Oxidized carbon nanofibers supporting PtRu nanoparticles for direct methanol fuel cells

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Abstract

Oxidized carbon nanofibers (CNFs) have been investigated as supports for PtRu nanoparticles. Two distinct CNFs characterized by different surface area and crystallinity have been considered and treated with nitric acid and a mixture of sulfuric and nitric acids to introduce oxygen functionalities. The oxidized CNFs have been then physico-chemically characterized and used for the preparation of PtRu/CNF catalysts by a modified microemulsion procedure. PtRu nanoparticles of ca. 2 nm size were obtained despite the relatively low surface area of CNFs (90–180 m² g⁻¹). A good particle distribution on the supports has been obtained, as confirmed by TEM micrographs and by the high values of electrochemically active surface areas (up to 200 m² g⁻¹). Catalysts based on oxidized carbon nanofibers present a significant increase of activity toward the electro-oxidation of methanol. The effect of oxidation treatments is not independent of the CNF properties, which must be considered for a convenient support optimization. Nevertheless, the optimum support is obtained when balancing three parameters: a sufficient electrochemical surface area, an improved metal-support interaction due to the effect of oxygen functionalities, and better methanol diffusion through the catalyst pores due to the wettability of oxidized CNFs.

Keywords: *carbon nanofibers, oxidation, functionalization, platinum-ruthenium, methanol oxidation*

1. Introduction

Direct alcohol fuel cells (DAFCs) represent a valid alternative to Li-ion batteries for small portable electronic devices and auxiliary power units, due to the high energy density of alcohols, lightweight, compactness, simplicity as well as easy and fast recharging [1-7]. The main drawbacks toward the commercialization of DAFC technologies are still the high cost and the unsatisfactory component lifetime, which are derived mainly from the use of noble metal catalysts and perfluorosulfonated polymer electrolyte membranes [8-11]. Regarding the use of noble metals, it is necessary to develop catalytic structures that maximize the utilization of platinum and platinum group metals for an adequate fuel cell performance. One of the most promising strategies is the use of advanced supports that stabilize metal nanoparticles, allow good diffusion paths for reactants and products, offer a high electrical conductivity and resist corrosion phenomena in the electrode environment [12-19].

Carbon supports still present the best compromise of properties to fulfill fuel cell requirements in terms of electrocatalytic activity. With the scope of improving the distribution of platinum-based nanoparticles on the surface of carbon supports, a plausible strategy is to create surface functionalities based on oxygen groups. Acid treatment is effective to introduce oxygen atoms on the carbon surface being part of functionalities such as carboxylic acids, anhydrides, lactones, hydroxyls or carbonyls [20, 21]. The functionalities may act as anchoring sites for the metal catalysts and eventually aid in their adsorption on the carbon surface by numerous mechanisms, which include adsorption, ion-exchange or coordination reactions [22, 23]. Moreover, the presence of oxygen-carrying polar functional groups enhances the surface hydrophilicity, which aids the diffusion of methanol fuel (aqueous solution) to achieve all the available catalytic active sites.

There are not yet clear indications in the literature about the real effect of oxygen groups on the electrochemical behavior of platinum-ruthenium catalysts. Carmo et al. [24, 25] found that oxidizing the benchmark support (carbon black Vulcan XC72R), with either nitric or sulfuric acids, results in a significant improvement of direct methanol fuel cell (DMFC) performance. They attributed the enhanced catalytic activity to a better distribution of PtRu nanoparticles on the surface, and/or the better wettability of the support, and/or a higher resistance to CO poisoning. Salgado et al.

[26] found that the electrochemically active surface area decreases from 70 to 54 m² g⁻¹ when using functionalized Vulcan, evidencing a detrimental effect on Pt dispersion, but still obtaining a significant improvement of DMFC performance. According to this, the positive effect of the oxidized carbon support is not attributed to a better nanoparticle distribution on the surface. The authors explain such enhancement in terms of surface polarity caused by the contribution of oxygen groups, leading to 2.5 times higher performance despite the worse noble metal surface area.

Not only conventional carbon blacks but also the functionalization of novel carbon structures has been investigated very recently. Figueiredo et al. reviewed the synthesis and functionalization of high surface area carbon xerogels (CXGs) [27]. They individuated the effect of different oxygen groups and rationalized the improvement of activity of PtRu catalysts as the result of two contrary effects: the presence of carboxylic and anhydride groups, which influences the stability and oxidation state of active metals; and the decrease of conductivity of the support influenced by the presence of surface oxygen groups. Alegre et al. also observed a significant variation of the oxidation state of Pt and Ru with the presence of carboxylic and lactone groups on CXGs [28]. However, although a significant improvement of the intrinsic activity of the catalysts is obtained with surface oxygen groups, the detrimental effect on nanoparticle dispersion and distribution, caused by a preferential metal growth on surface defects, results in no significant advantage for functionalized CXGs compared to untreated ones [28, 29]. All these works highlight the difficulties to individuate the effect of using oxidized carbon supports due to the scattering of data caused by different support properties and distinct catalyst preparation methods. To this purpose, Gómez de la Fuente et al. [30, 31] studied the combined effect of the functionalization of carbon black and PtRu synthesis methodologies. They concluded that the influence of both oxygen groups and synthesis procedures on the metal-support interaction and catalyst morphology are of key importance to maximize the PtRu utilization. In this regard, oxygen functionalities may play an important role in stabilizing Pt-based nanoparticles and influencing the electrochemical behavior of the catalyst.

The objective of the present work is to determine whether the functionalization of highly graphitic carbon nanofibers (CNFs) produces a significant enhancement of PtRu catalyst performance in DMFC. These CNFs possess a relatively low surface area

(100-150 m² g⁻¹), which hinders the dispersion of the active phase on the surface. High metal concentrations (≥ 50 wt%) on carbon are commonly used to minimize the electrode thickness and maximize fuel cell performance [1]. However, efforts are currently focused on the reduction of metal loading in the electrodes (≤ 1 mg cm⁻²) for cost-effective devices. This allows the electrode fabrication based on catalysts with low metal concentration on the carbon support in order to obtain a high surface area. In the present work, a microemulsion route was used to prepare high surface area 20 wt% PtRu nanoparticles supported on different CNFs in order to carry out an independent cross-analysis of support features and catalytic activity.

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2. Experimental details

2.1 Preparation and oxidation of carbon nanofibers

Carbon nanofibers were prepared at 600°C (named CNF600) and 700°C (named CNF700) by the catalytic decomposition of methane on a nickel-based catalyst, according to previous works [32, 33]. Two temperature values were selected to provide CNFs with two different diameters (28 nm for CNF600 and 54 nm for CNF700 [32]) and graphitization degrees, and consequently favor either the surface area (at 600°C) or the crystallinity (at 700°C). Both CNFs were functionalized by oxidation treatments, refluxing with concentrated acid solutions of HNO₃ or HNO₃:H₂SO₄ (1:1 v/v). In these solutions the nitronium ion, NO₂⁺, attacks the carbonaceous surface, which is presumably the first step in the introduction of oxygen surface groups. The addition of sulfuric acid increases the oxidation extent. With the purpose of maintaining a similar oxidation degree with both acid compositions, and based on previous studies [34, 35], boiling temperature (110 °C) was used for the HNO₃ treatment and room temperature for the HNO₃:H₂SO₄ treatment. The duration of the experiments was 30 minutes in all cases. The acid concentrations employed were 65 wt% for nitric acid and 96 wt% for sulfuric acid in water, as purchased from Panreac. After oxidation, samples were thoroughly washed with deionized water until neutral pH and subsequently dried at 100 °C overnight.

2.2 Deposition of PtRu nanoparticles on oxidized carbon nanofibers

The scope of the synthesis of PtRu catalysts was to obtain similar particle sizes independently of support surface area and surface chemistry. For this reason, a microemulsion route was employed [36-38], in which the encapsulation of metal precursors in reverse micelles limits the metal crystallites growth to a few nanometers. Briefly, it consists of preparing a microemulsion composed by 16.5 % surfactant (polyethylene glycol dodecyl ether, Brij®30, Sigma-Aldrich), 3.9 % aqueous solution containing the metal precursors (0.05 M H₂PtCl₆ and 0.05 M RuCl₃) and n-heptane as the hydrophobic phase. Subsequently, the appropriate amount of carbon support is dispersed in the microemulsion under sonication for at least one hour in appropriate amount for a metal concentration in the catalyst of 20 wt%. The reduction step involves the slow addition of sodium borohydride in excess at room temperature and under

vigorous stirring for 16 hours. Finally the catalyst is thoroughly washed with ethanol and water to remove the microemulsion components used during the synthesis, and dried overnight at 60°C.

2.3 Physico-chemical characterization

Textural properties of carbon supports such as the specific surface area and the pore volume were determined from nitrogen adsorption-desorption isotherms, measured at -196 °C using a Micromeritics ASAP 2020. Total surface area and pore volume were calculated using the Brunauer-Emmet-Teller (BET) equation and the single point method, respectively.

The quantitative and qualitative determination of the oxygen surface groups was carried out by means of temperature programmed desorption (TPD) experiments. Typically, 300 mg of carbon material was placed in a U-shaped quartz reactor. The temperature was increased at a rate of 10 °C min⁻¹ from room temperature up to 1050 °C under a helium flow of 30 cm³ min⁻¹. The amounts of CO and CO₂ desorbed from the carbon samples were analyzed by gas chromatography. The distribution of oxygen functional groups was estimated from the deconvolution of TPD curves into the different contributions by Gaussian functions and numerical routines. According to previous publications [21, 34, 39], in order to determine the relative amount of each surface group, some assumptions were considered for the deconvolution of CO₂ and CO curves: CO₂ profile is decomposed into three contributions corresponding to carboxylic acids, anhydrides and lactones (in increasing order of desorption temperature), whereas, CO profile is decomposed into three contributions corresponding to anhydrides, hydroxyls and carbonyls. An anhydride group decomposes releasing 1 mol of CO and 1 mol of CO₂, thus the corresponding peak must have the same shape and magnitude in the deconvolution of both CO and CO₂ curves.

The crystallinity of platinum-ruthenium crystallites and carbon was studied by X-Ray Diffraction. XRD patterns were performed using a Bruker AXS D8 Advance diffractometer, using Cu-K α radiation. Crystallite sizes were calculated from the Scherrer's equation applied to the (220) peak for platinum related reflections.

High-resolution transmission electron microscope (HRTEM) micrographs were obtained using a JEOL-2000 FXII microscope at 200 kV and with a spatial resolution of 0.28 nm. To obtain the micrographs, the catalyst samples were finely grinded and ultrasonically dispersed in ethanol. A drop of the resultant dispersion was deposited and dried onto a standard copper grid coated with Lacey carbon.

Energy dispersive X-ray (EDX) analyses and thermogravimetric analyses (TGA) in air were performed to quantify the metal loading and composition of the PtRu/CNF electrocatalysts. EDX measurements were also used to determine the Pt:Ru atomic ratio. An EDX analyzer Röntec XFlash Si(Li) coupled to a Hitachi S-3400N scanning electron microscope (SEM) was used for that purpose. For TGA experiments in air, a Setaram Setsys Evolution thermogravimetric analyzer was used at atmospheric pressure, and the temperature was varied from room temperature to 950°C with a constant rate of 5 °C min⁻¹.

2.4 Electro-chemical characterization

PtRu/CNF electrocatalysts were characterized in half-cell. Half-cell set-up consisted in a three-electrode assembly and an Autolab Potentiostat-Galvanostat. A large area pyrolytic graphite rod served as the counter electrode and a reversible hydrogen electrode (RHE) system was used as the reference electrode. The working electrodes were composed of the electrocatalysts deposited as a thin layer over a pyrolytic graphite disk (0.38 cm²). An aqueous suspension of the catalyst under study was prepared by ultrasonically dispersing it in ultrapure water (Milli-Q) and Nafion. An aliquot of the well-dispersed suspension was pipetted on the pyrolytic carbon disk substrate surface and dried at 80°C under nitrogen atmosphere, resulting in a platinum loading of 0.1 mg cm⁻² (33 wt% Nafion). After preparation, the electrode was immersed into the deaerated 0.5 M H₂SO₄ electrolyte, prepared from high purity reagents (Merck) and water purified in a Milli-Q system. The electrolyte was saturated with pure N₂ or CO gases (99.997%, Air Liquide), depending on the experiments.

For the electrochemical characterization, cyclic voltammograms were recorded in the electrolyte solution (0.5 M H₂SO₄) between 0.05 V and 0.85 V vs. RHE at a scan rate of 0.02 V s⁻¹. CO stripping voltammograms were obtained after bubbling this gas in the cell for 10 min at 0.2 V vs. RHE, followed by nitrogen purging to remove the excess

1 of CO. The admission potential was selected considering that for this value maximum
2 adsorbate coverage is achieved for CO adsorption [40]. Electrochemical surface active
3 areas were determined from the integration of the CO oxidation region (0.45-0.85 V vs.
4 RHE), after correction for double layer capacitance, and assuming $420 \mu\text{C cm}^{-2}$
5 involved in the process. Methanol electrochemical oxidation reaction was studied by
6 linear sweep voltammetry, with a scan rate of 0.005 V s^{-1} , substituting the base
7 electrolyte for a deaerated solution of methanol (2 M) in the base electrolyte (0.5 M
8 H_2SO_4).

3. Results and discussion

Main textural differences between the two pristine CNFs are the higher surface area and the higher pore volume of CNF600, this is, the CNF characterized by a relatively low synthesis temperature (600°C), as summarized in Table 1. Despite its lower surface area, CNF700 (synthesized at 700°C) has shown a better performance than CNF600 when used as PtRu support [41], because of the influence of support graphitization degree, which leads to an enhanced metal-support interaction. Consequently, we have included both supports, CNF600 and CNF700, with high and low surface area, respectively.

Notice that the treatment of CNFs with nitric acid at 110 °C (named ‘N’) and with nitric and sulfuric acids at room temperature (named ‘NS’) leads to the same oxygen content: 4.9 wt% for oxidized CNF600 and 2.8 wt% for oxidized CNF700. Similar oxygen contents will allow the comparison of supports and individuation of the influence of other parameters on the catalytic performance, *e.g.* the surface chemical composition or the textural properties. In general terms, both the surface area and the pore volume increase after these oxidation treatments, prompt by the roughening of the surface and the removal of nickel traces [34]. The oxygen content is clearly higher for the CNF600 based materials due to the larger surface area. Actually, the surface density of oxygen atoms, calculated taking into account the BET surface areas, indicates an oxygen concentration of about 6-7 atoms nm⁻² for the untreated CNFs, which increases to about 10-12 atoms nm⁻² after treatment, independently of surface area or type of oxidation process. This increase in oxygen is high enough to make the hydrophobic pristine nanofibers well dispersible in water, as evidenced in Fig 1. To this purpose, CNFs (1 mg) were mixed in a vial containing n-heptane and water, kept under sonication for 1 hour and then the vials were left to settle for 24 hours. The untreated sample presents no affinity with the aqueous phase, remaining mainly in the organic one (upper phase), whereas the treated samples remain well dispersed in the aqueous phase even after 24 hours. This indicates a significant improvement in terms of wettability for the CNFs with both acid treatments.

Fig. 2 shows the composition of the different types of oxygen groups. Temperature programmed desorption (TPD) experiments were carried out to estimate the content in carboxylic acids, anhydrides, lactones, hydroxyl and carbonyl groups

from the desorbed CO or CO₂ at different temperatures, according to previous studies [21, 34]. The treatments of CNFs significantly increase the net content of carboxylic acid (-COOH), lactone (-C₂OOH) and carbonyl (-C=O) groups while decreasing the hydroxyl group (-COH) concentration. Although carbonyl groups are abundant in the pristine CNFs, coming from exposure to air at ambient temperature, they do not seem to favor the wettability of the samples as evidenced in Fig. 1. The significant increase of the concentration of carboxylic acids and lactones explains the better wettability of the oxidized CNFs despite the relatively low increase of surface oxygen concentration.

Table 2 shows some of the main physico-chemical properties of PtRu catalysts supported on the different pristine and oxidized carbon nanofibers. The metal concentration is close to the nominal one in all cases (20 wt%), as confirmed by EDX and TGA experiments, with an atomic Pt:Ru ratio of approximately 50:50. The maximum catalytic activity for methanol oxidation has been reported to be given by a broad interval of bulk compositions near 40-60 Pt at.% [42, 43, 44]. In the present work, the variation of this atomic ratio within catalysts (46-52 at.%) will be considered low enough to influence the electrochemical behavior (at low temperature) in a much lesser extent than the variation of support features.

X-ray diffractograms (Fig. 3) correspond to the face centered cubic (fcc) structure of platinum together with the graphitic carbon reflections. The reflections attributed to metal particles are slightly shifted towards higher angles than the corresponding supported Pt (lattice parameter of 0.392 nm for Pt supported on carbon), as a result of the alloy with ruthenium. This is also evidenced by the lattice parameter, calculated from the Bragg equation (Table 2). The values obtained are lower than that of pure platinum supported on carbon nanofibers (ca. 0.392 nm) [17] and no reflections associated to Ru, or metal oxides are present, indicating that Ru is alloyed to the platinum structure. A high degree of alloy has demonstrated to offer a better catalytic activity in PtRu catalysts supported on carbon nanofibers [45].

PtRu crystal sizes, calculated from the broadening of the (220) reflection and applying the Scherrer's equation, were found between 1.8 and 2.3 nm. With the treatment labeled as NS, there is a slight increment in crystal size of PtRu alloys, not observed for the support treated with nitric acid alone. Taking into account that PtRu nanoparticles have been obtained by the microemulsion procedure, an increase of

particle size is attributable to a certain agglomeration of nanodroplets on the surface of CNFs. As this phenomenon is not observed with CNF treated with nitric acid (PtRu particle size is the same as on the untreated based CNF), differences in surface oxygen composition may explain such tendency to agglomerate during either the growth or deposition of metal particles. On the other hand, the carbon related peak (at ca. 26°) is more intense and narrow for the CNF700 related catalysts according to the more graphitic character of this support and derivatives compared to CNF600 related ones, maintaining in all cases a high ordering degree.

Theoretical mass surface areas (TMSAs) were calculated from the crystallite sizes determined by XRD analyses and assuming spherical nanoparticles. More details can be found in references [40, 43, 46]. In the present paper, both the particle size and the degree of alloy were considered to derive the TMSA, assuming spherical nanoparticles and correcting for the value of density. It is remarkable that high theoretical values up to 207 m² g⁻¹ are obtained, which highlights the importance of synthesizing small PtRu nanoparticles to maximize the noble metal utilization.

Regarding the electrochemical characterization, Fig. 4 shows the response in the oxidation of a CO monolayer, adsorbed at 0.2 V vs. RHE. The oxidation of CO occurs in a single peak starting at a potential of ca. 0.5 V vs. RHE. It is well known that the electrochemical oxidation of CO is a surface structure sensitive reaction [47, 48]. The center of the peak for the catalysts based on pristine CNF600 and CNF700 is indicated with a dashed vertical line. Notice that the oxidation of CO occurs at slightly more negative potential (30 mV) for the catalysts based on oxidized CNFs (excepting PtRu/CNF700NS). These minimum differences in CO oxidation potential could be attributed to the variation of surface characteristics, which in turn may derive from differences in particle size or different metal-support interaction. In the case of the treatment with nitric acid the same crystal size was obtained. The better CO oxidation behavior for PtRu/CNF600N and PtRu/CNF700N with respect to the corresponding untreated supports is consequently attributed to the effect of surface oxygen groups that favor the electrooxidation of CO at more negative potential values.

The electrochemical surface areas (ECSAs) were calculated from CO stripping curves assuming a charge of 420 μC cm⁻² in the oxidation of a monolayer of linearly adsorbed CO normalized by the total amount of metal (PtRu) [48], and the values are

summarized in Table 2. It is remarkable that the catalysts supported on the oxidized CNFs present, in general terms, considerably lower ECSA. This effect is attributed to metal nanoparticles agglomeration on the defects of CNFs. Similar decrease of ECSA was also reported by other authors [26, 49]. They observed a decrease of ECSA between 20 and 50% with respect to untreated support. It is worth to mention that the effect of the same oxidizing treatment on different CNFs does not result in the same trend with respect to ECSA. Firstly, regarding the treatment based on nitric acid at high temperature (N), the catalyst PtRu/CNF600N presents a ca. 30% lower ECSA with respect to PtRu/CNF600, whereas the catalyst PtRu/CNF700N presents a negligible variation of ECSA with respect to PtRu/CNF700. This means that the presence of carboxylic acid groups on the low surface area CNF700 favors the homogeneous dispersion of PtRu nanoparticles whereas the same treatment on the high surface CNF600 results in a higher density of defects and consequent lower ECSA [17]. Secondly, regarding the treatment based on nitric and sulfuric acid at room temperature (NS), catalysts are characterized by a slightly higher PtRu particle size, which results in a lower theoretical surface area. This inevitably leads to lower ECSA values with respect to the catalysts based on pristine CNF600 and CNF700.

The electro-oxidation of methanol (2M CH₃OH in 0.5M H₂SO₄) was studied at room temperature by linear sweep voltammetry in a half-cell set-up. Fig. 5 includes the polarization curves in terms of mass and specific activity obtained for the PtRu catalysts supported on CNF600-related samples. Two opposite effects are clearly observed when oxidized CNFs are used. Notice that from ECSA determination, lower mass activity should be expected for both CNF600N and CNF600NS supported catalysts since a significant decrease of the number of active sites was found in CO stripping. In fact, PtRu/CNF600N follows this trend with a 40% lower current density compared to PtRu/CNF600. However, the catalyst supported on CNF600NS shows a higher current density than CNF600. In this case, the significant increase of intrinsic activity, as evidenced in Fig. 5(b), compensates the decrease of electrochemical surface area. The increased mass activity is due to the higher intrinsic activity for PtRu/CNF600NS, thus, a higher rate of methanol oxidation per catalytic active site. PtRu/CNF600NS presents a higher particle size than PtRu/CNF600 as shown in Table 2. Garcia et al. observed a volcano-shaped curve with a maximum activity in a range of particle size of 1.6-2.2 nm for methanol oxidation at low temperature of highly alloyed PtRu catalysts [46].

Furthermore, the highest activity obtained for PtRu/CNF600NS is not only explained by the different particle size, but a significant contribution of metal-support interaction influences the catalyst behavior. The two most active PtRu catalysts based on CNF600 and CNF600NS were further analyzed by HRTEM, as shown in the representative images of Fig. 6. The images confirm the better distribution of particles and slightly bigger PtRu particles (2.3 nm) on the CNF600NS support. Indeed, the ratio ECSA/TMSA, which indicates the efficiency of metal distribution on the surface, is 84% in PtRu/CNF600NS but 74% in PtRu/CNF600 due to the presence of fewer agglomerates on the oxidized CNF.

The activity towards the oxidation of methanol for the CNF700-related catalysts is shown in Fig. 7. Notice that both the mass and specific activities of PtRu/CNF700 are higher than that of PtRu/CNF600 (Fig. 5). In a previous work we reported the favorable effect of crystallinity of CNF700 based catalyst when compared to catalysts based on CNFs synthesized at lower temperature [41]. With regard to functionalization, as previously pointed out, oxidation of CNFs results in different trends depending on the properties of the original carbon material. In the case of highly graphitic CNF700, the oxidation with nitric and sulfuric acid leads to a dramatic decrease of both mass and specific activity. This is in accordance with the CO oxidation shift to more positive potential of 80 mV (Fig. 4), which accompanied by a significant decrease of ECSA (40% lower), results in a poor activity for the electro-oxidation of methanol. On the other hand, the oxidation with nitric acid (PtRu/CNF700N) results in a better activity (both mass and specific) in the high current density region. This region is controlled by the diffusion of methanol to the active sites. As PtRu/CNF700 and PtRu/CNF700N present similar features, the better wettability of CNF700N may favor the oxidation at high current demand, where it is envisaged an improved accessibility of methanol to the active sites. The two best catalysts based on highly graphitic CNF700 were also analyzed by HRTEM, as shown in the representative images of Fig. 8. In this case, no significant differences were encountered within the catalysts structure and distribution of PtRu nanoparticles, confirming the physico-chemical properties analyzed in the previous discussion.

The effect of oxidizing CNFs is strongly related to their properties. High surface area CNF600 behaves like the well-studied carbon blacks [24-26, 30, 31]. A detrimental effect on the electrochemically active surface area comes with support oxidation. This is

1 only compensated by the presence of certain oxygen functionalities like lactones or
2 carbonyl whereas hydroxyl or carboxylic acid groups seem to hinder metal-support
3 interaction. On the other hand, highly graphitic carbon nanofibers present a good
4 catalytic activity with no necessary oxidizing treatment. Only at high current density,
5 where the diffusion of methanol is more hindered, the enhancement of surface polarity
6 might aid to obtain up to 20% higher activity.

7

4. Conclusions

Highly graphitic carbon nanofibers have been oxidized by two different acid treatments and studied as PtRu supports. Pristine CNFs are characterized by different surface areas (87 and $143 \text{ m}^2 \text{ g}^{-1}$) derived from the synthesis at two distinct temperatures. Acid treatments are effective to introduce oxygen groups. These produce hydrophilic CNFs with similar surface oxygen content of $2.8 \text{ wt\%}$ for the low surface CNF (CNF700) and $4.9 \text{ wt\%}$ for the high surface CNF (CNF600). Moreover with the oxidation both surface area and pore volume increase.

The microemulsion route used to synthesize PtRu nanoparticles leads to a particle size of about 2 nm . The CO electro-oxidation occurs at slightly more negative potential on the PtRu catalysts based on oxidized CNFs, which evidences a better metal-support interaction. The latter results in an improved catalytic activity toward the methanol electro-oxidation as evidenced from the polarization curves. Nonetheless, the effect of oxidation treatments is not independent of the CNF properties, which is a key parameter for a convenient support optimization. The optimum oxidized CNF support is thus obtained when balancing three factors: a sufficient electrochemical surface area, an improved metal-support interaction due to the effect of oxygen functionalities, and a better methanol diffusion through the catalyst pores due to the wettability of oxidized CNFs.

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Captions to figures

Figure 1. Dispersion of CNFs in water and n-heptane, 24 hours after sonication: pristine CNFs (left), CNFs treated with nitric acid (middle) and CNFs treated with nitric and sulfuric acids (right).

Figure 2. Oxygen groups concentration estimated by TPD experiments of (a) CNF600 related samples and (b) CNF700 related samples.

Figure 3. XRD patterns of the PtRu catalysts supported on pristine and oxidized CNFs.

Figure 4. CO oxidation stripping profiles of the different PtRu catalysts.

Figure 5. Polarization curves in the oxidation of 2M methanol at room temperature of catalysts supported on CNF600 related samples. (a) Mass activity; (b) Specific activity.

Figure 6. HRTEM representative images of (a) PtRu/CNF600 and (b) PtRu/CNF600NS.

Figure 7. Polarization curves in the oxidation of 2M methanol at room temperature of catalysts supported on CNF700 related samples. (a) Mass activity; (b) Specific activity.

Figure 8. HRTEM representative images of (a) PtRu/CNF700 and (b) PtRu/CNF700N.

1 **Table 1.** Properties of the pristine and the oxidized carbon nanofibers.

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Oxygen content (wt%)	Oxygen atoms surface density (at. nm^{-2})*
CNF600	143	0.58	2.6	6.9
CNF600N	178	0.77	4.9	10.8
CNF600NS	158	0.70	4.9	11.7
CNF700	87	0.30	1.5	6.4
CNF700N	93	0.29	2.8	11.2
CNF700NS	101	0.38	2.8	10.2

* Taking into account the surface area determined by BET equation.

2

3

Table 2. Properties of the PtRu catalysts supported on the pristine and on the oxidized CNFs.

	PtRu concentration (wt%)	PtRu crystal size (nm)	Pt:Ru atomic ratio	Lattice parameter (nm)	TMSA (m ² g ⁻¹)	ECSA (m ² g ⁻¹)
PtRu/CNF600	18	1.8	46:54	0.387	192	142
PtRu/CNF600N	23	1.8	52:48	0.385	207	103
PtRu/CNF600NS	18	2.3	47:53	0.389	132	111
PtRu/CNF700	21	1.9	47:53	0.388	172	113
PtRu/CNF700N	23	1.9	46:54	0.387	191	115
PtRu/CNF700NS	21	2.2	50:50	0.389	145	67

TMSA: theoretical mass surface area, calculated assuming spherical particles with an average diameter equal to PtRu crystal size and considering the density of the alloy [43, 46].

ECSA: electro-chemical surface area, determined by the electrochemical stripping of a CO monolayer.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8