1. Introduction

A direct methanol fuel cell (DMFC) based on a polymer electrolyte membrane is attractive for transport and portable applications [1,2]. The fuel is cheap, widely available and can be handled and distributed easily. It could be directly supplied to the anode, then, the hydrogen ions (protons) migrate through the electrolyte membrane to the cathode, electrons move through an external circuit, and thus, the oxygen reduction occurs at the cathode [1,3]. The steps and total reaction are:

Anode : CH₃OH(l) + H₂O(aq) → CO₂(g) + 6H⁺ + 6e⁻  \hspace{1cm} (1)

Cathode : (3/2)O₂(g) + 6H⁺ + 6e⁻ → 3H₂O(l) \hspace{1cm} (2)

Overall reaction : CH₃OH(l) + (3/2)O₂(g) → CO₂(g) + 2H₂O(l) \hspace{1cm} (3)

However, several problems still prohibit their practical uses, such as [2]: (i) the contamination of the cathode by migration of methanol through the electrolyte membrane, (ii) the high cost, (iii) the low electrocatalytic activity and the durability of the electrocatalysts impregnated and lastly (iv) the poisoning of the platinum electrocatalysts that are used for methanol oxidation in the anodic electrode.

Concerning the last point, the use of platinum–ruthenium alloy electrocatalysts can increase the current densities and to avoid the formation of carbon monoxide (CO) on the electrocatalysts (poisoning) [3]. Ru forms oxygenated species at lower potential than Pt and its presence in the electrocatalysts promotes oxidation of CO into CO₂ by the bifunctional mechanism and/or a “ligand effect” [4–8].

To effectively use these metals as electrocatalysts, they have to be well dispersed in small particles on a carbon support [9]. Although carbon is an excellent electronic conductor it is a very poor proton conductor. This is mainly because carbon is hydrophobic. However, on the carbon surface some hydrophilic groups like carboxyl, carboxyl, phenolic, quinone and lactone groups can be inserted [10]. These groups are normally introduced in the carbon by various oxidation treatments (e.g., nitric acid, hydrogen peroxide, hypochlorite and others) [10–12].

Several material supports, such as black carbon, mesoporous carbon, carbon nanofibers and carbon nanotubes have been researched and used for the manufacture of commercially available metal electrocatalysts, as reported in the literature [9,13–22]. However, the nature of the carbon structures...
modified with oxygen surface groups (functionalized carbon) and their interaction with the metal are not completely established.

The role of oxygenated groups on the formation of the dispersed Pt/C [16,22–24] and Pt–Ru/C [25–28] electrocatalysts has been investigated. Carino et al. synthesized Pt–Ru electrocatalysts by the impregnation method and subsequent alcohol reduction on both as received carbon and functionalized carbon with H2O2 [27] and HNO3 [28] solutions. The authors found that the Pt–Ru electrocatalysts supported on functionalized carbon are more homogeneously distributed than other studied materials and the electrochemical results showed higher activity for the Pt–Ru/C. This latter effect was attributed to better nanoparticles distribution/utilization on functionalized carbon.

In the same material support but using other reduction method (ethylene glycol), the effect of the carbon treatment on the stability of Pt/C electrocatalysts was investigated by Chen et al. [23]. The authors showed that after oxidative treatments with H2O2 and HNO3 solutions, the carbon became rich in oxygen-containing functional groups. They observed also that oxidative treatments of the carbon increased the interaction between the metal particle and the support, and that resulted in an improved electrochemical stability of Pt/C electrocatalysts. They showed that the Pt/C electrocatalyst prepared on the H2O2 solution treated carbon exhibited a higher stability than that prepared on the HNO3 solution treated carbon. In other reference, using colloidal method with a solution of NaHSO3, to obtain a colourless soluble intermediate of platinum and ruthenium, which was then oxidized with H2O2, Pt–Ru/C electrocatalysts showed also better CO tolerance and superior methanol oxidation [25].

In other type of carbon specimen (Korea Black Carbon), the effect of the chemical treatment on the electrochemical behaviour of Pt/C electrocatalysts was studied [24]. The authors showed that the size and the loading level of Pt metal clusters were dependent on the surface characteristics of the carbon and the electrocatalytic activity of the Pt electrocatalysts was enhanced when the black carbon was treated by basic or neutral agents, while the activity decayed for the acid-treated black carbon supported Pt [29].

The ordered mesoporous carbon (OMC) treated with HNO3 solution for preparation of Pt/C and Pt–Ru/C electrocatalysts for the carbon monoxide and methanol oxidation reactions was also investigated [17,18]. In this work, before deposition of the metals, the carbon was functionalized with the purpose to generate oxygenated groups for anchoring the Pt and Pt–Ru nanoparticles by the formic acid and borohydride reduction methods. The authors observed that CO stripping occurs at more negative potentials than for Vulcan XC-72R, and the best results for both methods were achieved with OMC functionalized with concentrated nitric acid for 0.5 h. Both Pt and Pt–Ru/OMC electrocatalysts presented better electrocatalytic activity towards CO and methanol oxidation.

In our previous studies [30], platinum electrocatalyst supported on functionalized carbon for methanol oxidation was prepared and characterized physically and electrochemically. The results showed that functionalized carbon using H2SO4 + HNO3 and HNO3 solutions contains more surface oxygenated functional groups than untreated carbon (Vulcan XC-72K), carbon treated with H2O2 solution or carbon thermally treated in helium atmosphere. In addition, the electrochemical results showed that the Pt electrocatalyst prepared on those functionalized carbons presented a significant improvement of the electrocatalytic activity due to the synergistic effect of carboxyl (–COOH), hydroxyl (–OH) and carbonyl (C=O) groups on functionalized carbon and Pt metal nanoparticles.

2. Experimental

2.1. Preparation of Pt–Ru electrocatalysts on functionalized carbon

Commercial carbon Vulcan XC-72R (Cabot), used as primary support material, was modified by chemical treatments (functionalized carbon) in order to create surface reactive groups. Then, the chemical treatment was done as follows: (i) H2O2 (30%, v/v) solution stirred at 60 °C for 10 h; (ii) 3 mol L−1 HNO3 solution and (iii) H2SO4+HNO3 (1:1) solution in both cases at 80 °C for 12 h, followed by washing in hot water [30]. Previously, the carbon was kept in contact with the chemicals in an ultrasonic bath for 40 min. In order to compare the results, the carbon was thermally treated in He atmosphere for 3 h in an oven at 300 °C.

The functionalized carbon supported Pt–Ru electrocatalyst was prepared by reduction with formic acid [18,30]. In this method, the formic acid solution was added to the functionalized carbon under sonication during 40 min. Afterwards, hexachloroplatinic acid (H2PtCl6·6H2O) and ruthenium chloride (RuCl3·3H2O) solutions, both from Johnson Matthey, were slowly added to obtain a good dispersion of Pt and Ru on the functionalized carbon support at temperature of 80 °C. Appropriate concentrations of the precursors were used to obtain a platinum–ruthenium loading of 30 wt.% on the different functionalized carbon materials.

2.2. Physical characterization

The atomic ratios of the Pt and Ru in the electrocatalysts were determined by the EDX technique in a FEG-SEM analytical microscope: JEO1 7001F with Oxford light elements EDS detector.

The content of platinum–ruthenium (metal) in the Pt–Ru/C electrocatalysts was determined by thermogravimetric analysis (TGA) carried out in a Lahysy-SETARAM equipment, under controlled atmosphere using O2 as reactive gas and a heating rate of 10 °C min−1. The weight loss and the heat flow were recorded for each sample from 25 to 1000 °C.

X-ray diffractograms of the electrocatalysts were obtained in a Rigaku D/MAX-B diffractometer operating with Cu Kα radiation (X-ray wavelength, λ = 0.15406 nm) generated at 40 kV and 35 mA and a graphite monochromator. Scans were done at 3° min−1 for 2θ values between 30° and 90°. In order to estimate the crystallite size of the Pt–Ru nanoparticles from XRD, the Scherrer’s equation was used [31]. For this purpose, the (220) peak of the Pt fcc structure around 2θ = 67.7° was selected. The lattice parameters were obtained by fitting the unit cell dimensions by the least squares method using the values of θ for all peaks assuming a Gaussian profile to subtract the background contributions [32]. In a first approach, the atomic fraction of Ru (xRu) in the Pt–Ru electrocatalysts was calculated by Vegard’s law with the expression:

$$x_{Ru} = \frac{a - a_0}{a - a_0 - a_1 - a_2}$$  \tag{4}

where a is the experimental lattice parameter; a0 is the lattice parameter assuming that all the ruthenium is alloyed, and a1 and a2 are the lattice parameter of supported platinum. This equation is known to explain the dependence of Pt–Ru lattice parameter of unsupported alloy on Ru content [33–35]. However, in the present case the low nominal Ru content of the sample and, thus, the small variations in the experimental lattice parameters, did not allow to obtain accurate values from Vegard’s expression. According to Antolini and Cardellini [34], if the dependence of the lattice parameter on Ru content is the same for supported and unsupported Pt, then the lattice constant of carbon supported Pt–Ru, a, results:

$$a = a_0 - kx_{Ru}$$  \tag{5}
Table 1 Structural characteristics, nominal atomic composition (EDX), analysis thermogravimetric (TGA), crystallite size ($d$), lattice parameter ($a$), atomic fraction in the alloy ($x_{Ru}$), degree of alloying ($x_{Ru}$) and electroactive area ($S_{a}$) of Pt-Ru/C alloy electrocatalysts.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ru (at.%)</th>
<th>TGA (wt.%)</th>
<th>$d$ (nm)</th>
<th>$x_{Ru}$ (%)</th>
<th>$S_{a}$ (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeTT</td>
<td>14</td>
<td>31</td>
<td>3.0</td>
<td>3.9187 ± 0.0007</td>
<td>3.5</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>13</td>
<td>31</td>
<td>3.3</td>
<td>3.9177 ± 0.00258</td>
<td>4.4</td>
</tr>
<tr>
<td>H₂SO₄ + HNO₃</td>
<td>10</td>
<td>28</td>
<td>4.3</td>
<td>3.9153 ± 0.00075</td>
<td>6.3</td>
</tr>
<tr>
<td>HNO₃</td>
<td>12</td>
<td>28</td>
<td>4.5</td>
<td>3.9165 ± 0.00057</td>
<td>5.3</td>
</tr>
</tbody>
</table>

where $a$ is the lattice parameter of pure carbon supported platinum, taken as 3.9231 Å, and $k = 0.124$ Å is a constant, obtained from data related to unsupported alloys [34].

Nanoparticle size and metal dispersion images of Pt–Ru/C electrocatalysts were obtained using a transmission electron microscope (TEM) Hitachi H8100. For such measurements, the samples were immersed in water and ultrasonically dispersed for 3 min. Then a drop of this suspension was deposited on a carbon grid and, after drying, the grid was ready for observation. Histograms of particles size supported on carbon were obtained using about 400 particles, excluding the agglomeration region. High resolution TEM (HR-TEM) experiments were carried out in the Synchrotron Light Brazilian Laboratory (LNLS, Campinas, SP, Brazil) using a microscope JEOL, JEM 3010, URP, operating at 300 kV and having a resolution of 0.17 nm.

X-ray photoelectron spectra (XPS) were acquired using the monochromatic Al Kα radiation ($hν = 1486.6$ eV) from a Kratos Analytical XSAM8000 equipment. Carbon powder samples as well as Pt–Ru/C electrocatalysts were mounted on the sample holder by pressing the powder against a double-faced tape. For details about the operation parameters, data treatment and charge accumulation correction see [30]. The sensitivity factors used for quantification purposes were: C 1s: 0.25; O 1s: 0.66; N 1s: 0.42; S 2p: 0.54; Pt 4f: 4.4 and Ru 3p₃/₂: 1.8.

2.3. Electrochemical characterization

A conventional one-compartment glass cell with a Luggin capillary was used in the electrochemical experiments. A large area graphite bar served as the counter electrode and a reversible hydrogen electrode (RHE) was used as the reference electrode. All potentials in the text are referenced to this electrode.

The working electrodes were composed by the electrocatalysts deposited as a thin layer over a pyrolytic graphite disk (5 mm diameter, 0.196 cm² geometric area) for conventional electrochemical studies. An aqueous suspension of 2.0 mg of the metal/C electrocatalyst was prepared by ultrasonically dispersing in 15 μL of NaFon® (5 wt.%, Aldrich) and 500 μL of pure water (Millipore).

An aliquot of the dispersed suspension was pipetted on the top of the graphite disk and dried. All the experiments were conducted at room temperature (22 ± 1 °C). After preparation, the electrode was immersed into deaerated 0.5 mol L⁻¹ H₂SO₄ (base electrolyte), prepared from Panreac reagent and water purified in a Milli-Q system. The electrolyte was saturated with pure nitrogen (Air Liquide).

To characterize the Pt–Ru/C electrocatalysts, cyclic voltammograms (CV) were recorded in the base (supporting) electrolyte solution between 0.05 and 0.80 V vs. RHE at a scan rate of 0.05 V s⁻¹. In the electrochemical experiments, the current values were normalized (specific activity) through division by the area of underpotential deposited copper (Cu_UPD) [36–39]. This was done using an aqueous electrolyte (0.5 mol L⁻¹ H₂SO₄; 0.5 mol L⁻¹ H₂SO₄ + 0.001 mol L⁻¹ CuSO₄) solution. Prior to each measurement, the electrolytes were purged with nitrogen.

The amount of platinum (mass activity) was calculated considering the mass of the Pt–Ru electrocatalyst present in the working electrode and the percentage of Pt (Table 1). Electrochemical studies were carried out using a Radiometer-Voltalab PGZ 100 apparatus.

Cyclic voltammograms in 0.5 mol L⁻¹ methanol (Fluka reagent) + 0.5 mol L⁻¹ H₂SO₄ solution to evaluate the performance of the electrocatalysts for the oxidation of methanol were also obtained.

Soon after, in a new solution with the same composition, current–time curves (chronoamperometry) were recorded at 0.60 V vs. RHE, in order to evaluate the performance of the electrocatalysts for the methanol oxidation.

Electrochemical impedance spectroscopy (EIS) measurements were carried out immediately after chronoamperometry by sweeping the frequency in the range of 10 kHz to 0.1 Hz. dc electrode potential was kept at different values in the range of 0.30–0.65 V vs. RHE and a 0.01 V ac signal was applied for the measurements. Spectra were treated with the Z-view Software (Scribner Associates, Inc.), using the adequate equivalent electric circuits. The EIS experiments were carried out using a Gamry, Reference 600 Potentiostat/Galvanostat/ZRA with a PC4 Controller Board.

3. Results and discussion

3.1. Characterization of the electrocatalysts

The EDX compositions of Pt–Ru electrocatalysts on support functionalized carbon are shown in Table 1. It can be seen that the average EDX compositions of electrocatalysts are near the nominal value (Pt:Ru; 85:15). In a previous paper [35] it was mentioned that it was not possible to anchor more than 25 at.% of Ru on Pt–Ru-supported materials using formic acid as reducing agent. One possible explanation for this is the formation of a complex between Ru and formic acid which partially prevents its anchoring on the carbon support.

TGA results in O₂ (reactive gas) controlled atmosphere are shown in Table 1. After thermal treatment at 1000 °C the carbon Pt–Ru samples keep a constant mass, around 28–31% of the original materials that corresponds to the metal load of the electrocatalysts. These values were used in the calculation of mass for each electrode.

X-ray diffraction spectra for the Pt–Ru electrocatalysts prepared on the carbon supports treated thermally and chemically modified are shown in Fig. 1. It is noticeable that the crystalline structure of the metal in the nanoparticles is apparent and all the XRD patterns clearly show the five main characteristic peaks of the face-centred cubic (fcc) crystalline Pt, namely at 39.7°, 46.3°, 67.7°, 81.5° and 85.9° assigned to planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), respectively.

Diffraction peaks of the Pt–Ru electrocatalysts on functionalized carbon treated with H₂SO₄ + HNO₃ and HNO₃ solutions are sharp indicating large crystallite size. The diffusion peak of the Pt (2 2 0) plane was selected to calculate the mean crystallite sizes for the electrocatalysts and the Scherrer equation was applied. The crystallite sizes obtained are given in Table 1. It can be observed that the size depends on chemical treatment of the carbon support. The mean crystallite size for the Pt–Ru/C electrocatalyst varies from 3.00 to 4.49 nm. It can be observed that the crystallite size for the Pt–Ru electrocatalysts on carbon heat treated under helium
atmosphere or treated with hydrogen peroxide is smaller than for Pt–Ru on functionalized carbon treated with mixed H₂SO₄ + HNO₃ and HNO₃ solutions, as shown in Table 1. These results agree with previous values found in the literature [7,16,40–42], namely those for reduction of the platinum–ruthenium electrocatalysts on carbon with acidic formic solution [40,41].

The five diffraction peaks in the Pt–Ru electrocatalyst on functionalized carbon (H₂SO₄ + HNO₃ and HNO₃) are modestly shifted to higher angles with respect to the corresponding peaks for the Pt–Ru on H₂O₂ and HeTT carbon (Fig. 1, inset), indicating a contraction of the lattice and Pt–Ru alloy formation due to the possible incorporation of Ru atoms. No peaks for metallic ruthenium and/or its oxides were observed, but their presence cannot be discarded because they may be present in a small amount or even in an amorphous form.

The lattice parameter values of Pt–Ru/C electrocatalysts are also summarized in Table 1. In all cases, the lattice parameters are smaller than those found for pure Pt (3.9231 Å), JCPDS card no. 04-0802, which indicates the presence of Ru substituting Pt in the lattice, leading to a smaller value and indicating the formation of the Pt–Ru alloy in the electrocatalyst [34,35,43–46]. Moreover, the values for Pt–Ru on functionalized carbon were smaller than for Pt–Ru/C (HeTT and H₂O₂) and show a tendency to decrease with increasing of the crystallite size, as show in Table 1. This behaviour was already seen for other alloys supported on carbon as Pt–Co, Pt–Cr and Pt–Ni electrocatalysts [17,47–49].

From the values of lattice parameters obtained by XRD, and according to Eq. (5) proposed by Antolini et al., the atomic fraction of Ru in the electrocatalyst supported on carbon was calculated (Table 1). Moreover, the percentage of alloyed Ru (Ru_AL) was calculated from the nominal Ru content of the sample (Ru/PT)nom and the atomic fraction in the alloy (xRu), according to the following equation [34]:

\[ \text{Ru}_{\text{AL}} = \frac{x_{\text{Ru}}}{(1 - x_{\text{Ru}})} \] (Ru/PT)nom

According to Table 1, the unfunctionalized carbon Pt–Ru electrocatalysts show a higher nominal atomic ruthenium content but only have in average about 25% of ruthenium alloyed with Pt, while for functionalized carbon supported electrocatalysts (H₂SO₄ + HNO₃ and HNO₃) a slight lower nominal Ru content was found but with a higher alloyed percentage (ca. 50% in average). Therefore, not all the ruthenium present in the Pt–Ru electrocatalysts is alloyed with platinum, as shown in Table 1.

Fig. 2 shows TEM images of the nanoparticles of platinum–ruthenium supported on HeTT treated carbon (Fig. 2, left) and HNO₃ functionalized carbon (Fig. 2, right). The corresponding particle size distribution histograms are also reported in Fig. 2 – below. As can be seen, TEM images present in both cases a homogeneous dispersion of Pt–Ru alloy on the carbon support. It is possible to observe in Fig. 2 that some areas of the electrocatalysts supported on carbon present agglomeration due to approximation of the smaller nanoparticles. The presence of functional groups derived from chemical oxidation treatment likely act as reactive site for the metal particles and would help in anchoring these particles on its surface [9].

High resolution TEM micrograph, obtained with a magnification of 800,000 for Pt–Ru on functionalized carbon treated with HNO₃ solution also is represented in Fig. 2. It is possible to see an image of a single particle where the crystalline (1 1 1) plane of the spherical Pt–Ru is evident [50]. The 0.2143 nm spacing which is attributed to the Pt–Ru (1 1 1) plane of the fcc lattice is indicated in figure. Compared to the nominal Pt (1 1 1) spacing of 0.226 nm [JCPDS 04-0802] [51], the spacing is lower indicating again smaller lattice parameter, consequently, the formation of Pt–Ru/C alloy electrocatalyst [50]. This result from HR-TEM analysis for the Pt–Ru/C agrees well with the XRD results.

Moreover, Pt–Ru electrocatalyst on functionalized carbon (HNO₃ solution) shows a particle size distribution broader than that of Pt–Ru on carbon thermally treated. For the Pt–Ru electrocatalysts prepared on carbon treated with HNO₃ solution, 60% of the particles have diameters between 3.5 and 4.5 nm with a mean particle size of 4.0 nm, while for the Pt–Ru electrocatalysts on HeTT carbon 60% of the particles have diameters between 2.5 and 3.5 nm with a mean particle size of 3.1 nm (Fig. 2). Therefore, the particle sizes obtained from the TEM images are compatible with the crystallite sizes calculated from the XRD (2 2 0) peak.

The four Pt–Ru/C electrocatalysts samples were characterized by XPS. Table 2 displays the peak binding energies, assignment and atomic percentages. XPS C 1s, O 1s, N 1s, S 2p, are very similar to those described in a preceding paper [30], both from the qualitative and quantitative point of view.

The most studied XPS region for ruthenium is Ru 3d. However, this region partly overlaps the C 1s region: Ru 3d₅/₂ presents binding energies ranging from 279 to 285 eV and, since the spin orbit splitting is 4.15 eV, Ru 3d₃/₂ has binding energies ranging from ~283 to ~289 eV fully overlapping the C 1s region. Moreover, when the substrate is mainly carbon, as it is the case in this work, the C 1s peak is so intense that completely masks even the component 3d₅/₂.

In this work, to study the oxidation state and the relative amount of ruthenium, the Ru 3p₃/₂ region was chosen. It was found in the literature that the ruthenium oxides are conductive [52] and, then the peaks were fitted with an asymmetrical pseudo-Voigt profile (Gaussian–Lorentzian product). The Excel Solver for minimizing the quadratic differences sum was used [53].

The profile is shown in Fig. 3 just for one of the Pt–Ru/C electrocatalysts samples, since it is qualitatively very similar in all the samples. In all the cases, the maximum was at 462.1 eV. This value is slightly smaller than the range existing in the literature for the RuO₂ oxide (462.7 ± 0.3 eV) [53]. This may be associated to the fact that an intimate mixture with platinum oxide exists changing the binding energy of Ru 3p. However, the binding energy for Pt⁴⁺ 4f keeps the same value, within the experimental error, obtained in the absence of ruthenium [30].

Due to the overall low nominal Ru compositions and, in particular, to the small atomic fraction of Ru in the Pt–Ru/C electrocatalyst, it was not possible to deconvolute the XPS spectra in order to separate the contributions of the metallic Ru and of ruthenium oxide. Even in the case of RuO₂, only a small amount was observed in the quantitative analysis by XPS technique. However, it was possible to plot this RuO₂ quantity (Table 2) as a function of the lattice parameter values from XRD data (Table 1), as shown in Fig. 4.
Fig. 2. TEM micrograph of Pt–Ru/C: (left) HeTT, (right) HNO₃ and (below) higher magnification of Pt–Ru/C, HNO₃. Histogram of Pt–Ru particles supported on HeTT and HNO₃ functionalized carbon.

Table 2
XPS binding energies and atomic percentages in Pt–Ru/C alloy electrocatalysts.

<table>
<thead>
<tr>
<th></th>
<th>HeTT</th>
<th>H₂O₂</th>
<th>HNO₃ + H₂SO₄</th>
<th>HNO₃</th>
<th>Assignment [65,66]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s 1</td>
<td>284.6 ± 0.1</td>
<td>70.1</td>
<td>71.6</td>
<td>65.0</td>
<td>65.9</td>
</tr>
<tr>
<td>C 1s 2</td>
<td>286.2 ± 0.1</td>
<td>11.6</td>
<td>10.5</td>
<td>11.1</td>
<td>10.1</td>
</tr>
<tr>
<td>C 1s 3</td>
<td>287.7 ± 0.2</td>
<td>4.4</td>
<td>4.5</td>
<td>4.4</td>
<td>4.7</td>
</tr>
<tr>
<td>C 1s 4</td>
<td>289.3 ± 0.1</td>
<td>2.9</td>
<td>3.0</td>
<td>3.8</td>
<td>3.6</td>
</tr>
<tr>
<td>C 1s 5</td>
<td>291.1 ± 0.3</td>
<td>2.4</td>
<td>2.5</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>O 1s 1</td>
<td>531.3 ± 0.4</td>
<td>2.2</td>
<td>2.5</td>
<td>7.6</td>
<td>5.4</td>
</tr>
<tr>
<td>O 1s 2</td>
<td>533.0 ± 0.6</td>
<td>2.5</td>
<td>2.2</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>O 1s 3</td>
<td>536.0 ± 0.1</td>
<td></td>
<td></td>
<td>0.4</td>
<td>H₂O</td>
</tr>
<tr>
<td>N 1s 1*</td>
<td>399.2 ± 0.2</td>
<td>0.38</td>
<td>0.35</td>
<td>0.35</td>
<td>0.30</td>
</tr>
<tr>
<td>S 2p½/2</td>
<td>163.9 ± 0.2</td>
<td>0.13</td>
<td>0.09</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Pt 4f½/2 1</td>
<td>165.1 ± 0.2</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Pt 4f½/2 1</td>
<td>71.7 ± 0.1</td>
<td>0.85</td>
<td>0.84</td>
<td>0.95</td>
<td>0.84</td>
</tr>
<tr>
<td>Pt 4f½/2 2</td>
<td>75.9 ± 0.1</td>
<td>0.64</td>
<td>0.63</td>
<td>0.71</td>
<td>0.63</td>
</tr>
<tr>
<td>Pt 4f½/2 2</td>
<td>72.8 ± 0.1</td>
<td>0.75</td>
<td>0.66</td>
<td>0.81</td>
<td>0.68</td>
</tr>
<tr>
<td>Pt 4f½/2 2</td>
<td>76.1 ± 0.1</td>
<td>0.56</td>
<td>0.49</td>
<td>0.61</td>
<td>0.51</td>
</tr>
<tr>
<td>Ru 3p½/2</td>
<td>462.1 ± 0.1</td>
<td>0.43</td>
<td>0.41</td>
<td>0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>Percentages</td>
<td>Total C</td>
<td>91.4</td>
<td>92.2</td>
<td>86.5</td>
<td>86.2</td>
</tr>
<tr>
<td></td>
<td>Total O</td>
<td>4.8</td>
<td>4.7</td>
<td>9.7</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Total Pt</td>
<td>2.81</td>
<td>2.61</td>
<td>3.08</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td>Total Ru</td>
<td>0.43</td>
<td>0.41</td>
<td>0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>Pt:Ru composition</td>
<td>86.6:13.4</td>
<td>86.6:13.5</td>
<td>92.9:7.1</td>
<td>88.6:11.4</td>
<td></td>
</tr>
</tbody>
</table>
It is observed that the smaller the lattice parameter the lower is the ruthenium oxide quantity present in the Pt–Ru alloy electrocatalysts on functionalized carbon. In fact, the Pt–Ru on functionalized carbon presents the larger Pt–Ru alloying degree, as observed in Table 1 [14,34,35].

3.2. Electrochemical studies of Pt–Ru/C electrocatalysts

Cyclic voltammograms (CV) performed in a single cell with H2 saturated base electrolyte, of Pt–Ru on carbon treated under helium atmosphere (HeTT) and carbon chemically treated are shown in Fig. 5. Due to preferential dissolution of ruthenium potentials were swept only between 0.05 and 0.8 V vs. RHE [54].

In the potential range 0.05–0.4 V (RHE) of the CV curves for the Pt–Ru electrocatalysts, the hydrogen adsorption/desorption peaks characteristics of a polycrystalline Pt are shown [30,38]. In the present work, the current densities were larger compared to platinum supported on carbon in our reference [30]. Moreover, the hydrogen peaks (Fig. 5) are a slightly more sharper for the Pt–Ru on functionalized carbons (H2SO4 + HNO3 and HNO3) than for carbons treated under helium atmosphere (HeTT) and with H2O2 solution due to some enrichment of Pt character (confirmed by the EDS spectrum) on those Pt–Ru on functionalized carbon.

In the potential range 0.4–0.8 V (RHE), the oxidation of the oxygen-containing surface groups present on carbon after the chemical treatment with acid solutions occur as it was already observed before [30]. These results imply that the surfaces of the functionalized carbon with acid solutions have been activated with the oxygen that was introduced into the carbon structure, as observed by Fourier transform infrared spectroscopy and XPS results [30].

As mentioned above, in the electrochemical experiments the current values for methanol oxidation were normalized to the CuUPD area [36–38]. The method to determine CuUPD electroactive areas (SCV) is associated to monolayer saturation of copper that is adsorbed on the Pt–Ru surface in the UPD region, as adopted by Green and Kucernak [37]. The SCV values are summarized in Table 1. It can be observed that electroactive areas for Pt–Ru electrocatalysts on carbons treated with HeTT and H2O2 solution are larger compared to those of Pt–Ru on functionalized carbons. As pointed out in the literature, monolayer adsorption of copper on the surface of Pt–Ru/C electrocatalysts is a ‘tempting’ assumption, which might introduce some error [55]. However, the result presented here is expected since the electroactivity area decrease with the particle sizes increase, as observed by XRD/TEM results. However, the presence of Nafion® that may block the contact of surface particles with the electrolyte cannot be discarded. In spite of this potential limitation the CuUPD process is suitable and it was found to be consistent and reproducible for determination of the Pt–Ru electroactive area under the present conditions [37,39].

The voltammograms for the methanol oxidation on the Pt–Ru/C electrocatalysts in 0.5 mol L−1 H2SO4 + 0.5 mol L−1 CH3OH solution at room temperature are shown in Fig. 6 where current densities are normalized with respect to (a) mass activity or to (b) specific activity (per area of CuUPD). The methanol-containing electrolyte was previously purged with nitrogen in order to avoid oxygen contamination. Again it should be observed that the Pt–Ru/C electrocatalysts supported on functionalized carbon (H2SO4 + HNO3 and HNO3) showed higher current densities for methanol...
oxidation compared to Pt–Ru/C electrocatalysts on carbon treated under helium atmosphere and with H₂O₂ solution. The difference between them is more pronounced when the current densities are normalized with respect to specific area, as showed in Fig. 6b. These results imply that both the oxygenated groups present in the functionalized carbon and the oxygen species due to dissociation of water on Pt–Ru/C electrocatalysts surface are responsible for the high current densities [30].

This result also indicates that the alloying degree can affect the electrocatalytic activity for methanol oxidation [56]. Higher alloy degree of Pt–Ru electrocatalyst on functionalized carbon can form surface oxygen containing species at slight lower potential in comparison with Pt–Ru electrocatalysts having lower alloying degree. In addition, the current density became higher for Pt–Ru electrocatalysts on functionalized carbon. The difference in current density can be explained by the surface composition of Pt–Ru/C electrocatalyst. In Pt–Ru electrocatalyst, which surface is formed with Pt metal and Ru oxide (site), intermediates of methanol dehydrogenation can adhere to the metal surface. This is in contrast with Pt–Ru electrocatalyst on unfunctionalized carbons richer in Ru oxide, as can be seen in the XPS results (Table 2).

The onset potential during the anodic scan for the methanol oxidation on Pt–Ru/C electrocatalysts was around 0.37 V vs. RHE. It was also observed that for Pt–Ru electrocatalysts supported on functionalized carbon the increase of current above 0.37 V has been ascribed to dissociation of water to form O-containing species. It is reasonable to admit that dissociation of water on Ru through the so-called bifunctional mechanism is easy [4–8,57]. It plays an important role in the promotion of methanol oxidation on Pt–Ru/C electrocatalysts compared to pure platinum where the corresponding process occurs above ~0.47 V vs. RHE. Namely, for Pt–Ru/C it is ±110 mV lower than for Pt/C [30].

Another way of interaction between the oxygenated groups on carbon and the methanol oxidation on the Pt–Ru electrocatalysts could be related with the solubility in water. Due to their nature, carbon materials, such as carbon nanofibers, mesoporous carbon and carbon nanotubes, are hydrophobic, so they exhibit low dispersibility in water and organic solvents [12,58,59]. However, chemically treated carbon shows hydrophilic behaviour. As seen in Fig. 7, the HNO₃ functionalized carbon shows better dispersibility in comparison with HeTT carbon [60]. This may be due to the higher interaction with water of the surface of Pt–Ru electrocatalysts supported on functionalized carbon, which should contribute more easily to the permeation of methanol and, consequently, to increase of the oxidation current, mainly at high potentials.

Fig. 8 shows the chronoamperometry plots at 0.60 V (RHE). Current density normalized with respect to (top) mass activity and (below) specific activity. The curves show a decreasing of current densities of the electrocatalysts with time in presence of methanol solution. It was also observed in the figure, that the Pt–Ru on carbon treated with HNO₃ solution presents the highest current densities for oxidation of methanol compared with the other three sup-

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**Fig. 5.** Cyclic voltammograms (thirty cycle) and stripping of copper for Pt–Ru/C electrocatalysts in 0.5 mol L⁻¹ H₂SO₄ and 0.5 mol L⁻¹ H₂SO₄ + 0.001 mol L⁻¹ CuSO₄ solution, respectively. The scan rate was 0.05 V s⁻¹.

**Fig. 6.** Part of cyclic voltammograms (fifth cycle) for Pt–Ru/C electrocatalysts in 0.5 mol L⁻¹ CH₃OH + 0.5 mol L⁻¹ H₂SO₄ solution at a scan rate of 0.05 V s⁻¹. Current density normalized with respect to (a) mass activity and (b) specific activity.
ports. The current densities normalized in terms of mass activity were of 0.7–0.9 mA cm\(^{-2}\) after 30 min. For the curves normalized with respect to specific activity (below), the current density after 30 min for Pt–Ru/C electrocatalysts functionalized with HNO\(_3\) solution reached a value of 0.18 mA cm\(^{-2}\) which is higher than those for Pt–Ru on carbon treated H\(_2\)SO\(_4\) + HNO\(_3\) solution (0.15 mA cm\(^{-2}\)), HeTT (0.12 mA cm\(^{-2}\)) and in H\(_2\)O\(_2\) solution (0.10 mA cm\(^{-2}\)). Then, the platinum–ruthenium on carbon that presented higher alloying degree and larger amount of oxygenated species on functionalized carbon (Pt–Ru/C, HNO\(_3\) solution) is better than Pt–Ru supported on carbon without or few oxygenated groups (HeTT and H\(_2\)O\(_2\) solution).

Electrochemical impedance spectra (EIS) for the Pt–Ru electrocatalysts on functionalized carbon at different potentials are given in Fig. 9. The EIS studies confirm the trend observed in cyclic voltammograms and chronoamperometry studies. In the impedance plots, a semicircle was observed for all carbon supported materials. For Pt–Ru supported on carbon treated in the different conditions, the charge transfer resistance (Rct) decreased, as the applied potential increases with an inductive loop at low frequencies for the samples at higher applied potentials (0.60 and 0.65 V vs. RHE). For Pt–Ru electrocatalysts on functionalized carbon with HNO\(_3\) solution the Rct is lower than for the other cases. Similar results have been reported for Pt and other materials for methanol and ethanol oxidation reactions [30,61–64], where the response at low potentials has been mainly associated with reactions of methanol dehydrogenation taking place at the interface between the Pt/C electrocatalyst and the aqueous electrolyte. With increasing potential, as the semicircle diameter and, thus, the Rct value decreases, the rate of methanol electrooxidation becomes higher. The inductive part of the plot was attributed to the bifunctional mechanism of electrooxidation of the methanol and, in particular, to the presence of adsorbed intermediates.

The methanol oxidation reaction should involve many parallel processes with reaction intermediates [4–8,57,61–64], according to the following reactions:

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt} - \text{CH}_2\text{OH} + \text{H}_\text{ads} \\
\text{Pt} - \text{CH}_3\text{OH} + \text{Pt} & \rightarrow \text{Pt} - \text{CHOH} + \text{H}_\text{ads} \\
\text{Pt} - \text{CHOH} + \text{Pt} & \rightarrow \text{Pt} - \text{COH} + \text{H}_\text{ads} \\
\text{Pt} - \text{COH} & \rightarrow \text{Pt} - \text{CO} + (3 - y)\text{Pt}, \quad 1 < y < 2 \\
\text{H}_\text{ads} & \rightarrow \text{H}^+ + e^- \\
\text{Pt} - \text{Ru} & + \text{H}_2\text{O} \text{(or oxygenated species)} \rightarrow \text{Pt} - \text{Ru} - (\text{OH})_\text{ads} \quad + \text{H}^+ + e^- \\
\text{Pt} - (\text{CO})_\text{ads} + \text{Ru} - (\text{OH})_\text{ads} & \rightarrow \text{Pt} - \text{Ru} + \text{CO} + \text{H}_\text{ads} + \text{H}^+ + e^- 
\end{align*}
\]

In this study, the impedance data were analyzed assuming two major equivalent circuits shown in Fig. 10. A serial association of two parallel networks was considered in both cases: one (RC) network, consisting of a constant-phase element (CPE\(_p\)) and a resistor (R\(_p\)), accounts for the high frequency impedance data, being attributed to the presence of a surface film; the other represents the processes occurring at the electrode/electrolyte interface [63,64], including a constant phase element (CPE\(_\text{dl}\)) for the double layer and the charge transfer resistance of the oxidation process (R\(_{\text{ct}}\)). Finally, R\(_\text{ads}\) is the solution resistance. In circuit of Fig. 10b, an additional RC network is included in series with the charge-transfer resistance, where R\(_\text{ads}\) and C\(_\text{ads}\) are related to adsorbed intermediates [61–64], including the oxygenated groups present on electrode surface. The first equivalent circuit (Fig. 10a) corresponds to the results obtained for potentials in the range 0.30–0.45 V vs. RHE. At these low potentials, the dehydrogenation of methanol involves the oxidation of H, according to Eqs. (7)–(11) and although the platinum active sites on platinum–ruthenium alloy are already covered with (CO)\(_{\text{ads}}\), the oxidation of CO\(_{\text{ads}}\) is still not taking place. On the other hand, ruthenium is covered with OH\(_{\text{ads}}\) coming from the dissociation of water and possibly oxygenated groups (coadsorption) present on carbon surface, specifically after the acid functionalization (Eq. (12)). The presence of these species was confirmed by FTIR as previously shown [30].

For higher potentials (above 0.45 V), the weakly bonded (CO)\(_{\text{ads}}\) groups suffer oxidation producing Pt active sites (Eq. (13)) where methanol molecules can be absorbed and react, and the equivalent circuit (Fig. 10b) must account for this feature through the presence of the (RC) network corresponding to the adsorbed intermediates and responsible for the inductive loop. Moreover, as mentioned above, the bifunctional mechanism, occurring for potentials higher than 0.47 V is faster than the processes observed at lower potentials, which may explain the decrease in the charge–transfer resistance as the potential increases (Fig. 11).

It is also important to note that the EIS results obtained for the Pt–Ru supported on functionalized carbon (HNO\(_3\)) are in agreement...
with the results obtained by cyclic voltammetry and chronamperometry, as the charge-transfer resistance is lower when compared with the other materials (Fig. 11), confirming a faster methanol oxidation process.

The hydroxyl ions are continuously regenerated by dissociation of water. In this case, the water breaking replaces the electrochemical regeneration process. The possibility of oxygenated groups is regenerated from degraded electrolyte solution can not to be also discarded. This is, the oxygenated groups on functionalized carbon at the starting of the reaction, if consumed in the earlier stages of the methanol oxidation reaction, can be continuously regenerated by secondary products increasing the electrocatalytic activity.

![Fig. 9. Complex-plane impedance plots for Pt–Ru/C electrocatalysts at 0.55, 0.60 and 0.65 V vs. RHE. The solid lines represent the fitted data to equivalent circuit in Fig. 10.](image)

![Fig. 10. Equivalent circuit for modelling the impedance plots (a) with and (b) without inductive behaviour.](image)

![Fig. 11. Relation between the reaction charge-transfer resistance and the potential on Pt–Ru/C electrocatalysts obtained by fitting the impedance data using the equivalent circuit.](image)
Therefore, the present discussion admits that the carbon functional groups provide oxygen species for methanol oxidation enhancing the electrocatalytic activity. Indeed, the electrochemical results are consistent with the presence of a high amount of those species on the carbon surface.

4. Conclusions

Platinum–ruthenium alloy electrocatalyst supported on carbon (Vulcan XC–72R) treated with H2SO4 + HNO3, HNO3 and H2O2 solution, and carbon thermally treated in helium atmosphere for methanol oxidation was prepared and characterized physically and electrochemically. The functionalized carbons using acid solutions contain more surface oxygenated functional groups than carbons treated with H2O2 solution or HeTT. In addition, uniform dispersion of Pt–Ru nanoparticles on the surface of carbons by acid formic reduction method was achieved. The electrocatalytic activity towards methanol oxidation was assessed by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. It was found that Pt–Ru alloy electrocatalysts on functionalized carbons increase the methanol oxidation rate when compared to Pt–Ru on unfunctionalized carbons. In addition, the XRD/HR-TEM analysis has confirmed the existence of a higher alloying degree for Pt–Ru electrocatalysts supported on functionalized carbon that is responsible for the superior electrocatalytic performance, as compared to electrocatalysts on unfunctionalized carbon. A mechanism is proposed, where OH species generated from dissociation of water and from oxygenated groups are adsorbed on Pt–Ru electrocatalysts, leading to the enhancement of the electrocatalytic activity of the methanol oxidation reaction.

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