours for as-synthesized and graphitized OMC, which could be related to differences in the oxidation mechanism. In particular, gOMC-R5 experiences a constant current plateau at potentials over 1.4 V vs. RHE upon 400 s of experiment (Figure 1). In this regard, Gallagher et al.⁵⁰ found that the electrooxidation pathway might be determined by the strength of the local graphene sheet interaction. They reported that weak interlayer interaction carbons display a quasi-linear behaviour with a very high initial rate of CO_2 formation. On the other hand, strongly interacting sheets in ordered carbons exhibit a quick current decay related to the growth of surface oxides with a low CO_2 evolution, followed by a plateau when the CO_2 formation rate reaches a maximum value. In agreement with these results, non-graphitized OMC with amorphous structure behave as weak graphene sheet interaction, whereas gOMC with crystalline structure exhibit strong interlayer interaction. The relative contribution of these two phenomena defines the type of current-time correlation, either linear in the first case or linear followed by a plateau for the second one. As a consequence, for prolonged oxidizing conditions, the oxidation current of the graphitized material can even surpass that of the bare material

at highly positive potentials, which would respond to a severe oxidation condition.

The linear part of the double-logarithmic representation of the current decay with time was fitted following equation 2 (Kinoshita-Giordano equation):⁵¹

$$j = k t^{-n} \quad (2)$$

being j the current density normalized per gram of carbon ($A g^{-1}$) and t the time. k and n are constants. A summary of the fitting parameters can be found in Table 1. The slope (n) is representative of the electrooxidation mechanism.⁵⁰ In general, bare OMC (not graphitized) present a higher value of the slope in comparison to graphitized carbons under comparable conditions. This supports the differences in the oxidation pathway in line with the results reported by Gallagher et al.⁵⁰ As a general trend, higher values of n were observed as the oxidation potential decreases,⁵¹ with the exception of gOMC-R2. Herein, it is important to note that a direct comparison of k is not accurate since different n factors were obtained depending on the applied potential and the carbon nature (graphitized or not graphitized). This variance in the values of n leads to not dimensionally identical kinetic constants, i.e. k units depend on the n factor. This is applicable to all the discussion in the text. However, the constant n presents similar values, with an average of 0.67 considering all tests. Thus, significant differences of the parameter k are valuable to evaluate variations of carbon oxidation rates. The comparison of k evidences that OMC-R2 and OMC-R5 carbons oxidize quicker than their graphitic analogues. Additionally, a higher value of the oxidation constant is observed as the applied potential increases for all the carbons studied in this work. This increase is more important for graphitized carbons, probably due to the good oxidation resistance under the less severe oxidation conditions (1.2 V). In this context, rate parameters of 1.4 and 0.74 $A s^n g^{-1}$ were obtained for gOMC-R2 and gOMC-R5 at 1.2 V, whereas their non-graphitized analogues exhibited one order of magnitude higher with k values of 20.9 and 11.0 $A s^n g^{-1}$, respectively.

The charge associated to the electrooxidation for 30 minutes was calculated from the area enclosed under the current vs. time curves (Table 1). In agreement with the previous discussion, graphitization strategy led to a significant decrease of the carbon electrooxidation charge at 1.2 and 1.4 V for both materials (in the range 93-61% depending on the potential and the material). At 1.6 V, the reduction of the associated charge was not as evident, especially for the material synthesized using a ratio TEOS/P123 = 2 (7% vs a reduction of 47% for OMC-R5). This behaviour indicates that a combination of graphitization strategies with proper textural/structural properties of carbon is mandatory to prevent or ameliorate degradation at highly positive potentials (like the case of 1.6 V vs. RHE).

Cyclic voltammograms (CV) were recorded at 50 $mV s^{-1}$ in the base electrolyte from 0.4 to 1.6 V. Figure 2 shows the CV of fresh electrodes (before oxidation, black curves) and after electrooxidation at 1.2 (red), 1.4 (blue) and 1.6 (green) V vs. RHE. A comparison of the fresh electrodes can be found in Figure S1. From these current –potential curves, the capacitance of the electrodes was calculated (Table 1) before ($C_{t=0}$) and after CA tests ($C_{t=30}$). A progressive increase of the double layer current was obtained for graphitized carbons as the potential applied increases, which may be related to the formation of oxygenated species, responsible of enhancing carbon wettability by the electrolyte.^{52–55} In contrast, as-synthesized carbons (OMC-R2 and OMC-R5) exhibited a decrease of the capacitance after electrooxidation tests.^{52,53,55,56} The latter may be related to: i) the alteration of the porosity of the electrodes and the decrease of the available sites by the irreversible degradation of carbon to CO_2 (COR); and/or ii) the formation of a passivating oxide on the electrode, which prevents electrolyte access. Interestingly, OMC-R2 behaves differently after potential holding at 1.2 V and an increase of the capacitance was

obtained, which may be related to the formation of polar oxygen containing species on this carbon surface under these conditions.

EIS is a powerful tool to study the different processes taking place at the electrode/electrolyte interface. EIS measurements were carried out at 1.4 V vs. RHE. Bode-impedance and Bode-phase plots are given in Figure 3 for all electrodes, before (black) and after (coloured) CA tests. Nyquist plots can be found in Figure S3. Firstly, comparing EIS measurements for fresh electrodes (see Figure S2 for a better understanding), similar equivalent series resistance (R_s) are observed for all OMC ($\sim 1.8 \Omega \text{ cm}^2$) by analyzing impedance (Z) at high frequencies ($> 10 \text{ kHz}$), which is mainly related to ion conductivity of the electrolyte. However, OMC-R2 showed a higher value ($5.7 \Omega \text{ cm}^2$) could be attributed to a lower electrical conductivity of this electrode influencing the total resistance.

Regarding the effect of CA tests on the EIS measurements, as-synthesized materials presented an increase of the impedance value at low frequencies as the applied potential in the CA increases, indicating a higher charge transfer resistance in the COR upon the electrooxidation experiments, in line with CV results. In contrast, graphitized OMC exhibited a decrease of the impedance at low frequencies, which might be related to the formation of oxygen species favouring charge transfer processes. Interestingly, non graphitized electrodes presented characteristic frequencies presumably correlated to carbon electrooxidation at 1.4 V vs. RHE, being evident in the Bode-phase plot of Figure 3. The lowest frequency contribution, appearing at about 5-8 Hz might be ascribed to diffusional processes, typically characterized by low characteristic frequencies. The second one, in between 300-500 Hz is probably correlated to charge transfer in the electrooxidation of carbon, and is only evident in OMC-R5. Indeed, the fresh OMC-R2 electrode (without previous oxidation) does not present this behaviour. In contrast, capacitive features drive the impedance in a larger extent than the oxidation process in graphitized electrodes.

Electrooxidation studies: influence of the temperature. Electrooxidation studies were also performed for two selected materials (OMC-R5 and gOMC-R5) at different temperatures (25, 40 and 60 °C) to deeper understand the carbon degradation mechanism.

Figure 4 shows the current vs. time at 1.4 V (double logarithmic scale) of OMC-R5 and gOMC-R5. In general, an increase of the oxidation current and the charge associated after 30 minutes (see Table 1) was observed with the raise of the temperature for both carbons. Interestingly, gOMC-R5 subjected to the most severe oxidation conditions (60 °C) exhibited an increase of the current after 300 s of experiment. According to the literature, this behaviour might be explained by a maximum in CO_2 formation⁵⁰ or by the formation of a high amount of oxygen-containing species.⁵⁷ XPS analysis evidenced a high oxygen enrichment at the surface of gOMC after the CA tests at 60 °C (see next section). In line with these results, a 10-fold increase of the capacitance was observed (Figure 5). However, experiments monitoring the CO_2 evolution would be required to provide deeper insights. On the other hand, a higher oxidation current is observed for gOMC-R5 after 300 s of experiment at 60 °C in comparison to OMC-R5. The latter is explained by a strong degradation of the last material even during the first seconds of the CA test under these conditions. Indeed, OMC-R5 exhibited a decrease of the carbon oxidation current (and the associated charge) with the temperature shift from 40 to 60 °C even at the starting of the experiment, which may be related to a strong alteration of the electrode by the irreversible oxidation to CO_2 or by the formation of an irreversible passivation layer. Additionally, CV studies (Table 2) evidenced an almost complete loss of the initial capacitance at 25°C (93%) after CA at 1.4 V and 60 °C.

Fitting parameters of the linear part of the double-logarithmic current vs. time are

given in Table 2. OMC-R5 exhibits a faster oxidation than gOMC-R5 for the studied temperature window, with k values in the range 24.4-32.4 A sⁿ g⁻¹ and 0.77-3.47, respectively. In general, both the bare and the graphitized materials oxidize faster with the raise in the temperature, as evidence the higher values of k . The rate increase with the temperature is comparatively lower for OMC-R5 due to the fast oxidation that this material presents even at the milder conditions (24 °C and 1.4 V).

The apparent activation energies were determined for both OMC-R5 and gOMC-R5, considering the Arrhenius equation (equation 3):

$$k = k_0 e^{\frac{-E_a}{RT}} \quad (3)$$

where k is the rate (A sⁿ g⁻¹), k_0 is the frequency factor (A sⁿ g⁻¹), E_a is the apparent activation energy (J mol⁻¹), R is the gas constant (8.314 J K⁻¹ mol⁻¹), and T is the absolute temperature (K). Figure S4 shows the fittings for both materials. A higher apparent activation energy for carbon electrooxidation was obtained for the graphitized material in comparison to OMC-R5, with values of 35 and 5 kJ mol⁻¹, respectively. These results show that the graphitization treatment is a good strategy to obtain carbons less prone to oxidation. It has to be noted that the kinetic constants k are not dimensionally identical since different n values were obtained for OMC-R5 and gOMC-R5 depending on the temperature. This is the best approximation to correlate oxidation kinetics with the variation despite it might lead to some inexactitude in the calculation of the apparent activation energies.

CV of fresh electrodes (before oxidation, black curves) and after electrooxidation at 1.4 V at 25 °C (red), 40 °C (blue) and 60 °C (green) are given in Figure 5. The shift of the temperature resulted in a progressive higher capacitance for the graphitized material, while OMC-R5 showed a drastic decrease of the double layer current upon CA tests. Thus, the trend is the same than that discussed above for the influence of the potential. However, the raise of the temperature seems to have a higher impact on the oxidation extent for both materials. In this context, the capacitance of OMC-R5 decreased around 90-93% (Table 2) respect to the initial capacitance at 25 °C, when the potential holding was performed at 40-60 °C (vs. 58% at 25 °C). These results confirm the strong degradation that the non-graphitized material suffered with the increase of the temperature, resulting in practically a total loss of its initial double layer current. In contrast, a 3-fold and 10-fold increase of the capacitance was evident after tests at 40 °C and 60 °C, respectively.

Bode plots of EIS measurements recorded at 1.4 V are shown in Figure 6 for OMC-R5 and gOMC-R5, before (black) and after potential holding at the three temperatures. Nyquist plots are given in Figure S5. In agreement with the CV results, OMC-R5 presented a progressive increase of the impedance value at low frequencies as the temperature during CA increases, indicating a higher resistance due to a slower charge transfer. In contrast, gOMC-R5 exhibited a decrease of the impedance at low frequencies, which might be related to the formation of oxygen species favouring the charge transfer for electrooxidation.

XPS analyses of fresh and oxidized electrodes. The electrodes were analysed by XPS prior and after CA experiments in order to gain insights in the variation of surface oxygen-containing species. C, O, S and F atomic contents obtained from the survey spectra can be found in Table 3. The deconvolution of the C1s spectra are shown in the Supporting Information (Figure S6 and Table S1). OMC- and gOMC-based electrodes contain around 33 wt. % of Nafion[®] ionomer, which is an acid sulfonated tetrafluoroethylene based fluoropolymer-copolymer, with chemical formula (C₇HF₁₃O₅S)_m·(C₂F₄)_n. Thus, both the carbon and the binder contribute to C1s and O1s spectra but F 1s and S 2p are only associated to the ionomer. In spite of the binder

contribution, the relative amount of oxygen and carbon may be used as an adequate estimation to study the alteration of chemical composition at the surface of the electrodes. As a matter of fact, fresh electrodes showed an atomic fluorine content around 46% and a S/F ratio of 0.03, indicating a similar Nafion[®] amount. Prior to the electrooxidation tests, gOMC-R5 showed a lower amount of oxygen than OMC-R5, confirming the removal of oxygenated species after the heat treatment at 1500 °C. After CA tests, the F content increases and the C amount decreases for all the electrodes, which is related to the carbon loss by the COR. In line with these results, the S/F ratio decreases probably due to a partial loss of sulfonic groups in the ionomer, which should contribute to a decrease of the O amount. However, the relative amount of oxygen, expressed as either O/C or O/Csp², increases after CA tests due to the formation of oxygen-containing species.

A deeper insight of the variation in the relative amount of oxygen with respect to the total C1s amount (O/C) and Csp² (O/Csp²) can be found in Table 3. The first normalization considers the carbon-fluorine species in the binder, carbon bond to oxygen and Csp², whereas O/Csp² includes only the last group. Thus, this last ratio allows a better individualization of carbon species related to OMC. Electrooxidation of the electrodes by CA during 30 min led to a progressive increase of the ratio O/C as the potential increases for the experiment set run at 25 °C for both OMC-R5 and gOMC-R5. The same trend was observed after potential holding at 1.4 V at different temperatures, i.e. a surface enrichment of oxygen was obtained when the temperature was shift from 25 °C to 60 °C. Additionally, the effect of temperature seems to be more relevant than the increase in the potential from 1.4 to 1.6 V, since higher values of both O/C and O/Csp² were found for both OMC-R5 and gOMC-R5. These results confirm that the carbon surface is enriched with oxygen-containing species upon CA experiments.

Carbon electrooxidation takes place through a complex process involving the formation of different oxygenated species, such as carbonyls/quinones, phenols, hydroxides and carboxylic acids.^{15,58–60} Some of these oxygen species may act as inert carbon sites to the COR, and hence, creating a passivated surface reducing the density of available sites.⁴⁹ In contrast, carboxylic acids may be further oxidized in the presence of water forming CO₂, being this reaction the rate determining step.^{58,59}

The deconvolution of C1s spectra showed an increase of the C=O relative content for both materials upon CA tests at 25 °C, which is related to a formation of oxygen species like carboxylic acids or quinones. On the other hand, C-O species, related to the formation of hydroxides and phenols, only increased substantially for gOMC-R5. Regarding the effect of temperature, the shift from 25 to 60 °C led to a progressive increase of C-O species for OMC-R5 and gOMC-R5, being this effect again more evident for the last material. On the other hand, the relative content of C=O functionalities was almost duplicated for the graphitized carbon, whereas a decrease was evident for OMC-R5, implying a reduction of carboxylic acids/quinones at the surface.

As a summary, the increase of both the potential and the temperature resulted in an enrichment of C-O and C=O functionalities for gOMC-R5. In the case of the bare material, the formation extent of C-O and C=O groups is lower. These results indicate that OMC-R5 is less prone to form oxygenated species than its graphitic analogous. Additionally, OMC-R5 exhibited an evident decrease of the C=O species with the raise of the temperature, and a practically total loss of the capacitance was observed (90-93%). Previous works^{58,59} have found that carboxylic acids can be oxidized to CO₂. Thus, the reduction of C=O groups could be related to the oxidation of these groups to CO₂. In contrast, oxidation tests led to a significant formation of oxygenated species in the graphitized material. These groups may be further oxidized to CO₂ or act as a reversible

passivation layer inhibiting carbon degradation.^{49,58,59}

Conclusions

The electrooxidation behaviour of as-synthesized and graphitized OMC has been studied at 1.2, 1.4 and 1.6 V vs. RHE under different temperatures (25, 40 and 60 °C) in acid media (0.5 M H₂SO₄). Accelerated stress tests showed differences in the oxidation behaviour for OMC. A linear current-time correlation was observed for bare materials, whereas graphitized carbons exhibited an initial current decay followed by a plateau. Graphitization conducted to a significant decrease of the oxidation extent with a reduction of the electrooxidation associated charge from 7% to 93% depending on the carbon features, applied potential and temperature. Additionally, a quicker oxidation rate was obtained for as-synthesized materials with higher *k* values for all potentials and temperatures studied. Temperature was found to play a significant role in the electrooxidation process. Indeed, a non-graphitized material exhibited an important loss of the initial capacitance (90-93%) after the oxidation tests at 1.4 V under 40 °C and 60 °C, related to carbon loss by the irreversible oxidation to CO₂. The formation of an irreversible passivation layer cannot be discarded. In contrast, graphitized OMC evidenced a strong enhancement of the capacitance (4 to 10-fold increase) by the creation of oxygen-functional groups. Post-mortem XPS analysis evidenced that the relative amount of oxygen progressively increased as the applied potential or the temperature increases. A higher oxygen enrichment was observed for graphitized materials. From the electrooxidation tests under different temperatures, apparent activation energies for carbon electrooxidation were calculated. A higher value was obtained after graphitization (35 kJ mol⁻¹ vs. 5 kJ mol⁻¹), indicating that thermal treatment is an adequate approach to obtain carbons less prone to electrooxidation. The results are of interest to design strategies for minimizing electrooxidation of carbon supports, and consequently, for obtaining stable catalysts for PEMFC.

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Table 1. Electrooxidation parameters of ordered mesoporous carbons upon current transients at 1.2, 1.4 and 1.6 V in 0.5 M H₂SO₄.

Electrode	Potential (V)	k (A s ⁿ g ⁻¹)	n	Q _{t=30} ^a (C g ⁻¹)	C _{t=0} (F g ⁻¹)	C _{t=30} (F g ⁻¹)	$\frac{C_{t=30}-C_{t=0}}{C_{t=0}}$ (%)
OMC-R2	1.2	20.9	0.78	424	26	37	44
	1.4	61.4	0.79	1098		21	-20
	1.6	67.6	0.73	1885		9	-67
OMC-R5	1.2	11.0	0.74	238	15	6	-58
	1.4	24.4	0.72	574		5	-68
	1.6	28.2	0.67	866		4	-69
gOMC-R2	1.2	1.4	0.52	96	7	22	202
	1.4	9.2	0.65	431		67	806
	1.6	18.6	0.61	1748		79	970
gOMC-R5	1.2	0.74	0.76	17	5	7	45
	1.4	0.77	0.67	48		10	101
	1.6	3.08	0.52	457		24	363

^aQ_{t=30} = carbon oxidation charge in 30 minutes

Table 2. Electrooxidation parameters of OMC-R5 and gOMC-R5 upon current transients at 1.4 V in 0.5 M H₂SO₄ at 25, 40 and 60 °C.

Electrode	Temperature (°C)	k (A s ⁿ g ⁻¹)	n	Q _{t=30} ^a (C g ⁻¹)	C _{t=0} ^b (F g ⁻¹)	C _{t=30} (F g ⁻¹)	$\frac{C_{t=30}-C_{t=0}}{C_{t=0}}$ (%)	E _a (kJ mol ⁻¹)
OMC-R5	25	24.4	0.72	574	15	6	-58	5
	40	31.6	0.74	949		1	-90	
	60	30.8	0.78	616		1	-93	
gOMC-R5	25	0.77	0.67	48	5	10	101	35
	40	2.04	0.61	215		25	385	
	60	3.47	0.50	1342		60	1081	

^aQ_{t=30} = carbon oxidation charge in 30 minutes. ^bC_{t=0} is given at 25 °C

Table 3. Chemical composition from XPS analysis of the OMC-R5 and gOMC-R5 electrodes before and after chronoamperometric experiments in 0.5 M H₂SO₄.

Electrode	C	O	S	F	S/F	O/C	O/Csp ²	C-O/Csp ²	C=O/Csp ²
	(at %)								
OMC-R5	45.5	6.3	1.5	46.6	0.033	0.14	0.72	0.22	0.17
+ 1.2 V. 25 °C	44.5	6.3	1.3	47.8	0.028	0.14	0.78	0.14	0.16
+ 1.4 V. 25 °C	42.6	6.9	1.5	48.9	0.032	0.16	0.88	0.22	0.20
+ 1.4 V. 40 °C	37.5	8.4	1.7	52.4	0.032	0.23	1.22	0.25	0.17
+ 1.4 V. 60 °C	34.9	7.9	1.5	55.7	0.026	0.23	2.07	0.30	0.11
+ 1.6 V. 25 °C	41.1	7.4	1.4	50.1	0.028	0.18	1.17	0.23	0.26
gOMC-R5	48.0	4.8	1.4	45.8	0.031	0.10	0.56	0.28	0.33
+ 1.2 V. 25 °C	45.7	5.1	1.1	48.0	0.024	0.11	0.57	0.34	0.35
+ 1.4 V. 25 °C	39.5	4.5	1.2	54.8	0.022	0.11	0.69	0.36	0.45
+ 1.4 V. 40 °C	40.1	7.0	1.5	51.4	0.029	0.18	2.78	0.96	0.78
+ 1.4 V. 60 °C	39.1	7.0	1.5	52.3	0.028	0.18	2.07	1.31	0.84
+ 1.6 V. 25 °C	41.9	5.6	1.1	51.2	0.022	0.13	0.87	0.42	0.51

Figure 1. Current-time curves for electrooxidation tests at 1.2 V (black curves), 1.4 V (red curves) and 1.6 V (blue curves) in 0.5 M H₂SO₄ of ordered mesoporous carbons. Solid curves: bare OMC. Dashed curves: graphitized OMC.

Figure 2. CV from 0.4 to 1.6 V vs. RHE at 50 mV s in 0.5 M H₂SO₄ of fresh electrodes (not oxidized, black curves) and after holding the potential to 1.2 (red curves), 1.4 (blue curves) and 1.6 V (green curves) vs. RHE.

Figure 3. Bode plots: impedance modulus (left panel) and phase angle (right panel) vs. frequency in 0.5 M H_2SO_4 of fresh electrodes (not oxidized, black curves) and after holding the potential to 1.2 (red curves), 1.4 (blue curves) and 1.6 V (green curves) vs. RHE.

Figure 4. Current-time curves for electrooxidation tests at 1.4 V at 25 °C (red curves), 40 °C (blue curves) and 60 °C (green curves) in 0.5 M H₂SO₄ of OMC-R5 and gOMC-R5.

Figure 5. CV from 0.4 to 1.6 V vs. RHE at 50 mV s in 0.5 M H_2SO_4 of OMC-R5 and gOMC-R5 fresh electrodes (not oxidized) and after holding the potential to 1.4 V at 25 °C (red curves), 40 °C (blue curves) and 60 °C (green curves).

Figure 6. Bode plots, impedance modulus (left panel) and phase angle (right panel) vs. frequency in 0.5 M H_2SO_4 of OMC-R5 and gOMC-R5 fresh electrodes (not oxidized, black curves) and after holding the potential to 1.4 V at 25 $^\circ\text{C}$ (red curves), 40 $^\circ\text{C}$ (blue curves) and 60 $^\circ\text{C}$ (green curves).