# Electrochemical behavior of the carbon black Vulcan XC-72R: influence of the surface chemistry

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## Abstract

The effect of chemical surface oxidation of the carbon black Vulcan XC-72R on the capacitance, tolerance to corrosion and electrochemical activity toward the hydrogen evolution reaction (HER) has been studied in 0.1M NaHCO<sub>3</sub>. Acid treatments with HNO<sub>3</sub> or a HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> mixture resulted in a progressive introduction of oxygencontaining groups which led to a strong increase of the capacitance and a higher tendency to carbon corrosion. In contrast, an inhibition of the hydrogen evolution current (at potentials more negative than -1.0V) was observed for oxidized samples in comparison to the un-treated material. HER was also tested in the presence of dissolved CO<sub>2</sub> to study the influence of the surface chemistry on the CO<sub>2</sub> electroreduction. An inhibition of the H<sub>2</sub> evolution current was evidenced in the CO<sub>2</sub> saturated electrolyte due to the adsorption of species from CO<sub>2</sub> reduction. A strong hydrogen current decrease (65-78%), and thus a higher tendency to adsorb (CO<sub>2</sub>)<sub>red</sub> species, was obtained on the original Vulcan and the HNO<sub>3</sub>-treated samples, in comparison to the carbon oxidized with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> (15%), which could be related to the highest content of basic groups of the last carbon.

**Keywords:** carbon black, oxygen functionalization, carbon electrooxidation,  $H_2$  evolution,  $CO_2$  electroreduction.

## **1. Introduction**

Carbon blacks have been extensively used in the field of electrochemistry owing to their high mesoporous distribution, good electrical properties, as well as their low cost and high availability since they are usually obtained by thermal decomposition of hydrocarbons derived from petroleum sources [1-4]. Different carbon blacks, such as acethylene black, Ketjen Black, Black Pearl or Vulcan XC-72, have been used as electrodes in supercapacitors or catalyst supports in electrochemical applications [1-8]. Among them, Vulcan XC-72R (industrially produced by Cabot Corporation) has attracted special attention due to its good compromise between adequate surface area (~ 250 m<sup>2</sup>g<sup>-1</sup>) and high electric conductivity (~ 2.77 Scm<sup>-1</sup>) [1, 9].

In general, carbon applications involve interfacial interactions, where different reactants and ions access to the carbon surface. As a result, a great effort has been devoted to study the effect of surface chemical properties of carbons (including carbon blacks) on the electrochemical performance for energy-conversion and storage devices, such as supercapacitors, polymer electrolyte membrane fuel cells (PEMFC) and electrolyzers [3, 10-15]. Particularly, the chemical introduction of oxygen-containing species on the carbon structure has been extensively investigated [3, 10, 16-21]. Different chemical oxidation procedures have been studied using oxidizing solutions (such as NaClO, HNO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>) or gases (e.g. CO<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub>, NO, etc.) [5, 22, 23], which result in the generation of different oxygen functionalities on carbon surfaces, such as carboxyls, carbonyls, phenols, quinones or lactones.

These oxygen functionalities has been found to play an important role on the electrochemical behavior of carbon-based electrodes and their activity toward main reactions involved in PEMFC and electrolyzers [3, 10, 16-21]. Particularly, the introduction of oxygen-containing species has been reported to be advantageous for

attaining a better dispersion and anchoring of the electrocatalytic active phase onto the carbon surface [5, 24, 25]. In addition, oxygen functionalities decrease the hydrophobic character of carbons, enhancing the capacitance, and thus the accessible electrochemical area [21, 26-29].

In contrast to the advantages of improved capacitance or good dispersion of the active phase, the introduction of oxygen functional groups may promote the carbon electrochemical corrosion, which is one of the main problems facing the PEMFC efficiency [26, 30]. During the electrooxidation of the carbon support, oxygen adsorbed species are progressively introduced on the carbon surface which are converted to CO<sub>2</sub> at high overpotentials, resulting in a substantial decrease of the active surface area of the catalyst, and consequently a severe loss of the PEMFC performance [26, 30, 31]. It has been found that the presence of oxygen functionalities onto the carbon surface may facilitate the gasification of the carbon support [26, 30]. These studies generally involve the progressive electrochemical oxidation of carbon-supported catalysts [11, 21, 26, 32]. However, to our best knowledge, there are still few studies dealing with both the influence of previous chemical oxidation of carbon blacks (not only by the electrochemical route) and the corrosion resistance of metal-free carbon electrodes [33].

On the other hand, few efforts have been made in the role of oxygenfunctionalized carbons on the electrochemical activity toward the hydrogen evolution reaction (HER) [20, 34], which is the cathodic half reaction in electrochemical water splitting. In this context, Bleda-Martínez et al. [20] found an improved hydrogen storage capacity in carbons with a low content in surface oxygen complexes. On the other hand, a previous work showed that carbon electrooxidation might decrease the active sites and hence, inhibit the hydrogen formation [34]. Nevertheless, the effect of the chemical introduction of oxygen species on carbon surfaces on the activity for the HER remain largely unknown.

Electrocatalysts supported on carbon materials have been also used for other electrochemical applications, such as the hydrogenation of  $CO_2$  into energy-rich products [35-44]. In this context, Hossain et. al have recently showed the effective reduction of  $CO_2$  to CO, HCOOH and CH<sub>4</sub> with a faradaic efficiency of 76.6% in a  $CO_2$ saturated NaHCO<sub>3</sub> solution on a nanocomposite consisting of Cu nanoparticles deposited on reduced graphene oxide [41]. Interestingly, high efficiencies to the formation of hydrocarbons and oxygenates have been recently reported on metal-free Ndoped carbon electrodes [45-49]. However, scarce studies about the effect of the oxygen functionalization on the electrocatalytic activity toward the  $CO_2$  conversion can be found in the literature [35, 42, 48]. In addition, these studies usually involve metal-base electrodes or trace metals and the role of the support has not been stated.

A recent report has evidenced that the presence of oxygen functionalities may play an important role on the capacitance and on the corrosion tolerance of carbon materials, as well as on the electrocatalytic activity toward H<sub>2</sub> evolution and CO<sub>2</sub> reduction reactions [34]. However, carbons of different nature with different morphology, structure, textural properties and surface chemistry were considered in this previous work [34], making difficult to clarify the role of surface oxygen-containing species. The current report addresses this issue by gradually introducing oxygen functional groups on the carbon surface of Vulcan XC-72R. Different chemical oxidation treatments with concentrated nitric acid or a nitric-sulphuric acid mixture over a prolonged period of time (from 0.5 to 2 hours) at 30 or 120 °C were used. The electrochemical behavior of the original and oxidized carbon samples was studied by cyclic voltammetry in aqueous 0.1 M NaHCO<sub>3</sub>. The obtained results are discussed in terms of the capacitance, tolerance to corrosion and activity toward the HER, which are key issues on energy-conversion devices. The study is extended to the evaluation of the performance of carbons for the  $CO_2$  electrochemical reduction.

# 2. Experimental

#### 2.1 Functionalization of Vulcan XC-72R

Functional groups were generated on Vulcan XC-72R (supplied by Cabot) surface by using concentrated HNO<sub>3</sub> (65%, Panreac) or a HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (95%, Sigma Aldrich) mixture 1:1 (v/v) as oxidizing agents. Three different chemical oxidation procedures were employed: (i) oxidation with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> at 30 °C for 30 min; (ii) oxidation with HNO<sub>3</sub> at 120 °C during 30 min and (iii) oxidation with HNO<sub>3</sub> at 120 °C during 120 min. The resulting oxidized samples were denoted as Vulcan-O1, Vulcan-O2 and Vulcan-O3, respectively. After the oxidation treatments, carbons were filtered, thoroughly washed and dried at 60 °C.

## 2.2 Physicochemical characterization

Temperature programmed desorption (TPD) experiments were obtained in an AutoChem II 2920 analyzer. Carbon materials were heated at 10 °C min<sup>-1</sup> up to 1000 °C in a quartz reactor under an Ar atmosphere (50 mLmin<sup>-1</sup>). The CO and CO<sub>2</sub> amounts were monitored online by mass spectrometry. The TPD deconvolution was performed adjusting the experimental profiles to a multiple Gaussian function using the Fytik software [5, 34, 50]. The CO and CO<sub>2</sub> evolutions and the deconvoluted profiles are displayed in Figure S1 and S2.

X-ray photoelectron spectroscopy (XPS) spectra were performed in an ESCAPlus OMICRON system operating at 150 W (15 mA, 10 kV) under vacuum ( $<5\cdot10^{-9}$ ), using a non-monochromatized MgKa (1253.6 eV) anode. Survey scans (1sweep/200 ms dwell) were recorded at 0.5 eV step size, 0.2 s dwell time and 50 eV pass energy, while detailed scans for C1s and O1s were acquired at 0.1 eV step size, 0.5 s dwell time and

20 eV pass energy. The XPS spectra were calibrated with the C1s graphitic peak (284.6 eV). C and O contents were obtained after Shirley background subtraction using the CASAXPS software. Figure S3 displays the results for a selected material, Vulcan-O3.

Elemental analysis (EA) were obtained in a Thermo FlashEA 1112 analyzer.

Transmission electron microscopy (TEM) micrographs were performed with a JEOL-2000 FXII microscope at 200 kV. Previously, the carbon materials were dispersed in ethanol under sonication and deposited on a copper grid.

X-Ray diffraction (XRD) diffractograms were measured in a Bruker AXS D8 Advance diffractometer using Cu K $\alpha$  radiation. The graphite interlayer spacing (d<sub>002</sub>) of carbon materials was calculated from the Bragg's equation on the (002) graphite peak, while crystallite sizes (Lc) were obtained applying the Scherrer's equation with a K value of 0.89 [38].

 $N_2$  adsorption-desorption isotherms of samples were recorded in a Micromeritics ASAP 2020 at -196 °C. The specific surface area (S<sub>BET</sub>) was calculated from the BET equation and the total pore volume (V<sub>T</sub>) by means of the single point method at P/P<sub>0</sub> = 0.99. Mesopore volume (V<sub>meso</sub>), pore diameter (D<sub>p</sub>) and pore size distributions were determined by the BJH methodology considering the desorption branch of the N<sub>2</sub> isotherm. Mesopore fraction was obtained in terms of pore volume [38]. Figure S4 shows the N<sub>2</sub> adsorption-desorption isotherms and the BJH pore size distributions.

Thermal resistance of the materials was studied by thermogravimetric (TG) analysis in air using a SETARAM Setsys Evolution system. The carbon materials were heated from room temperature to 950 °C at a heating rate of 5 °C min<sup>-1</sup>.

## 2.5. Spectro-electrochemical measurements

Electrochemical measurements were monitored in an Autolab PGSTAT302 (Ecochemie) potentiostat-galvanostat at room conditions using a conventional threeelectrode electrochemical cell. For the differential electrochemical mass spectrometry (DEMS) characterization, the electrochemical cell was connected in-situ to a mass spectrometer (Balzers Omnistar). The details of the experimental installation can be found in [51]. Carbon suspensions were obtained dispersing 2 mg of the carbon material in 15  $\mu$ L of Nafion dispersion (5 wt.%, Aldrich) and 500  $\mu$ L of ultrapure water. Then, a thin-layer of the carbon suspension was deposited onto a glassy carbon (GC) disk ( $\phi = 7$  mm, SIGRADUR® G) and dried at room temperature, resulting in the working electrodes. This Nafion amount allows a good deposition of carbons to the GC electrode without large surface blocking [34, 52]. A large surface area carbon rod was employed as a counter electrode and an Ag/AgCl/3M KCl electrode as reference (0.21 V vs. NHE, normal hydrogen electrode).

The influence of oxygen functionalization on the electrochemical behavior of Vulcan was studied in a N<sub>2</sub>-deaerated 0.1 M NaHCO<sub>3</sub> (Merck, p.a.) electrolyte solution. First, an aliquot (10  $\mu$ L) of the carbon solution was deposited on the GC to evaluate the capacitance and the corrosion of untreated and functionalized Vulcan samples. The capacitance was obtained by integration of the current vs. potential curve in the region 0.3-0.8 V vs. RHE (reversible hydrogen electrode) considering the mean value of positive and negative going scans of cyclic voltammograms (CVs) recorded in the base electrolyte at 50 mV s<sup>-1</sup> from 0.1 to 1.0 V. Then, other aliquot of 10  $\mu$ L was deposited on a fresh GC electrode to evaluate the activity of carbon materials for the hydrogen evolution and CO<sub>2</sub> reduction reactions. To correct the differences of pH between the electrolytes (8.4 in the solution saturated with N<sub>2</sub> and 6.8 in the presence of CO<sub>2</sub>), all potentials in the text are referred to the RHE.

#### 3. Results and discussion

#### 3.1 Physicochemical characterization of carbon Vulcan materials

TPD experiments were performed to study the amount and kind of oxygen surface species originated during oxidation treatments. Table 1 displays the total amounts of CO and CO<sub>2</sub> desorbed obtained from the integration of the TPD profiles vs. time and the oxygen content ( $O_{TPD}$ , wt.%). The CO/CO<sub>2</sub> ratio and the oxygen atoms per surface area calculated from the S<sub>BET</sub> obtained by N<sub>2</sub> physisorption (see later Table 4) are also given in Table 1.

**Table 1.** Surface chemistry of untreated and functionalized Vulcan samples from TPD,EA and XPS.

Sample	CO (µmol g <sup>-1</sup> )	CO <sub>2</sub> (µmol g <sup>-1</sup> )	CO/CO <sub>2</sub>	O <sub>TPD</sub> (wt.%)	O (atoms nm <sup>-2</sup> )	OEA (wt.%)	Oxps (wt.%)
Vulcan	174	106	1.6	0.6	1.0	0.4	2.3
Vulcan-O1	927	468	2.0	3.0	5.0	3.5	8.1
Vulcan-O2	1252	763	1.6	4.4	8.2	5.1	8.2
Vulcan-O3	1603	957	1.7	5.6	11.7	7.0	12.0

Original material contains a small content of oxygenated groups mainly derived from the contact with the atmosphere. Oxidation treatments led to an important increase in the concentration of CO and CO<sub>2</sub> releasing groups. Consequently, oxygen was progressively intercalated into the structure of the carbon matter as the severity of the chemical treatments increased, following the sequence: Vulcan-O1 < Vulcan-O2 < Vulcan-O3. Thus, the longest treatment with nitric acid was the most effective for developing surface oxygen-containing groups.

The oxygen content was also obtained from EA and XPS (Table 1,  $O_{EA}$  and  $O_{XPS}$ ). Surface oxygen content is obtained by XPS, while TPD and EA are considered as bulk methods. EA results correlate quite well with the oxygen concentration obtained by TPD, while XPS values are higher for all the samples indicating that the surface is

enriched with oxygen.

Deconvolution of TPD profiles allowed to determinate the amount of the different oxygen-containing species (Table 2). Acid functionalities (carboxylic and lactones) are released as CO<sub>2</sub> and basic groups (phenols, quinones and carbonyls) are decomposed into CO. Anhydrides are desorbed as both CO<sub>2</sub> and CO [5, 34]. Oxidation treatments led to an important increase of carboxylic acids, phenols and quinone/carbonyls. The introduction of these species decreases the hydrophobic character of carbon materials, increasing the active electrochemical surface area (see later section 3.2.1). In addition, oxygenated functional groups enhance the active phase dispersion and the metal precursor impregnation when carbons are used as supports in the synthesis of electrocatalysts [25, 42]. However, a different distribution was obtained depending on the oxidation procedure. The treatment with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> resulted in a higher contribution of basic groups with a ratio CO/CO<sub>2</sub> of 2.0 (Table 1), whereas a similar surface basicity (with values of around 1.6-1.7) was obtained when HNO<sub>3</sub> was used as oxidant agent or for the bare material.

Sample	Carboxylic acid	Anhydride	Lactone	CO desorption	Phenol	Carbonyl/ quinone
Vulcan	39	6	20	11	5	25
Vulcan-O1	196	209	70	56	174	275
Vulcan-O2	375	300	82	38	338	388
Vulcan-O3	478	369	99	38	325	682

**Table 2.** Results from deconvolution of  $CO_2$  and CO (µmol g<sup>-1</sup>) TPD profiles of untreated and functionalized Vulcan samples.

However, these differences on the oxygen amount and the oxygen surface

distribution of the carbon materials did not present any influence onto the morphological properties. The bare material Vulcan was formed by spherical nanoparticles composed of small crystallites [34, 38]. Oxidized samples presented similar features, as displayed in Figure 1 for the carbon subjected to the most severe treatment (Vulcan-O3). Similarly, the commercial material preserved their crystalline structure upon functionalization since the  $d_{002}$  and the L<sub>c</sub> obtained from the graphite (002) peak of XRD diffraction patterns did not suffer significant changes with, values around 3.54-3.56 Å and 1.6-1.7 Å, respectively, for all the samples (Table S1).

The impact of chemical oxidation on the textural properties of Vulcan XC-72R was studied by  $N_2$  physisorption. Table 3 summarizes the results for all the carbons.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>T</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore fraction (%)	D <sub>p</sub> (nm)
Vulcan	238	0.38	0.31	83	10.4
Vulcan-O1	228	0.40	0.33	83	12.0
Vulcan-O2	204	0.38	0.32	84	12.4
Vulcan-O3	181	0.38	0.33	86	14.0

**Table 3.** Textural parameters of untreated and functionalized Vulcan samples.

The untreated material presents a developed porosity ( $S_{BET} = 238 \text{ m}^2 \text{g}^{-1}$ ,  $V_T = 0.38 \text{ cm}^3 \text{g}^{-1}$ ). After chemical functionalization, a decrease of the specific surface area was evidenced due to a partial destruction of the original textural structure. This decrease is more important as the treatment severity increases. In addition, a slight increase of the mesopore content was observed after oxidation which may be caused by a widening of the pores probably owing to a collapse of the pore walls by the creation of oxygen groups or by the severity of the oxidant conditions [53]. In correlation with

these results, the average pore size increased from 10.4 for the original material to 14.0 for the most oxidized sample, Vulcan-O3.

The influence of the oxygen functionalization on the thermal stability of Vulcan was studied by TG analyses. Figure 1 displays the TG profiles and mass variation velocity vs. temperature obtained for the original material and functionalized carbons. The bare material presents a high oxidation resistance with a gasification temperature at 672 °C. After functionalization, the oxidation temperature decreased which can be ascribed to a partial destruction of the textural structure of the original material [54], in agreement with the results obtained by N<sub>2</sub> physisorption. In fact, a decrease of around 50 °C was obtained for the most oxidized sample (Vulcan-O3). Moreover, functionalized samples show a soft weight loss at 100-400 °C in comparison to the original carbon. This initial decay is related to the desorption of oxygen surface species, which are unstable at high temperatures.



**Fig. 1.** TEM images of Vulcan and Vulcan-O3 (left). TG profiles in air of untreated and functionalized Vulcan samples (upper right panel) and mass variation velocity (bottom right panel) vs. temperature.

# 3.2. Electrochemical measurements of carbon Vulcan materials

## **3.2.1.** Capacitance properties

CVs were registered in the base electrolyte from 0.1 to 1.0 V at 50 mV s<sup>-1</sup> for the carbon materials. Capacitance (C) vs. potential curves were obtained from the faradic currents (I) and the scan rate (v) by means of the Equation 1;

$$C[F] = I[mA]/v[mVs^{-1}]$$
<sup>(1)</sup>

The results are shown in Figure 2.



**Fig. 2**. Capacitance vs. potential curves of untreated and functionalized Vulcan samples in 0.1 M NaHCO<sub>3</sub> ( $v = 50 \text{ mV s}^{-1}$ ).

The Vulcan curve shows a relatively low background capacitance for the original sample. After functionalization, the double layer capacitance increased due to an improved hydrophilicity and hence, an increase of the accessible area to aqueous electrolyte, as a result of the creation of oxygen-containing polar functionalities (such as hydroxyl, carboxyl, carbonyl, quinone and others) during oxidation treatments [55]. Average capacitance values for the mean value in the range from 0.3 to 0.8 V ( $C_{(0.3-0.8 V)}$ ) are given in Table 4.

In addition to improved wetting, a faradaic peak appeared between 0.3 and 0.9 V, which is attributed to redox reaction of surface-oxygen containing groups mostly quinones [27, 55-59], following the Equation 2:

$$C=O + e^{-} + H^{+} \leftrightarrows C - OH$$
<sup>(2)</sup>

This contribution becomes more distinguishable following the sequence: Vulcan-O1 < Vulcan-O2 < Vulcan-O3, in correlation with the carbonyl/quinone content obtained by TPD experiments. However, a quantification of the pseudocapacitance was not possible since the deconvolution of the faradaic peaks from the double layer capacitance is not precise.

#### 3.2.2. Electrochemical oxidation: corrosion tests

Several works have studied the electrochemical oxidation of carbon materials by electrochemical techniques [12, 26, 29, 30, 56, 60-62]. However, the influence of previous chemical surface oxidation of carbon blacks by acid treatments on the tolerance to electrooxidation has been seldom considered [33]. In the present work, the influence of the progressive oxygen functionalization of Vulcan on the carbon electrooxidation was studied by cycling the potential from -0.1 to 1.6 V at 5 mV s<sup>-1</sup> in 0.1 M NaHCO<sub>3</sub>. Figure 3 displays the results for all the samples. The voltammogram was also recorded for the GC confirming that the substrate does not contribute substantially to the total current of the carbons.



**Fig. 3**. CVs of untreated and functionalized Vulcan samples, from -0.1 to 1.6 V vs. RHE in 0.1 M NaHCO<sub>3</sub> (v = 5 mV s<sup>-1</sup>).

The anodic currents from 1.0 to 1.6 V in Figure 3 may be related to carbon corrosion and oxygen evolution reaction (OER) due to water oxidation. The understanding of the reaction mechanism and the actives sites of carbons play a key role in the development of active and stable electrocatalysts. Both reactions take place via multi-step processes involving the formation of different surface oxides [57, 63], and hence the presence of oxygen surface groups may present a strong influence. In order to distinguish between the current signals associated with the production of CO<sub>2</sub> by carbon corrosion and O<sub>2</sub> by OER, DEMS measurements were carried following the mass to charge (m/z) ratio m/z = 44 (ion current of  $[CO_2]^+$ ), m/z = 22 (doubly ionized carbon dioxide  $[CO_2]^{++}$ ) related to the formation of CO<sub>2</sub> and the m/z = 32 ( $[O_2]^+$ ) attributed to the generation of O<sub>2</sub>. Figure 4 shows the CVs and the corresponding mass spectrometric cyclic voltammograms (MSCVs) obtained for the untreated material. The m/z = 44

increased at potentials more positive than 1.0 V due to the CO<sub>2</sub> formation by corrosion. Similarly, the m/z =22 signal followed the same trend. Conversely, OER did not occur under these conditions since the mass signal m/z = 32 did not increase during the anodic scan. In agreement with these results, Asthon et al. [63] did not detected oxygen evolution by DEMS on a glassy carbon electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> cycling the potential from 0 to 2 V vs. RHE.



**Fig. 4.** CVs (upper panel) and MSCVs for CO<sub>2</sub>, m/z = 44 and m/z = 22 (middle panels) and for O<sub>2</sub>, m/z = 32 (bottom panel) of Vulcan in 0.1 M NaHCO<sub>3</sub> (v = 5 mV s<sup>-1</sup>).

Therefore, the faradaic currents observed in Figure 3 for the untreated material and functionalized samples are only associated with the irreversible carbon gasification

to  $CO_2$  by means of the Equation 3:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$
 (E<sup>0</sup>=0.207 V vs. RHE) (3)

During functionalization treatments, functional groups are progressively introduced on the carbon structure, increasing the double layer capacitance and the current associated with the hydroquinone/quinone redox couple becomes more evident, as confirmed in the previous section (section 3.2.1). This higher content of surface-oxygen containing functionalities seems to favour the  $CO_2$  formation by carbon corrosion at high potentials since a higher faradaic current is observed in Figure 3 as the severity of the chemical oxidation treatment increases.

In order to further research about the effect of oxygen functionalization on the electrochemical oxidation of Vulcan, corrosion tests were performed with all the samples by cycling the potential from 0.9 to 1.6 V at 50 mV s<sup>-1</sup> for 200 complete cycles. CVs obtained at 5 mV s<sup>-1</sup> from -0.1 to 1.6 V of untreated and functionalized carbons before and after the corrosion experiment can be seen in Figure 5. In addition, Table 4 displays the decrease of the anodic faradaic current at 1.6 V ( $\Delta I_{(1.6 V)}$ ) and the variation of the average double layer charge obtained from the integration of the current in the potential range from 0.3 to 0.8 V by considering the mean value from anodic and cathodic scans, before and after corrosion tests ( $\Delta C_{(0.3-0.8 V)}$ ).

Sample	C <sub>(0.3-0.8 V)</sub> (F g <sup>-1</sup> )	$\Delta C_{(0.3-0.8 V)}$ (%) <sup>a</sup>	$\begin{array}{c} \Delta \mathbf{I}_{(1.6 \text{ V})} \\ (\%)^{\mathbf{a}} \end{array}$	b (mV dec <sup>-1</sup> )	j <sub>0</sub> (A g <sup>-1</sup> )	α
Vulcan	5	(+) 45	(-) 9	235	5.38.10-4	0.25
Vulcan-O1	30	(+) 1	(-) 26	237	1.22.10-3	0.25
Vulcan-O2	36	(-) 17	(-) 33	288	1.72.10-3	0.21
Vulcan-O3	42	(-) 25	(-) 31	266	$1.04 \cdot 10^{-3}$	0.22

**Table 4.** Electrochemical features and electrokinetic parameters for the HER of untreated and functionalized Vulcan samples.

<sup>a</sup>An increase of the capacitance in the potential range from 0.3 to 0.8 V or the current faradaic at 1.6 V after the corrosion tests is specified by (+) and a decrease by (-).

Untreated Vulcan presented a slight decrease (9%) of the faradaic current at 1.6 V after the corrosion test, whereas the average capacitance increased substantially (45%). Therefore, potential cycling induces at untreated Vulcan an increase in the surface electroactive area due to the creation of O-containing species, and hence, an improved wetting of the carbon by the electrolyte during the cycling but a low trend to the irreversible corrosion is apparent. Similar results have been reported by other authors on different carbon materials including Vulcan XC-72R [26, 27, 34, 56, 64, 65].

In contrast, functionalized samples exhibited a higher decrease of the anodic current after electrochemical oxidation (around 26-33%). In addition, a progressive diminution of the double layer charge was displayed with a decrease value of 25% for the carbon subjected to the most effective treatment for creating functional groups, Vulcan-O3. This behavior has been recently described in literature for electrochemically oxidized carbon materials (including fresh Vulcan XC-72) after long cycling (more than 10000 cycles at Vulcan XC-72) from 1 to 1.5 V vs. RHE at a scan rate of 500 mV s<sup>-1</sup> [12, 62]. Okunew and coworkers [12, 62] associated this decrease to the progressive destruction of the porous structure of the material after long cycling. They evidenced two carbon-degradation stages depending on the cycle number: during the first stage an

increase of the double layer current was evident due to the creation of oxygen surface species, while after long cycling the carbon current-potential curve gradually become similar to the GC signal indicating the complete degradation of the samples. In this work, we show that the previous chemical oxidation of Vulcan XC-72R accelerates the carbon corrosion since a gradual decrease of the double layer charge (second degradation stage according to the mechanism proposed in [12, 62]) was evidenced for HNO<sub>3</sub>-treated carbons after 200 cycles from 0.9 to 1.6 V at 50 mV s<sup>-1</sup>. Vulcan-O1 showed a high decrease of the faradaic current at potentials above 1.2 V due to the irreversible carbon oxidation to  $CO_2$  but the double layer current (from 0.3 to 0.8 V) was preserved. Finally, the untreated material presented an important increase of the capacitance (first degradation stage according to [12, 62]). Thus, the introduction of surface oxygen species during chemical oxidation treatments promotes the irreversible gasification of the carbon matter to CO2 since these functional groups act as intermediates in the process favouring corrosion [21, 33, 56]. In addition, oxygencontaining polar groups enhance the hydrophilicity and consequently, the surface area accessible to aqueous electrolyte, increasing the probability of corrosion. In fact, the carbon electrooxidation resistance follows the sequence: Vulcan-O3 < Vulcan-O2 < Vulcan-O1 < Vulcan in correlation with the increase of the oxygen content obtained by TPD for these samples. This fact is important to be considered when designing a catalyst support, as the presence of oxygen groups improves the dispersion of metal particles [25, 42, 66] but favours the corrosion of the support, and consequently, the long term stability of the material.



**Fig. 5.** CVs of untreated and functionalized Vulcan samples, in 0.1 M NaHCO<sub>3</sub> (v = 5 mV s<sup>-1</sup>). Solid curves: prior to anodic experiments. Dashed curves: after 200 cycles at 50 mV s<sup>-1</sup> between 0.9 and 1.6 V vs. RHE.

# 3.2.3. H<sub>2</sub> evolution reaction

HER occurs at potentials below 0.0 V vs. RHE in energy-conversion devices. However, scarce works have studied in detail the performance of metal-free carbon electrodes for hydrogen evolution [67, 68]. In addition, the influence of oxygencontaining groups on hydrogen adsorption/evolution has been rarely studied [20, 34]. In the current work, the effect of oxygen treatments on the activity toward HER was studied by recording CVs at 5 mV s<sup>-1</sup> in 0.1 M NaHCO<sub>3</sub> in the potential range from -1.1 to 1.6 V and from -1.1 to 1.0 V. Figure 6 displays a comparison of the voltammograms recorded for the untreated Vulcan and Vulcan-O3.

An important influence of the upper potential on the onset and the current for the HER was observed. The hydrogen evolution current is significantly lower when the carbons are cycled up to 1.6 V than when the positive potential limit is 1.0 V, which has been recently explained by a decrease of the number of available actives sites for HER by carbon electrooxidation [34]. Interestingly, a slight higher current density decrease at -1.1 V was observed for Vulcan (72%) in comparison to Vulcan-O3 (62%) when cycling up to 1.6 V which could be explained by the negligible oxygen amount of the untreated material. In this context, Vulcan presented an O<sub>XPS</sub> amount of 2.3 wt.% and a high hydrogen evolution current was obtained at -1.1 V (13.3 A g<sup>-1</sup>) when the potential was cycled from -1.1 to 1.0 V (Figure 6, solid curve), while the oxidized sample Vulcan-O3 with a higher oxygen amount (O<sub>XPS</sub>: 12.0 wt.%) displayed a lower cathodic current (8.0 A g<sup>-1</sup>). Thus, the introduction of oxygen seems to inhibit the HER. However, when the carbons are cycled from -1.1 to 1.6 V (Figure 6, dashed curves) a similar cathodic current (around 3.0-3.5 A g<sup>-1</sup>) is obtained due to the electrooxidation of both carbons during the anodic scan. Thus, it seems that after electrochemical oxidation at potentials more positive than 1.0 V the initial O content does not affect severely in the electrochemical activity for H<sub>2</sub> evolution.



Fig. 6. CVs of Vulcan and Vulcan-O3 in 0.1 M NaHCO<sub>3</sub> from -1.1 to 0.2 V (solid curves) and from -1.1 to 1.6 V vs. RHE (dashed curves) ( $v = 5 \text{ mV s}^{-1}$ ).

In order to prevent the oxidation of carbons in the 1.0-1.6 potential range, linear voltammograms (LVs) between -1.1 V and 1.0 V were recorded for the different materials and compared (Figure 7). Firstly, it is remarkable that the contribution to the total hydrogen evolution current of the GC used for the deposit of the ink is negligibe. A different behavior for HER was found depending on the oxidation treatment. Indeed, a different onset potential for HER (defined at the current density of -1.3 A g<sup>-1</sup>) is evidenced in LVs. The HNO3:H2SO4-treated carbon (Vulcan-O2) displays the most positive onset potential (-0.72 V) showing an improved condition toward HER, in comparison to the un-treated carbon (-0.79 V) and the samples oxidized with HNO3 (around -0.82 V for both Vulcan-O3 and Vulcan-O4). Therefore, the oxidation treatment seems to play an important role on the electrochemical activity for HER: the treatments with HNO<sub>3</sub> inhibit the HER, whereas oxidation with a mixture of HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> shifts the onset potential to more positive values. The presence of H<sub>2</sub>SO<sub>4</sub> in the last treatment, which provides an enrichment of the carbon surface basicity, could be responsible for the different behavior for HER. However, the cathodic faradaic current in the 0.0 to -0.8 V potential range could be also related to the reduction of oxygenated species. Spectro-electrochemical techniques (such as DEMS) could provide a deeper insight of the onset potential for HER of carbon materials [34, 38]. Additionally, at more negative potentials than -1.0 V, the introduction of oxygen species inhibits the formation of H<sub>2</sub>, diminishing the cathodic current following the sequence: Vulcan > Vulcan-O1 > Vulcan-O3  $\approx$  Vulcan-O2.



**Fig. 7**. (a) LVs from 0.2 to -1.1 V vs. RHE in 0.1 M NaHCO<sub>3</sub> ( $v = 5 \text{ mV s}^{-1}$ ) and (b) Tafel plots of untreated and functionalized Vulcan samples.

The activity toward the HER of carbons was further studied by the Tafel plots (Figure 7b). The overpotential was compensated by the ohmic potential drop. The corresponding Tafel slopes (b), the exchange current densities  $(j_0)$  and the charge transfer coefficients ( $\alpha$ ) for the HER are shown in Table 4. The reaction pathway of the HER involves the initial electrochemical adsorption of H<sup>+</sup> (Volmer step) and followed by either the electrochemical desorption reaction (Heyrovsky step) or chemical desorption reaction (Tafel step) to obtain H<sub>2</sub> [69]. High Tafel slopes were obtained for all the samples with values in the range 235-288 mV dec<sup>-1</sup>, indicating high energy barriers for the HER with the rate limiting step in the initial  $H^+$  adsorption (slope > 120) [70]. Consequently,  $\alpha$  values around 0.21-0.25 were obtained for the carbon materials. Similar Tafel slopes and charge transfer coefficients have been obtained for metal-free carbon electrodes by other authors [70-75]. On the other hand, the original material and the carbon oxidized with HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> (Vulcan-O1), presented the lowest values of b (235 and 237 mV dec<sup>-1</sup>, respectively) and the highest  $\alpha$  (around 0.25 for both samples), showing favourable reaction kinetics for the hydrogen evolution in comparison to samples treated with only HNO<sub>3</sub> (Vulcan-O2 and Vulcan-O3). In contrast, the original material presented a j<sub>0</sub> of  $5.38 \cdot 10^{-4}$  A g<sup>-1</sup>, which is around 2-3 times lower than those observed for the oxidized samples, indicating a poorer intrinsic rate of electron transfer. In this context,  $j_0$  is determined at the reversible potential (i.e. zero overpotential). However, the HER occurs at high overpotentials at carbon electrodes, and thus the Tafel slope and  $\alpha$  are considered to be more practical parameters than  $j_0$  for evaluating their electrocatalytic activity [76].

# 3.2.4. H<sub>2</sub> evolution in the presence of CO<sub>2</sub>: evidences for CO<sub>2</sub> reduction

The HER on Vulcan, before and after functionalization, was also studied in presence of dissolved  $CO_2$  to study the electrochemical activity toward  $CO_2$ 

electroreduction. In this context, the performance of metal-free carbon electrodes for  $CO_2$  electroreduction has attracted special attention during the last years [34, 45-47, 49]. However, the effect of oxygen functionalization of porous carbon electrodes has been rarely considered [42, 48]. To the best of our knowledge it is the first time reporting the  $CO_2$  reduction on metal-free carbon porous electrodes subjected to different chemical oxidation treatments. The curves obtained for each sample in 0.1 M NaHCO<sub>3</sub> at 5 mV s<sup>-1</sup> from -1.1 to 0.2 V in absence or in presence of dissolved  $CO_2$  are displayed in Figure 8.



**Fig. 8**. CVs of untreated and functionalized Vulcan samples, in 0.1 M NaHCO<sub>3</sub> (v = 5 mV s<sup>-1</sup>) in absence and presence of CO<sub>2</sub>. Solid curves: Ar saturated solution. Dashed curves: CO<sub>2</sub> saturated solution.

A different activity was found at potentials more negative than -0.7 V for the carbon materials, as can be seen comparing the faradaic currents at -1.1 V in the presence and in the absence of CO<sub>2</sub>. In the base electrolyte saturated with Ar, the

currents at -1.1 V are associated with the  $H_2$  formation, whereas for  $CO_2$  dissolved solution are due to both HER and the electrochemical reduction of  $CO_2$ .

The original carbon and the samples treated with concentrated HNO<sub>3</sub> (Vulcan-O2 and Vulcan-O3) presented a strong decrease of the current at -1.1 V in presence of CO<sub>2</sub>, which could be associated to the adsorption of species from CO<sub>2</sub> reduction on carbon surfaces [34, 77, 78]. In other words, (CO<sub>2</sub>)<sub>red</sub> species (such as CO<sub>ad</sub> and formates) are adsorbed on carbon during the cathodic scan, inhibiting the formation of molecular hydrogen, and decreasing the total faradaic current. Interestingly, the diminution of the cathodic current was more evident for Vulcan and Vulcan-O2 than for the sample subjected to the most severe treatment, Vulcan-O3. In fact, an inhibition of the cathodic current at -1.1 V around 75-78% was obtained on the former materials in the presence of CO<sub>2</sub>, whereas Vulcan-O3 presented a value of 65%, which may be explained by a decrease in the amount of adsorbates from  $CO_2$  reduction for the last sample. As evidenced by TPD analysis longer treatment time of Vulcan in nitric acid led to the highest amount of O-containing species on the carbon surface which could result in a blockage of the porous structure to the active sites. On the other hand, Bandosz and coworkers [48, 49] have recently reported that micropores could enhance the CO<sub>2</sub> interaction and the (CO<sub>2</sub>)<sub>red</sub> species retention on carbon surfaces. According to  $N_2$  physisorption results, a higher mesopore fraction was obtained for Vulcan-O3 which might affect negatively in the formation of  $(CO_2)_{red}$  species.

In contrast, a small decrease of the cathodic current (15%) was obtained on the carbon treated with the  $HNO_3:H_2SO_4$  mixture in a  $CO_2$  saturated solution, showing that the adsorption of  $(CO_2)_{red}$  occurs to a much lower extent on this carbon. This behavior is associated with differences in the nature of the mix of functional groups since Vulcan-O1 presented a higher basic group contribution. According to [48, 49], the

electrochemical reduction of CO<sub>2</sub> is favourable on basic carbon surfaces, whereas acid surfaces enhance HER. However, a lower (CO<sub>2</sub>)<sub>red</sub> coverage seems to be obtained on the carbon with the most developed basicity, Vulcan-O1. In agreement with these results, Fe based electrodes supported on the Vulcan XC-72R subjected to similar oxidation treatments showed a different behavior for CO<sub>2</sub> reduction in acid media (0.5 M H<sub>2</sub>SO<sub>4</sub>) in a previous study [42]. In that manuscript a different reaction pathway was proposed depending on the oxidation treatment of the carbon surface: the formation of CO<sub>ad</sub> was favoured on Fe electrodes supported on HNO<sub>3</sub>-treated carbons and the original material, while formic acid was mainly obtained when the support was oxidized with HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub>, which again resulted in the highest CO/CO<sub>2</sub> ratio. The results obtained in that work evidenced that adsorbed species are mostly formed on the former electrodes, whereas the material with an improved surface basicity presented a lower tendency to the formation of adsorbates from CO<sub>2</sub> reduction, although a high activity toward the formation of formic acid. Thus, metal-free carbon electrodes seem to follow the same reaction pathway for CO<sub>2</sub> electroreduction in a neutral solution (0.1 M NaHCO<sub>3</sub>); i.e. adsorbed species could be obtained on the former electrodes, while volatile compounds would be mainly generated in the carbon oxidized with nitric-sulphuric acid.

According to these results, it is proved that the support and its chemical surface properties are modified during functionalization treatments conditioning the posterior electrochemical reactions taking place when carbon-based electrodes are used in electrochemical devices (e.g. fuel cells and electrolyzers).

## 4. Conclusions

The electrochemical behavior in 0.1 M NaHCO<sub>3</sub> of Vulcan XC-72R, before and after different chemical oxidation treatments has been discussed. Oxidized samples presented a noticeable increase of the capacitance due to an enhancement of the carbon

wetting by the creation of polar groups during oxidation treatments. In addition, the quinone/hydroquinone redox reaction became more distinguishable as the treatment severity increased, confirming that these groups were effectively introduced on the carbon surface. However, oxygen functionalization resulted in a gradual decrease of the corrosion resistance with the oxygen amount. Thus, the introduction of oxygen-containing functional groups on the carbon surface favours the electrochemical oxidation. On the other hand, lower hydrogen evolution currents (at potentials more negative than -1.0 V) were obtained for all oxidized samples in comparison to the untreated material.

Finally, an important effect of the oxygen functionalization on the electrochemical activity for  $CO_2$  reduction was evidenced. Vulcan and the samples treated with nitric acid showed a strong decrease of the HER current in presence of  $CO_2$  (around 65-78%) owing to the  $(CO_2)_{red}$  species adsorption. However, the formation of adsorbates was not as evident for the sample oxidized with nitric-sulphuric (with an inhibition of the cathodic current of 15%), which could be related to a different surface oxygen-containing group distribution. Indeed, this carbon presented a more developed surface basicity which seems to decrease the  $(CO_2)_{red}$  coverage.

As a conclusion, this study clearly indicates that both the amount and the nature of oxygenated species effectively affect the electrochemical behavior of carbon electrodes towards CO<sub>2</sub> reduction.

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