This study presents results on PtRu electrocatalysts supported on both as received and H₂O₂ treated carbon black. The electrochemical properties and fuel cell performance of both home-made and commercial PtRu electrocatalysts were compared to PtRu supported on H₂O₂ treated carbon black. The PtRu nanoparticles were synthesized by the impregnation method and subsequent alcohol reduction. Transmission electron microscopy experiments revealed that the PtRu electrocatalysts supported on H₂O₂ treated carbon black are more homogeneously distributed than all other studied materials. Cyclic voltammetry electrocatalyst curves, PEMFC and DMFC experiments showed higher activity for the PtRu supported on H₂O₂ treated carbon black. Such an enhanced performance is related to a better particle distribution of the treated carbon black and can also be inferred by the better nanoparticles utilization that are outside from the carbon pore structure, which are more exposed and available to the reactants, enhancing the fuel cell performance and avoiding the waste of noble catalysts.

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1. Introduction

Hydrogen is currently the most efficient and commonly used fuel for polymer electrolyte membrane fuel cells (PEMFCs). However, the cost of its production and the problems associated with its storage and distribution make the application of this fuel a challenge [1,2]. Several studies investigate the utilization of methanol as a fuel to operate the PEMFC [3–6]. In this case the cell is referred as direct methanol fuel cell (DMFC). However, there are still drawbacks regarding the use of such a fuel. The electrochemical oxidation of methanol is a less efficient process if compared to electrochemical oxidation of hydrogen, because poisoning intermediates are formed, mainly carbon monoxide. In order to overcome the CO poisoning, an alternative to favor the carbon monoxide (CO) oxidation is the use of a second metal, e.g. Ru [7]. The added ruthenium is able to form oxygenated species, facilitating the oxidation of the COₐds to carbon dioxide (CO₂) at lower potentials than platinum. This phenomenon is called bi-functional mechanism and was first considered by Watanabe and Motoo [8]. Moreover, an electronic effect, which weakens the COₐds bond on the surface and results in a higher power density for DMFC application was proposed [9]. Carbon black is frequently used as the catalyst support because of its...
relative high stability in both acid and basic media, good electronic conductivity and high specific surface area. The support material has a strong influence on the properties of the catalysts, such as metal particle size, electrochemical active area, size distribution, and morphology, degree of alloying, dispersion, stability, life time, mass transport, catalyst layer electronic conductivity and metal nanoparticle stability during operation. Hence, the optimization of carbon supports is very important for future DMFC technology developments. The support should be well selected, with a suitable specific surface area, porosity, morphology, surface groups and electronic conductivity. Corrosion resistance is also a crucial parameter in order to make an active commercial catalyst. Most of these parameters are affected by the preparation of the carbon black. However, the most commonly applied industrial material, the Vulcan XC72, still exhibits insufficient properties for these purposes [10,11]. Consequently, the carbon support can be modified at the micro(nano)scopic level by chemical reactions in order to encapsulate, protect, control the hydrophobic/hydrophilic character, change the reactivity, enhance catalytic properties, create composites, change polarity, zeta potential [12–17].

Supported catalyst over an adequate carbon black will maximize its surface area and decrease the total amount of material employed. The aim of supporting catalysts over carbon materials is to increase the fraction metal particles (active sites) exposed to the reactants vs. the total amount of metal contained within the catalyst. In this sense, in order to improve the metallic dispersion, it would be advantageous to use large surface supports that display a high number of anchoring sites. If we consider that increasing the quantities of carbon surface functional groups, without decreasing its surface area, would increase the dispersion of the catalysts function. The fraction of small particles would be more active than large ones since their surface area is maximized. Ideal catalysts are based on well dispersed nanoparticles deposited onto carbon supports.

Oxidative treatments (nitric acid, ammonium persulfate, hydrogen peroxide) can improve the performance of the carbon supported activated catalysts [18,19]. The presence of oxygen-containing surface functional groups influences the surface behavior of carbons to a considerable extent [20,21]. As examples, the wet ability and adsorptive behavior of a carbon, as well as its catalytic and electrical properties, are influenced by the nature and extent of such surface groups. The varying role of oxygenated functionalities on the formation of the dispersed platinum has been established [22–25]. Usually, additional treatments of the carbon support are important to remove (not entirely) any surface contaminant. Such contaminants are known to decrease the surface area of the deposited catalysts and result in a bad nanoparticle distribution (non-homogeneous) [26]. A suitable necessary relationship between the amount of oxide surface groups in the carbon support and the amount of anchored metal is still a controversy. However, several studies of supported electrocatalysts over modified carbon black have shown better performances than the commercial ones [27].

In this study, treatment of the carbon black with hydrogen peroxide was carried out by introducing oxygenated groups and modifying its properties and hindering both agglomeration and loss of active surface.

2. Experimental

A commercial carbon black Vulcan XC72 (Cabot Co.) was used as a support. This carbon was treated with hydrogen peroxide 30 volumes at 60 °C, stirred for 24 h. The H₂O₂ treated carbon was filtered, washed until water reached pH neutral and dried at 110 °C overnight. The treated carbon was labeled as XC72-H₂O₂.

Carbon supported electrocatalysts were prepared through impregnation method and subsequent alcohol reduction [28,29]. A mixture of the desirable metallic ions solution was used as precursor, where the ions were reduced to their metal forms, using ethylene glycol (Merck) as solvent and reducing agent in the presence of the carbon support. PtRu/C (20 wt%, Pt:Ru atomic ratio of 1:1) was prepared using this procedure. H₃PtCl₆•6H₂O (Aldrich) and RuCl₃•2H₂O (Aldrich) were used as metal sources. High surface area carbon black Vulcan XC72 as delivered and H₂O₂ treated carbon black XC72-H₂O₂ were used as supports. In this procedure the salts were first added to the carbon support, followed by an ethylene glycol solution (75:25 – ethylene glycol:water). The system was ultrasonically treated for 15 min. It was then refluxed and heated at 160 °C for 1 h. The resulting powder was filtered, washed with ultra-pure water and dried in air at 110 °C overnight. PtRu/C (20 wt%, Pt:Ru atomic ratio of 1:1) commercial electrocatalysts from E-TEK were used for comparative purposes.

A NOVA 300 Brunauer–Emmet–Teller (BET) analyzer was used to determine the specific surface area of the carbons. Prior to measurement, the carbon samples were purged with pure nitrogen gas overnight at a temperature of 150 °C to remove any contaminants and moisture that could be in the carbon support.

A laser scattering (LS) LS230 small volume module plus-coulter was used to estimate the average particle size of the carbons in an aqeous colloidal system. Before measurement, 5 mg of the sample was dispersed in water and ultrasonically dispersed for at least 48 h.

A thermal analysis system STAR TGA/SDTA851 module from Mettler Toledo with star version SW 8.01 software was used for thermogravimetric analysis (TGA). The TGA measurements were carried out under a nitrogen atmosphere at 50 mL min⁻¹ and at a heating rate of 10 °C min⁻¹ from 50 to 600 °C.

The Pt:Ru atomic ratios of the electrocatalysts were obtained by using a Philips XL30 scanning electron microscope coupled to an EDAX DX-4 microanalyser with a 20 keV electron beam. The X-ray Diffraction (XRD) analyses were performed using a STOE STADI-P diffractometer with germanium monochromated Cu Kα radiation and position-sensitive detector with 40 apertures in transmission mode. The X-ray diffractograms were collected with a scan rate of 1 ° min⁻¹ and an incident wavelength of 1.5406 Å (KαCu). The average crystal size was estimated using the XRD data and the Scherrer equation [30].

The transmission electron microscopy (TEM) characterization was done using a JEOL JEM-1200EX microscope and the average particle size was calculated using the image tool software with one TEM micrograph for each catalyst.
Electrochemical studies of the electrocatalysts were carried out by using the thin porous coating technique [31,32]. An amount of 10 mg of the electrocatalysts was added to 20 g of water, (0.1 mg precision). The mixture was submitted to a Unique Maxi Clean 1400A 40 kHz ultrasound bath for 5 min, where 3 drops of a 6% PTFE (polytetrafluorethylene) water suspension were added. Again, the mixture was submitted to the ultrasound bath for 5 min, filtered and transferred to the working electrode support cavity (0.30 mm deep and area of 0.36 cm²). The quantity of the electrocatalysts in the working electrode was determined with a precision of 0.0001 g. By the cyclic voltammetry (CV) experiments, the current values (I) were expressed in Ampere and were normalized per gram of platinum (AgPt). The reference electrode was an RHE (reversible hydrogen electrode) and the counter electrode was a platinized Pt net with 4 cm². Electrochemical measurements were taken using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a computer by using the Microquimica Software. Cyclic voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂.

The evaluation of the 1.0 mol L⁻¹ methanol oxidation was performed at 25 °C in H₂SO₄ 0.5 mol L⁻¹. For comparative purposes, a commercial carbon supported Pt and PtRu catalysts from E-TEK (20 wt%; Pt:Ru molar ratio 1:1) was used.

For the membrane electrode assembly (MEA) preparation, water and a desired amount of the Nafion® ionomer solution were added to the catalyst powder. The system was emulsified with a Quimis® Dispersor Extratur Q-252-28 500W ultra-turrax system for 10 min and mechanically stirred at 90 °C, until the loss of water was sufficient, resulting in an optimum paste consistency to be applied by the screen printing technique. Nafion® 117 was used as membrane. The amount of catalytic material (metal loading) was controlled after the printing process. After screen printing, heat treatment for the prepared MEA was carried out at 135 °C for 30 min. The membrane was treated with nitric acid at 100 °C and then washed in hot ultrapure water. The MEA was placed in the single cell, using a gas diffusion layer Toray paper (TGP-H-060) in the anode and Sigracet 10 cc in the cathode. For the fuel cell experiments PEMFC, it was applied at an air flow of 1.5 mL min⁻¹ (100% excess and 100% humidity) and at a hydrogen flow of 0.8 mL min⁻¹. For DMFC, it was applied at an air flow of 1.5 mL min⁻¹ (100% excess and 100% humidity); and at a CH₃OH 3.5% flow of 15 mL min⁻¹. For all experiments the cell temperature was 70 °C. The platinum loading for the anode was 0.6 mgPt cm⁻² and for the cathode 1.0 mgPt cm⁻².

<table>
<thead>
<tr>
<th>Table 1 – LS particle size, BET and CV surface area analyses obtained for the carbons support</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Vulcan XC72</td>
</tr>
<tr>
<td>Vulcan XC72 + H₂O₂</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Carbon support characterization

3.1.1. BET surface area results

The results of the BET surface area are summarized in Table 1. The BET surface area of the support decreased 31% after hydrogen peroxide treatment. It indicates that the treatment changed the carbon structure. A small reduction in the surface area of carbons after oxidants treatment was already observed [33]. The authors showed that these oxidants could penetrate into the carbon structure, resulting in a carbon pore blockage. As previously showed [34–39], oxidation treatments produce a large amount of oxygenated groups (carboxylic, hydroxyl, lactones, etc.) in the carbon surface [40]. These groups are responsible for changing both the acid–basic character of the carbon black and the pore structure. The carbon black pore structure is relevant for the development of electrocatalysts support for DMFC application. It is undesirable that the presence of micropores in the catalyst support filled with metal catalysts, which are inaccessible for the reactants, resulting in the waste of noble catalysts. It is suggested that the oxygen-containing surface functional groups are fixed at the carbon micropores entrance and probably blocking the diffusion of species into them. The same restricted diffusion effect in the carbon black micropores after a chemical treatment with hydrogen peroxide was already observed [12,13,15,27,41]. In this study, the possible blocking of the micropores could be previously evidenced by the BET results (Table 1).

3.1.2. X-ray diffraction (XRD) results

XRD diffractograms of the studied carbon black are shown in Fig. 1a. The broad diffraction peaks occurring at 2θ ≈ 24° and 43° are related to (002) and (10-1) peaks, respectively, analyzed. The location and width of these two diffraction peaks indicate that the carbon black has a coke-like structure with disordered carbonaceous interlayers [42]. The occurrence of the same pore restriction in terms of XRD results can also be discussed [15]. The authors took into consideration the strain exerted by selected oxygen-containing surface functional groups on the graphene layers. It can be seen in Fig. 1a that, after the H₂O₂ treatment, there was a change in the position of the peaks. This effect was also observed by previous studies [12,13,15,27] and can be possibly attributed to the incorporation of the oxygenated groups in the carbon black structure.

3.1.3. Laser scattering (LS) results

Fig. 2 displays the carbon particle size distribution obtained by the laser scattering technique. A reduction of the carbon black average particle size can be seen in Table 1. With the H₂O₂ treatment process, the carbon black became much more hydrophilic, as also observed by other studies [12,13,15,27] and consequently, the dispersion of the carbon black in water was easily achieved. In this case, the particle size of the treated carbon black dispersed in water is much smaller than the one of untreated carbon black. Such a beneficial property of the electrocatalysts preparation, results in a much more homogeneous particle size distribution.

3.1.4. Cyclic voltammetric (CV) results

Cyclic voltammograms obtained for the carbon black and XC72-H₂O₂ are shown in Fig. 3. They illustrate the effects of
the treatment procedure and of the scan rate variation on the current–potential profiles. Fig. 4 presents the plots of the anodic capacitive current $I_c$ vs. $v$ ($v =$ sweep speed) obtained at $E =$ 0.8 V vs. RHE, which were used for the calculation of the double layer capacitances and of the electrochemical active areas. These measurements were carried out at 0.8 V vs. RHE, because in this range the CV current is essentially constant and related to double layer charging, since most surface redox active groups must be oxidized at lower potentials. The currents were divided by the mass of the sample in order to allow easy comparison of the results. Fig. 3 shows that the responses of the electrodes are those typically observed for several types of high surface area carbons [43-46]. From the voltammograms in Fig. 3b, it is observed that for the XC72-H$_2$O$_2$ sample, the increase of scan rate leads to a distortion on the current–potential relationship, which is not observed for non-treated carbon black. This phenomenon is related to the presence of ohmic drop effects introduced by distributed resistance inside the electrode layer. This fact is confirmed by the results displayed in Fig. 4, depicting the deviation of
linearity at higher scan rates of some plots of $i_c$ vs. $v$ for the XC72-H$_2$O$_2$.

### 3.2. PtRu/C electrocatalysts characterization

#### 3.2.1. Energy dispersive of X-ray (EDX) and X-ray diffraction (XRD) results

The EDX and the mean crystallite size results of the electrocatalysts are presented in Table 2. The Pt:Ru atomic ratios of the obtained electrocatalysts were very close to the nominal composition, calculated from the masses of the used metallic components. All the electrocatalysts showed diffraction peaks at about $2\theta = 40, 47, 67$ and $82^\circ$, Fig. 1b, characteristic of the face-centered cubic (fcc) structure of platinum and platinum alloys [47–49]. Carbon black Vulcan XC72 and its treated derivatives show the characteristic diffraction pattern of graphitic carbon ($2\theta = 25^\circ$), as discussed before. Moreover, neither peaks of separate tetragonal RuO$_2$ nor of hexagonal close-packed (hcp) Ru phases are found. The average crystallite size, $L$, may be estimated according to the Scherrer equation using the platinum peak (220) [30].

$$L = \frac{0.9\lambda_{\text{pol}}}{B_{(20)} \cos \phi_{\text{max}}}$$  

where the wavelength $\lambda_{\text{pol}}$ is 1.54056 Å, and the full width half maximum $B_{(20)}$ is in radians.

The XRD average crystallite size, when compared to the TEM average particle size, was very similar. The values of the average particle and crystallite size are presented in Table 2.

These results show that the alcohol reduction produces nanoparticles in the desirable size range for fuel cell applications. Oxidation of the support did lead to changes in the PtRu particle size, which was smaller compared to the PtRu supported onto non-treated material. Agglomeration of small PtRu nanoparticles was found to occur on all materials. Hence, the slight discrepancy between particles size as determined from TEM and XRD techniques.

#### 3.2.2. Transmission electron microscopy (TEM) results

The TEM images are presented in Fig. 5. Fig. 5b shows a very homogenous and uniform particle distribution for the PtRu/C-H$_2$O$_2$ material and Fig. 5a reveals a less homogeneous distribution for the PtRu/C Etek material. The TEM particle size histograms are presented in Fig. 6 and the average particle size in Table 2. The TEM results of particle size are in agreement with the XRD crystallite size results (Section 3.2.1). Looking at the histograms, the material supported in H$_2$O$_2$ treated carbon black is more homogenous than all other studied materials. Also compared to the commercial PtRu/C Etek material, the electrocatalysts supported in treated carbon black present a more homogeneous distribution. In the commercial material, particles in the average range of about 2–3 nm correspond to no more than 40% of the particles, while for the treated carbon black material, in the average range (3–5 nm), the particles correspond to about 70%.

#### 3.2.3. Electrochemical results

The cyclic voltamgrams of PtRu/C 20% performed in 0.5 mol L$^{-1}$ H$_2$SO$_4$ are shown in Fig. 7. The cyclic voltammograms show characteristics for typical PtRu/C catalysts [50]. For PtRu catalysts the hydrogen UPD (Underpotential desorption) region (0.075–0.35 V vs. RHE) is less defined, because the adsorption/desorption hydrogen peaks are not developed on Ru. Some differences are apparent between the materials.

In Fig. 8 are presented the cyclic voltammetry (anodic sweep, first cycle) for 1 mol L$^{-1}$ methanol oxidation in H$_2$SO$_4$ 0.5 mol L$^{-1}$. It was discounted from each anodic sweep its respective base voltammograms from Fig. 7. Fig. 8 shows a higher activity performance for the PtRu/C-H$_2$O$_2$ catalyst for methanol oxidation, when compared to the other investigated catalysts. This enhanced performance is explained by the better particle distribution in the PtRu/C-H$_2$O$_2$ also be inferred by the functional mechanism [51]. Due to the high affinity of Ru towards oxygen-containing species, sufficient amounts of OH ad are formed to support reasonable CO oxidation rates. This effect leads to higher activities for the overall methanol oxidation process on PtRu compared to Pt. This high activity on PtRu/C-H$_2$O$_2$ can be better explained and understood by the oxygenated groups on the carbon surface.

### Table 2 - Pt:Ru atomic ratio (EDX analysis), particles size (from DRX and TEM), for the prepared electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatlysts</th>
<th>Pt (wt.%)</th>
<th>Ru (wt.%)</th>
<th>Pt:Ru atomic ratio</th>
<th>Pt:Ru atomic ratio</th>
<th>Particle size (nm) XRD</th>
<th>Particle size (nm) TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu/XC72, 20%</td>
<td>13.8</td>
<td>6.8</td>
<td>1:1</td>
<td>1:1</td>
<td>4.3</td>
<td>4.7</td>
</tr>
<tr>
<td>PtRu/XC72-H$_2$O$_2$, 20%</td>
<td>13.8</td>
<td>6.8</td>
<td>1:1</td>
<td>1:1</td>
<td>3.4</td>
<td>3.7</td>
</tr>
<tr>
<td>PtRu/C E-TEK, 20%</td>
<td>13.8</td>
<td>6.8</td>
<td>1:1</td>
<td>1:1</td>
<td>1.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>
The PEMFC polarization curves and power density curves working with hydrogen and air are presented in Fig. 9. The cathode was set as standard, using commercial materials such as Pt/C HISPEC and Pt/C E-TEK.

The PtRu/C-H2O2 treated catalyst realized a maximum power density of 519 mW cm⁻² gmetal⁻¹, the PtRu/C catalyst without treatment: 305 mW cm⁻² gmetal⁻¹, PtRu/C E-TEK: 35 mW cm⁻² gmetal⁻¹ and PtRu/C E-TEK with the HISPEC cathode: 200 mW cm⁻² gmetal⁻¹. The performance of the treated material was much better if compared to the non-treated material and to commercial materials.

The DMFC polarization curves and power density curves working with methanol at approx. 1.1 mol L⁻¹ (3.5 wt%) and air are presented in Fig. 10. The PtRu/C-H2O2 treated catalyst realized a maximum power density of 65 mW cm⁻² gmetal⁻¹, the PtRu/C catalyst without treatment: 50 mW cm⁻² gmetal⁻¹, PtRu/C E-TEK: 35 mW cm⁻² gmetal⁻¹ and PtRu/C E-TEK with the HISPEC cathode: 16 mW cm⁻² gmetal⁻¹. The performance of the treated material was better compared to the non-treated material and compared to commercial materials.

Fig. 5 – TEM micrograph for PtRu/C Etek and PtRu/C-H2O2.

Fig. 6 – TEM particle size histograms for PtRu/C Etek and PtRu/C-H2O2.

Fig. 7 – Cyclic voltammograms in H₂SO₄ 0.5 mol L⁻¹, 10 mV s⁻¹ for the different electrocatalyst systems.
For PEMFC and DMFC applications, the better performance can be attributed to the better nanoparticles utilization that are outside from the carbon pore structure, that are now available for the reactants oxidation, enhancing the fuel cell performance.

For DMFC application, the oxygenated groups that are in the carbon surface structure may be also working in a bifunctional mechanism, enhancing the carbon monoxide oxidation for DMFC applications.

The fuel cell polarization curves were collected after 24 h of stabilization in a potentiostatic mode (Potential applied: 600 mV) for PEMFC and (Potential applied: 200 mV) for DMFC operations. But long-term experiments must be conducted in order to evaluate the stability of the system.

Summarizing, the results presented the following performance order: PtRu/C-H2O2 > PtRu/C > PtRu/C Etek with Etek cathode > PtRu/C Etek with Hispec cathode.

4. Conclusions

BET results showed that the specific surface area for the carbon support after treatment was reduced by 31%, which indicates that the treatment used produced significant changes in the carbon structure. It was suggested that the oxygen-containing surface functional groups are probably fixed at the entrance of the micropores, after the carbon treatment and probably blocking the diffusion of species into them. The XRD results showed that after the treatment, there was a change in the location of the peaks. This effect can be possibly attributed to the incorporation of the oxygenated groups in the carbon black [12,13,15,27]. For the XC72-H2O2 sample the CV currents increased after the treatment. This behavior is probably related to a breaking of hydrophobicity and/or to an increase in the amount of surface electrochemically active groups. The TEM images reveal a very homogeneous and uniform particle distribution for the PtRu/C-H2O2 material and a less homogeneous distribution for the PtRu/C material. For the PEMFC and DMFC results, an increase in the performance for the PtRu/C-H2O2 electrocatalyst system was observed. This can be explained due to the better nanoparticle distribution in the carbon support. The better performance can be also attributed to the better "nanoparticles utilization", electrocatalysts nanoparticles that are outside from the carbon pore structure, enhancing the fuel cell performance.

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