Characterization and performance evaluation of Pt-Ru electrocatalysts supported on different carbon materials for direct methanol fuel cells

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Abstract

The paper addresses the effect of the carbon support on the microstructure and performance of Pt-Ru-based anodes for direct methanol fuel cells (DMFC), based on the study of four electrodes with a carbon black functionalized with HNO₃, a mesoporous carbon (CMK-3), a physical mixture of TiO₂ and carbon black and a reference carbon thermally treated in helium atmosphere (HeTT). It is shown that CMK-3 hinders the growth of the electrocatalyst nanoparticles (2.7 nm) and improves their distribution on the support surface, whereas the oxidized surfaces of HNO₃ carbon and TiO₂+carbon lead to larger (4 - 4.5 nm), agglomerated particles, and the lowest electrochemical active areas (54 and 26 m² g⁻¹, in contrast with 90 m² g⁻¹ for CMK-3), as determined from CO stripping experiments. However, HNO₃ and TiO₂ are characterized by the lowest CO

oxidation potential (0.4 V vs. RHE), thus suggesting higher CO tolerance for these electrodes. Tests in DMFC configuration show that the three modified electrodes have clearly better performance than the reference HeTT. The highest power density attained with electrodes supported on carbon treated with HNO_3 ($65 \text{ mW cm}^{-2} / 300 \text{ mA cm}^{-2}$ at 90°C) and the equally interesting performance of the TiO_2 -based electrodes ($53 \text{ mW cm}^{-2} / 300 \text{ mA cm}^{-2}$), is a strong indication of the positive effect of the presence of oxygenated groups on the methanol oxidation reaction. The results are interpreted in order to identify separate microstructural (electrocatalyst particle size, porosity) and compositional (oxygenated surface groups, presence of oxide phase) effects on the electrode performance.

Keywords: *Pt-Ru electrocatalyst; functionalized carbon; mesoporous carbon (CMK-3), oxygenated groups; TiO_2 +carbon support, methanol oxidation; DMFC.*

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1. Introduction

Liquid-fed direct methanol fuel cells (DMFC) based on a Nafion[®] polymer electrolyte membrane (PEM) have attracted much interest due to the simplicity in system design, e.g. no requirement for hydrogen storage or a fuel reformer, or humidification of the hydrogen and O_2 /air [1]. However, DMFC have demonstrated much lower peak power density than PEM fuel cells running on

hydrogen because the methanol oxidation kinetics in the anode electrocatalyst is slow, leading to a relatively large loss in cell potential. Moreover, the cell potential is further lowered by methanol permeating through the membrane toward the cathode [1].

Platinum-ruthenium are the preferred electrocatalysts for DMFC since they are more tolerant to CO and hence better promoters of the methanol oxidation reaction (MOR) than pure platinum. Ruthenium, even when alloyed with Pt, forms oxygenated species at lower potentials than Pt alone, thus facilitating the oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) [2-3]. However, Pt accounts for about 85 at.% of the Pt-Ru alloy electrocatalysts and hence cost is still an issue.

In order to avoid the massive use of platinum, these electrocatalysts are dispersed in the form of nanoparticles (~3 nm) on the surface of carbon support that provides the necessary electronic conductivity to the electrode. Porous carbon black (Vulcan XC-72R) particles are the most common supports, but alternatives such as mesoporous carbon (CMK-3), carbon nanofibers or nanotubes (CNF, CNT) have demonstrated better properties when compared to conventional carbon black. CNTs are cylindrical mono-dimensional structures with high aspect ratio, low density and high specific surface area. Such morphological characteristics provide a strong mechanical support and a porous open structure that improves mechanical behaviour and the stability upon on/off cycles of the cells. Mesoporous carbons have an extremely high surface area

(often close to $1000 \text{ m}^2 \text{ g}^{-1}$) due to a fine and homogeneous porosity (ordered or disordered), which leads to a high and uniform dispersion of catalytic metals, and enhanced mass transfer for improved electrode performance [4-8]. Moreover, it has been shown that CO stripping on Pt and Pt-Ru electrocatalysts occurs at less positive potentials when these are supported on CMK-3 than on the conventional Vulcan XC-72R [8-9]. The same study reveals that the best results for methanol oxidation were obtained when the CMK-3 surface was functionalized by a treatment with concentrated HNO_3 solution. Similar conclusions were drawn for Pt and Pt-Ru electrocatalysts on conventional carbon supports [10-11]. The acidic treatment leads to the formation of oxygenated groups at the surface that extend the ability of the electrode to promote the CO oxidation.

In line with this idea that surface oxygenated groups on the support of the metal catalyst improve the CO tolerance, and ultimately also the methanol oxidation and oxygen reduction reactions in fuel cells [12], a variety of alternative electrode materials were designed by substituting part of the carbon support in conventional Pt-carbon electrodes by a metal oxide, such as CeO_2 , SnO_2 , and principally TiO_2 [13-21]. While the effects in terms of oxidation potential have been confirmed for all these oxides, their low electrical conductivity (comparatively to carbon black) is an obvious drawback. Processing is thus key to ensure a homogeneous distribution of the oxide particles in the electrode in order to maximize the potential benefits of the enhanced CO tolerance, without compromising the conductivity of the electrode. For example, the Pt-Ru

electrocatalysts on TiO_2 +carbon support prepared by the polygonal barrel-sputtering method have demonstrated a high electrocatalytic activity for methanol oxidation [15]. Enhanced performance has also been reported for Pt/C- CeO_2 electrocatalysts obtained by β -cyclodextrin carbonization [19], and for carbon riveted microcapsule Pt/MWCNTs- TiO_2 electrocatalyst prepared by in situ carbonized glucose with ultrahigh stability for proton exchange [20] and stable carbon riveted Pt/ TiO_2 -C electrocatalyst prepared by in situ carbonized glucose [21].

It should be noticed that some of these works are based solely on cyclic voltammograms, without confirmation by true DMFC tests. On the other hand, there is no direct comparison of the different approaches allowing a fair assessment of the advantages and disadvantages of each one. Here we propose such systematic study with the aim to compare the effects of different carbon supports (surface modified with acid treatment, a mesoporous carbon and a carbon+ TiO_2 composite) on the electrocatalyst microstructure and composition, and how these correlate with activity for the CO oxidation reaction, and with the anode performance in real direct methanol cells. We further explore the benefits of the presence of surface oxygenated groups by extending the study to the effect of temperature on the methanol oxidation. The goal is to identify the most relevant factors determining the electrode performance, and in particular, to try to separate microstructural (electrocatalyst particle size, porosity) from compositional (oxygenated surface groups, presence of oxide phase) effects, thus providing guidelines for the optimization of electrode.

2. Experimental

2.1. Preparation and characterization of carbon supports

Four different kinds of carbon supports were used in this study, three based on modifications of the commercial Vulcan XC-72R (Cabot) carbon and a fourth material with mesoporous structure. The first modification of the Vulcan XC-72R was a thermal treatment at 300 °C in helium atmosphere for 3 h (HeTT). In a second sample, the carbon was chemically treated in a 3 mol L⁻¹ HNO₃ solution at 80 °C for 12 h (HNO₃), followed by washing in hot water.

The third sample was a composite consisting of a mixture of HeTT and titania nanoparticles in a (1:1) wt. proportion (approximately 40:60 vol.). Here, titania is actually a mixture of nanocrystalline TiO₂ with ~2 wt. % (~5 vol. %) of single-walled carbon nanotubes (SWCNT). The TiO₂ nanopowders were prepared by a combination of sol-gel and hydrothermal methods. First, a SWCNT soot was dispersed in a 1 % aqueous solution of sodium dodecylbenzene sulfonate, as previously described [22]. Then, titanium isopropoxide was diluted in isopropanol and added into a mixture of isopropanol with the aqueous SWCNT dispersion. The resulting suspension was aged overnight, filtered, washed and again dispersed in an isopropanol water solution (1:1) and treated at 200 °C for 24 h in an autoclave. This final suspension was filtered, rinsed with distilled

water, and dried at 105 °C to finally obtain the TiO₂ nanoparticles, which were then carefully mixed with HeTT in an agate mortar.

The fourth support is a mesoporous carbon (CMK-3) obtained by nanocasting with a hexagonally ordered mesoporous silica hard template (SBA-15) [23]. The SBA-15 was first prepared by well established self-assembly methods using tetraethyl orthosilicate (TEOS, 98%, Aldrich) as silica source and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) copolymer (20EO:70PO:20EO, P-123, Aldrich) as the structure directing agent [6,7,24]. In this procedure, the TEOS was slowly added to an acid solution of the surfactant. This solution, after a 5 min sonication at room temperature, was stirred for 24 h at 35 °C and then kept in autoclave at 100 °C for another 24 h. The resulting precipitate was filtered, washed with deionized water, dried at 60 °C and, finally, fired at 540 °C in air during 6 h. The expected structural and microstructural features of the final SBA-15 product were analyzed by nitrogen sorption isotherms, X-ray diffraction (XRD), scanning and transmission electron microscopies (SEM and TEM) coupled to energy dispersive X-ray spectroscopy (EDS). The SBA-15 was then impregnated with a carbon source by adding an acidic solution of sucrose (Fluka), drying it first at 100 °C for 6 h and subsequently at 160 °C for another 6h. The impregnation was repeated to increase the sucrose loading. The final pyrolisation step was carried out at 1100°C in Argon atmosphere during 2 h. The SBA-15 template was subsequently removed by washing with a 2 mol L⁻¹ NaOH solution. The resulting CMK-3 particles retain the typical vermicular morphology of the silica

template, whereas the hexagonal symmetry of the carbon nanorods is the exact inverse replica of SBA-15.

Surface area and the porosity of the carbon supports were estimated from nitrogen adsorption isotherms at -196 °C with a Micromeritics® ASAP 2020. Micropore surface areas and volumes were calculated through the V-t plot method (carbon black standard), whereas the mesopore volume was evaluated by the Barret-Joyner-Halenda (BJH) method.

2.2. Preparation and characterization of Pt-Ru/C electrocatalysts

Pt-Ru electrocatalysts were prepared by reduction with formic acid on the previously prepared carbon supports (HeTT, HNO₃, TiO₂ and CMK-3) [21,25]. In this method, the formic acid solution was added to the carbon under sonication during 40 min. Subsequently, hexachloroplatinic acid (H₂PtCl₆.6H₂O) and ruthenium chloride (RuCl₃.3H₂O) solutions, both salts from Johnson Matthey, were slowly added to the carbon suspension at 80 °C. Appropriate concentrations of the precursor salts were used to obtain a Pt-Ru atomic ratio of 85:15 and a final metal content of 30 wt. %.

The atomic Pt:Ru ratio was determined by semi-quantitative energy dispersive spectroscopy (EDS) analysis in a scanning electron microscope JEOL 7001F equipped with EDS detector (Inca pentaFETx3, Oxford Instruments).

The total metal content in the Pt-Ru electrocatalysts was determined by thermogravimetric analysis carried out in a LabSys-SETARAM equipment from 25 to 1000 °C with a heating rate of 10 °C min⁻¹ and under a controlled atmosphere of 100 kPa of O₂.

Powder X-ray diffraction (XRD) patterns were obtained in a Rigaku D/MAX-B diffractometer operating with Cu K_{α1} radiation ($\lambda=0.15406$ nm) generated at 40 kV and 35 mA and a graphite monochromator. Scans were done at 3° min⁻¹ for 2 θ values between 20 and 90°. Scherrer's equation was used to estimate the crystallite size of the Pt-Ru nanoparticles from the (220) XRD peak of the Pt face centered cubic structure (fcc) at around 2 θ = 67.7° [26]. The lattice parameter was obtained by the whole pattern fitting by a least squares method and assuming a Gaussian peak profile to subtract the background contributions [27]. The atomic fraction of Ru (x_{Ru}) in the Pt-Ru alloy was calculated according to Vegard's law by the expression [28-30]:

$$a = a_c - K x_{Ru} \quad (1)$$

where a is the experimental lattice parameter (Table 2), a_c is the lattice parameter of pure platinum (taken as 3.9231 Å, JCPDS card No. 04-0802) and $k=0.124$ Å is a constant, obtained from data related to unsupported alloys [28].

The distribution of the Pt-Ru/C electrocatalyst particles on the carbon support was assessed by a transmission electron microscope 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 film (copper grid) and, after drying, the grid was ready for observation.

X-Ray Photoelectron Spectroscopy (XPS) measurements were performed using a Microlab 310 F (Thermo Electron – former VG Scientific) equipped with a Mg (non-monochromated) anode and a concentric hemispherical analyzer. The XPS spectra were collected under pressures below 5×10^{-9} mbar and using Al radiation (no-monochromator) in CAE mode = 30 eV, with an accelerating voltage of 15 kV. The quantification was performed by an algorithm based on the simplex optimization, as used in the Advantage[®] software, after fitting, the peaks to a Gaussian – Lorentzian product function.

2.3. Electrochemical characterization

In order to test the electrochemical performance, the various anodes were used in a single DMFC configuration fed with methanol solution/oxygen. The electrodes were prepared on a diffusion layer made with carbon powder (Vulcan XC-72R) and 15 % w/w PTFE and applied on a carbon cloth (PWB-3, Stackpole). The electrocatalysts were applied on top of this layer in the form of a homogeneous dispersion of the catalyst powder (Pt-Ru/C for the anodes, or 30 % Pt/C ETEK for the cathodes) with addition of approximately 10 mg of Nafion[®] (5.5 % solution and 920 mg mL⁻¹, Aldrich) in isopropanol (Merck) for both anode and cathode (electrocatalysts layer). All electrodes were made with a geometric area of 4.62 cm² with 1 mg Pt cm⁻². After drying, the electrodes

were hot pressed on both sides of a Nafion[®] 117 membrane at 125 °C and 50 kg cm⁻² for 2 min. The Nafion[®] membranes were previously cleaned with a 3 % solution of H₂O₂, washed and then treated with a 0.5 mol L⁻¹ H₂SO₄ solution. The cells were operated at 60 and 90 °C with 2 mol L⁻¹ methanol solution and flow of 2 mL min⁻¹ at the anode, and 1 and 3 atm oxygen at the cathode. The flow of oxygen of the 80 mL min⁻¹ humidified of the same cell temperature. The anode polarization current-potential curves and the corresponding power density plots were recorded in these conditions.

Cyclic voltammograms (CV) were recorded in a single DMFC operating with hydrogen and argon (White Martins). Argon was passed for 30 min to eliminate oxygen. The reversible hydrogen electrode (RHE) was used as auxiliary and reference electrode. The CV were recorded in the potential interval 0.075-0.90 V vs. RHE at room temperature and at 10 mV s⁻¹. The electroactive areas of the electrocatalysts were determined in a separate experiment through the oxidation of adsorbed CO [21-32]. After recording a CV in a N₂ purged system, CO was admitted to the cell and adsorbed at 0.075 V for 15 min. The excess CO was eliminated with N₂ and the stripping charges determined between 0.075 and 0.9 V vs. RHE by using a scan rate of 10 mV s⁻¹ with correction of the currents by the background. Cyclic voltammograms and current-time curves at 0.60 V vs. RHE in 0.5 mol L⁻¹ methanol (Fluka reagent) + 0.5 mol L⁻¹ H₂SO₄ solutions were recorded between 30 and 60 °C to evaluate the activation energy of the oxidation of methanol on the Pt-Ru electrocatalysts. All electrochemical measurements were carried out with a 1285A Solartron

Potentiostat connected to a personal computer and using the software CorrWare[®] for Windows (Solartron).

3. Results and Discussion

3.1. Physical characterization

The porosity characteristics of the different carbon supports are listed in Table 1. The thermal treatment of the pristine Vulcan XC-72R carbon leads to a slight decrease of the surface area (about 10 %) and pore volume (~15 %), suggesting that some level of sintering may occur, probably accompanied by partial oxidation of the carbon. The acid treatment induces much larger microstructural changes, with reductions in excess of 30 % for both the surface area and the pore volume. These important microstructural changes upon the treatment with strong oxidant agents such as HNO₃ are well known and are usually ascribed to the formation of large amounts of acidic groups (e.g. carboxyls and phenols) on the surface [33]. The addition of the TiO₂ nanoparticles to the HeTT carbon slightly reduces the overall micropore surface area due to the substitution of porous carbon by dense titania nanoparticles with high external surface area. Due to the mesoporosity, the surface area of the CMK-3 support (904 m² g⁻¹) is, as expected, much higher than that of the other supports.

Table 2 shows relevant compositional, structural and microstructural data obtained for the Pt-Ru nanoparticles on the different carbon supports. It can be seen that the average Pt:Ru atomic ratio measured by EDX is near the nominal composition (Pt:Ru = 85:15) for the four anodes. On the other hand, TGA results show a residue after firing at 1000 °C in pure oxygen corresponding to 28-31 % of the initial weight of the Pt-Ru electrocatalysts on functionalized carbon, HeTT and CMK-3-based anodes, which nearly corresponds to the nominal 30 wt. % electrocatalyst load. The result for the TiO₂+carbon anode is obviously higher (54 %) due to the inorganic titanium nanoparticles replacing 50 % of the carbon support, but it is somewhat lower than the nominal value (65 %). This difference suggests that some organics were still present in the initial TiO₂ nanoparticles. These experimental values were used to correct the mass of each electrode.

The powder XRD patterns for the Pt-Ru electrocatalysts prepared on the different carbon supports are shown in Figure 1. The five main reflections of the fcc crystalline platinum metal (JCPDS card No.: 4-0802) are apparent on the four patterns. As expected, the TiO₂ anatase (A) peaks can also be seen in the TiO₂ support (JCPDS card No.: 21-1272), as shown in Figure 1.

The average crystallite sizes estimated from these patterns are given in Table 2 and show that the carbon support has a substantial effect on the crystallization of the Pt-Ru electrocatalysts. Here, the effects may be related to the porosity characteristics of the support, to the chemical nature of the surface or to a

combination of the two. Assuming that the electrocatalyst nanoparticles are predominantly formed inside the pores, one expects a strong correlation between the pore volume and the crystallite size. The results indeed show the smallest crystallites for the CMK-3-supported anode, but the differences are minor if taking into account the huge differences in the pore volume and in particular in the volume of mesopores (Table 1), which are more restrictive of the crystallite growth. The other three anodes (HeTT, HNO₃ and TiO₂+carbon) have similar pore volumes and display a distinct trend of increasing crystallite size with increasing S_{BET} , which is closely related to the increase of the micropore surface area (S_{mic}) fraction of S_{BET} . These observations suggest that the microstructure and, in particular, the micropore surface area are the main factors determining the crystal growth. It is interesting to note that the approximately 40 vol % of TiO₂ has a small effect on the crystallite size of the electrocatalyst nanoparticles.

The lattice parameters, also summarized in Table 2, are smaller than for pure Pt (3.9231 Å, JCPDS card No. 04-0802), which indicates the presence of Ru substituting Pt in the lattice. However, the atomic fraction of Ru in the electrocatalysts estimated from the lattice parameters (Equation 1) are 3.5, 5.3, 9.2 and 14.7 % for HeTT, HNO₃, CMK-3 and TiO₂ supports, respectively. With the exception of TiO₂-containing material, these are surprisingly low values in comparison with the expected nominal composition (15 %). Since there is no evidence in the XRD pattern for the presence of pure Ru or RuO₂ reflections (XPS indicates less than 1 % RuO₂, see Table 2), such differences in lattice

parameter can only be explained by differences in the crystallinity of the samples, possibly linked with the existence of amorphous Ru. The fact that there is no correlation of the fraction of alloyed Ru with the crystallite size nor with porosity, may suggest that, contrary to the crystal growth (primarily influenced by porosity), the surface chemistry of the support plays a key role on the crystallization of the Pt-Ru alloy electrocatalysts. This is a subject for a systematic study in future work.

The Pt-Ru nanoparticles are homogeneously distributed on the carbon support, as shown by the TEM images in Figure 2. Some agglomeration of the smaller nanoparticles is also apparent, which is particularly noticeable in the TiO₂+carbon sample. These clusters are formed by a mixture of carbon, TiO₂ and Pt-Ru nanoparticles. Such clustering has been previously reported for carbon nanotubes/titanium dioxide nanocomposites prepared by sol–gel methods, but the distribution of the clusters was far from being homogenous [12].

A detailed XPS study was conducted in order to assess the compositional differences of the anodes. The C 1s, O 1s, Pt 4f, Ru 3p and Ti 2p XPS ionisations of the Pt-Ru electrocatalysts on CMK-3 and TiO₂+carbon supports are shown in Figure 3 and the binding energies and the atomic percentage for each signal are listed in Table 3.

The binding energies for C 1s and O 1s ionisations are very similar in both materials. The total oxygen relative intensities were 26.6 and 35.1 % for the CMK-3 and TiO₂+carbon supports, respectively. In both materials the percentages were higher than for the HNO₃ (10.8%) and HeTT (4.8%) supports from reference [18]. The presence of oxygenated groups is confirmed by high contents of oxygen present in the different supports in comparison to the HeTT reference (with a single thermal treatment). Another relevant feature is the predominance of functional C-O groups in the TiO₂ +carbon support. There is a clear inversion concerning the C-C and C-O contents. The former is higher for the CMK-3, while the second predominates on the TiO₂.

The binding energies for Pt 4f_{5/2} and Pt 4f_{4/2} ionisations are very similar in both materials and correspond to different oxidation states as illustrated in Figure 3b. The peak with greater relative intensity centered at 71.7 eV can be assigned to Pt in the metallic state (Pt⁰), in spite of the slight shift toward higher values with respect to the literature value of 71.2 eV [34]. In fact, a slight shift of the Pt⁰ peak to higher binding energies is a known effect of small particles [35].

The binding energies of the Pt 4f_{5/2} components centered at 74.7 eV and 76.1 eV can be attributed to the Pt²⁺ (PtO) and Pt⁴⁺ (PtO₂) species, respectively. Figure 3b shows the Ru 3p and Ti 2p ionisations. In this case the binding energy of both metals is similar, with Ru 3p appearing at 465.5 eV and being ascribed to RuO₂, whereas Ti 2p has the high intensity at 459.5 eV [36-37]. This means that the titanium in the oxide form (TiO₂) may also contribute to the

unexpectedly high relative intensity of RuO₂ (anhydrous) found for the titania-based catalyst, when compared to CMK-3 based catalyst (Table 3). In fact, while for the Pt-Ru/CMK-3 electrocatalyst only a small amount of the RuO₂ is estimated (0.2 %), this is about five times higher (1.07 %) for the Pt-Ru/TiO₂+carbon. The very low quantity of RuO₂ estimated by XPS is in good agreement with the XRD results suggesting that most of the ruthenium is metallic and alloyed with platinum. It is also interesting to note the XPS data showing that the oxygen content in the CMK-3 (26 %) and TiO₂+carbon (35 %) electrocatalysts is considerably higher than for the HeTT (about 10 %, according to ref. [11]). However, the actual composition of the Pt-Ru alloy is similar (according to XRD, Table 2). Important differences are however observed in the crystallite size and agglomeration condition, but, as noticed above, without any apparent correlation with the oxygen content.

3.2. Electrochemical studies

Figure 4 shows the CO stripping oxidation of a monolayer formed at 0.075 V by adsorption of CO for 15 min (first positive going sweep), as well as, the cyclic voltammogram (second cycle) in the base electrolyte for the clean surface of Pt-Ru/C electrocatalysts. The current density of CO stripping is similar for all electrodes (about 15 mA cm⁻²), with the exception of the titania-based electrocatalyst, where it occurs for much lower currents (about ~5 mA cm⁻²). It can also be seen that the onset of CO_{ads} oxidation is observed at 0.4 V vs. RHE for the electrocatalysts deposited on HNO₃ and TiO₂ carbon supports, whereas

it appears at slightly higher potential (about 0.45 V vs. RHE) for the CMK-3 and HeTT supports. While the overall activity for the CO oxidation is negatively affected in the HNO₃ and TiO₂ samples by the larger Pt-Ru particle size, the lower CO oxidation potential suggests an enhanced CO tolerance when using supports with oxidized groups. It is interesting to note that all voltammograms exhibit three peaks that overlap to various degrees, that may be ascribed to variations in the coverage of adsorbates (e.g. CO_{ads} and OH species) on Pt-Ru sites [33]. It has been proposed that the formation of oxygenated species in the ruthenium-containing alloys can promote the oxidation of CO to CO₂ by the bifunctional mechanism and/or a “ligand effect” [2,3,38-42].

The specific electrochemical active area (in MEA configuration), determined from the CO-stripping experiments, are listed in Table 2. The S_{cv} values vary from 87 m² g⁻¹ for the mesoporous carbon support down to 26 m² g⁻¹ for the titania-containing electrode. The most likely explanation for the smaller S_{cv} for PtRu-TiO₂/C when compared to the other electrodes is the noticeable agglomeration of the Pt-Ru nanoparticles, as shown in Figure 2, which obviously reduce the surface area available for CO adsorption. In fact, the TEM images for the other three electrodes (HeTT, HNO₃ and CMK-3) display well dispersed nanoparticles, showing an obvious contrast with the titania-containing electrode. Considering just these electrodes, it can be seen that the S_{cv} values increase with decreasing Pt crystallite size, as expected from the assumed increase in specific surface area (of these particles).

The polarization curves in single DMFC for the four anodes and the corresponding power densities are compared in Figure 5a), where the current density normalized by the geometric area. The performance of Pt-Ru on the acid functionalized carbon (HNO_3) in the DMFC is the highest of all tested supports in all potential ranges. The cell performance at 60 °C decreases in the sequence: $\text{HNO}_3 > \text{CMK-3} > \text{TiO}_2 \gg \text{HeTT}$, with the double $\gg$ indicating a larger difference. The clearly worse behaviour of HeTT anode may be due to activation polarization losses, as suggested by the steep decrease of the voltage for low current density. In fact, the onset of the ohmic part of the polarization curve for this sample can hardly be perceived. On the contrary, the linear part of the curves for the three best cells are clearly apparent and suggest similar ohmic resistances. As expected, the current density increases with increasing temperature and increasing the oxygen activity at the cathode due to a faster reaction rate or the improvement of the mass transport, but the sequence is slightly different in these conditions, with a much improved performance of the HeTT cell, and the CMK-3 and TiO_2 –based cells displaying essentially the same performance. Under these more favourable electrode kinetics, the linear part of the I-V curves is observed for all samples, and the smaller slope with respect to the low temperature data, confirms the expected decrease of the ohmic resistance. The better performance at low temperature of the cells with modified anodes thus suggests a strongly enhanced reaction rate, or a different rate limiting step.

Figure 5b shows the corresponding power density curves for both test conditions (60 °C / 1 atm O₂ and 90 °C / 3 atm O₂). The values of power density found in this work are two times larger if compared to Pt electrocatalysts [45]. The differences in performance between the four cells (particularly with respect to the HeTT-based cell) tend to decrease with the simultaneous increase of temperature and oxygen pressure at the cathode. Since the cathodes are identical for all cells, it is reasonable to assume that the differences are essentially related to the anode behaviour and that the enhanced low temperature performance of the cells with modified anodes (by chemically modified or increased surface area) is indeed related to these modifications.

A possible explanation of the better performance of Pt-Ru/C on TiO₂+carbon compared to HeTT in direct methanol fuel cells can be the strong electronic interaction between the Pt-Ru nanoparticles and the TiO₂+carbon support that might weaken the chemisorption strength of CO_{ads} on the Pt-Ru electrocatalyst, enhancing the CO electrooxidation activity [43-45]. On the other hand, it is known that increasing the amount of alloyed ruthenium on Pt-Ru enhances the electrocatalytic activity for methanol oxidation due to an easier chemisorption of labile oxygen species (and CO oxidation) [46,47]. The higher fraction of alloyed Ru on the CMK-3 and the HNO₃-functionalized carbon anodes could thus allow the formation of species containing surface oxygen at slightly lower potentials than the reference Pt-Ru/HeTT anode (which is expected to have a lower content of Ru in the alloy). In the case of the CMK-3-based electrodes, there is also the likely benefit from the extraordinary high surface area of the

mesoporous carbon, in principle allowing a more efficient distribution of the reactants.

In order to gain further insight of the possible effect of the presence of oxygenated groups on the methanol oxidation reaction, a more detailed study of the effect of temperature was carried out by cyclic voltammetry in methanol solution. Figure 6 shows the cyclic voltammograms (fifth cycle) for Pt-Ru electrocatalysts on HeTT and HNO₃ carbon supports. The current density was normalized with respect to specific electrochemical active area (see reference 18). It is possible to see that when increasing the temperature from 30 to 60°C, the electrocatalytic activity is enhanced and, again, the Pt-Ru supported on functionalized carbon presents higher current densities compared to unfunctionalized carbon in agreement with previous half-cell studies [20,48] and the above data.

The results (not presented) of chronoamperometry at 0.5 V (RHE) and 30 min were used to determine the activation energy for the methanol oxidation on Pt-Ru, as shown in Figure 7. The values obtained are similar for both electrodes (42 and 47 kJ mol⁻¹ for HNO₃ and HeTT, respectively) and are in good agreement with literature data for Pt-Ru electrocatalysts supported on highly ordered pyrolytic graphite support [49] or on fishbone-type carbon nanotubes [50]. This apparent insensitivity of the activation energy with regard to the carbon support suggests a similar rate-limiting mechanism for all electrodes, in agreement with the polarization results (Figure 5a). One possible explanation

for this behaviour can be found in the possible roles of other ionic species in the methanol oxidation. For example, the carbonyl, hydroxyl or carboxyl groups present on oxidized carbon supports may also play an active role on methanol oxidation. These functional groups could transform into $-\text{COOH}^{2+}$, $-\text{OH}^{2+}$ or $-\text{C}=\text{OH}^+$ by reaction with H^+ in the electrolyte solution thus contributing to:

thus contributing to the surface polarity and also to the heat of immersion of the carbon black by interaction with water [51].

4. Conclusions

Four Pt-Ru electrocatalysts for DMFCs were prepared using different carbon supports, including a reference carbon black submitted to a simple thermal treatment (HeTT), the same carbon chemically treated with in a HNO_3 solution (HNO_3), a mesoporous carbon (CMK-3) and finally a mixture of the HeTT and titania nanoparticles. These electrodes were extensively characterized by a range of physico-chemical and electrochemical methods. The following conclusions can be drawn from this investigation:

- The carbon support has a significant impact on the electrocatalyst particle size and state of agglomeration. Differences on the Pt:Ru ratio were minor between the four electrodes. Titania-containing materials tend to have highly

agglomerated particles and of larger size than in the reference material. On the contrary, mesoporous carbon ensures the highest level of dispersion of the electrocatalyst particles in the support surface and is very effective in restricting the crystal growth. The functionalized carbon supports contain a much larger fraction of surface oxygenated groups than the reference HeTT; this however, does not correlate with any of the characterized microstructural features.

- Cyclic voltammetry and carbon monoxide (CO) stripping experiments showed a strong correlation between the size and agglomeration of the electrocatalyst, with smaller, well dispersed particles yielding the highest specific electrochemically active area. The HNO₃ and TiO₂+carbon supports are able to promote CO oxidation at a lower potential than CMK-3 and HeTT, whereas the low surface area of the TiO₂ leads to the lowest activity for CO oxidation of the four tested electrodes. This comparatively poor performance is not confirmed in DMFC testes, where this electrode displays the second highest electrocatalytic activity towards methanol oxidation (56 mW cm⁻² / 300 mA cm⁻² at 90 °C). The cell with the acid-treated carbon electrodes has the best performance at 63 mW cm⁻² in the same conditions, which is an excellent value.

- The results indicate that a suitable combination of microstructure and composition is necessary to achieve the best performance since the proposed modifications often have opposite effects. For example, in order to fully benefit from the potentially better CO and methanol oxidation activities of supports with high surface oxygen contents such as the titania-containing electrodes, it is important to prevent the agglomeration or the growth of the catalyst particles.

This work suggest that this may be achieved by a combination of the oxide with a mesoporous carbon with a surface acidic treatment.

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Figure captions

Figure 1. Powder XRD diffractograms of the Pt-Ru electrocatalysts on different carbon supports.

Figure 2. TEM micrographs of the Pt-Ru electrocatalysts on different carbon supports.

Figure 3. (a) C 1s and O 1s and (b) Pt 4f and Ru 3p and Ti 2p XPS spectra for Pt-Ru electrocatalysts on CMK-3 and TiO₂ carbon supports.

Figure 4. Cyclic voltammograms for Pt-Ru electrocatalysts on carbon supports (dashed lines) and stripping scans for CO adsorbed (solid lines) at a scan rate of 0.01 V s⁻¹.

Figure 5. a) Polarization curves and b) power density curves for a single DMFC with anodes of Pt-Ru on various carbon supports (cathode is a conventional Pt/C) measured at 60 °C / 1 atm O₂ pressure (closed symbols) and 90 °C / 3 atm O₂ pressure (open symbols) using a 2 mol L⁻¹ methanol solution as fuel.

Figure 6. Cyclic voltammograms (fifth cycle) at different temperatures for the Pt-Ru electrocatalysts deposited on HNO₃ functionalized carbon (dashed) and HeTT (solid) in 0.5 mol L⁻¹ CH₃OH + 0.5 mol L⁻¹ H₂SO₄ solution. The scan rate is 0.05 V s⁻¹.

Figure 7. Arrhenius plots of the current density at 0.5 V vs. RHE for Pt-Ru electrocatalysts on functionalized carbon with HNO₃ solution (open symbols) and carbon treated in He atmosphere supports (solid symbols).

Table 1. Porosity characteristics of the supports: specific surface area (S_{BET}), micropore surface area (S_{mic}), external surface area (S_{ext}), micropore volume (V_{mic}) and mesopore volume (V_{mes}).

Support	S_{BET}	S_{mic}	S_{ext}	V_{mic}	V_{mes}
	($\text{m}^2 \text{g}^{-1}$)	($\text{m}^2 \text{g}^{-1}$)	($\text{m}^2 \text{g}^{-1}$)	(mL g^{-1})	(mL g^{-1})
Vulcan (as-received)	260	108	152	0.05	0.29
HeTT	232	98	134	0.04	0.25
HNO₃	167	76	91	0.03	0.20
TiO₂	212	66	146	0.03	0.31
CMK-3	904	144	760	0.07	1.26

Table 2. Summary of the structural characteristics, platinum and ruthenium nominal atomic compositions by EDX (Pt and Ru), thermogravimetric analysis (TGA), crystallite size (d), lattice parameter (a) and CO electroactive area in MEA's (S_{cv}) of Pt-Ru/C electrocatalysts.

Support	Pt (at. %)	Ru (at. %)	TGA (wt. %)	d (nm)	a (Å)	S_{cv} (m² g⁻¹)
HeTT	86	14	31	3.0	3.9187	70
HNO₃	88	12	28	4.5	3.9165	54
TiO₂	86	14	54	4.0	3.9049	26
CMK-3	83	17	30	2.7	3.9117	87

Table 3. XPS binding energies and atomic percentages in Pt-Ru alloy electrocatalysts on CMK-3 and TiO₂+carbon supports.

	Binding Energy (eV)	CMK-3 relative intensity / %	TiO ₂ relative intensity / %	Assignment
C 1s 1	284.3	31.1	44.1	sp ² and sp ³ C-C,
C 1s 2	285.9	21.5	11.6	C-O
C 1s 3	287.3	14.4	4.30	C=O
C 1s 4	289.8	3.8	-	O-C=O
O 1s 1	531.4	3.3	8.0	Metal oxide + C=O
O 1s 2	533.2	18.7	22.8	C-O
O 1s 3	535.5	4.60	4.30	H ₂ O
Pt 4f_{7/2}	71.7	1.37	0.46	Pt
Pt 4f_{5/2}	76.1	1.03	0.25	Pt-O + Pt(OH) ₂
Ti 2p_{3/2}	459.3	-	1.63	TiO ₂
Ru 3p_{3/2}	465.0	0.20	1.07	RuO ₂ (anhydrous)
N 1s 1	395.7	-	1.49	amine
Percentages	Total C	70.8	60.0	
	Total O	26.6	35.1	
	Total Pt	2.40	0.71	
	Total Ru	0.20	2.70

Figure 1.

Figure 2.

3a)

3b)

Figure 3.

Figure 4.

a)

b)

Figure 5.

Figure 6.

Figure 7.