The effect of carbon nanofiber properties as support for PtRu nanoparticles on the electrooxidation of alcohols

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Abstract

Carbon nanofibers (CNFs) characterized by different mean diameter, BET surface area, pore volume and crystallinity were prepared and studied as supports for PtRu nanoparticles to investigate the influence of the support characteristics on the performance for the electrooxidation of alcohols. A modified microemulsion procedure was used to deposit the metal nanoparticles minimizing the effect of the support on the catalyst particle size.

PtRu nanoparticles of ca. 2 nm size were obtained despite the relatively low surface area of CNFs (95-185 m² g⁻¹) with a good distribution on the surface as confirmed by TEM micrographs and the high values of the electrochemically active surface areas (110-140 m² g⁻¹) determined by electrochemical CO stripping. The most appropriate PtRu dispersion was achieved for those carbon nanofibers showing the best compromise in terms of BET surface area and graphicity.

A cross-analysis of the supports physico-chemical properties, ECSA and mass activity for the methanol and ethanol oxidation reactions suggests that both PtRu dispersion and electronic properties as determined by the effect of CNF crystallinity play a significant role in determining the electrocatalytic activity. Different electrocatalytic activity behavior with CNF properties were found for methanol and ethanol. Methanol oxidation is favored using highly crystalline CNFs as PtRu support, despite their low surface area, whereas ethanol oxidation is hindered by diffusional problems when using highly graphitic CNFs due to their low pore volume, so the activity is maximized supporting PtRu on CNFs with a more accessible porosity.

Keywords: PtRu catalyst, carbon nanofibers, fuel cell, methanol, ethanol
1. Introduction

Energy distribution in low molecular weight alcohols, such as methanol or ethanol, is an attractive option in terms of sustainability and low environmental impact. For their direct conversion into electrical energy, direct alcohol fuel cells (DAFC) are regarded as a very interesting choice in terms of efficiency for portable devices [1-7]. Methanol and ethanol are the most appropriate alcohols in DAFC. Methanol has been widely considered because it is the smallest alcohol molecule and its electrochemical oxidation is relatively fast if compared to alcohols with a higher number of carbon atoms [8]. The use of ethanol instead of methanol has gained interest as it has a higher energy density (about 30% higher), ethanol itself and its oxidation products are less toxic, the cross-over effect is less detrimental and can be easily produced from biomass (a renewable source) [9, 10]. Unfortunately, the kinetics of ethanol oxidation reaction (EOR) is even slower than that of methanol oxidation reaction (MOR), where the challenge is the cleavage of C-C bond at low temperature. The improvement of the oxidation kinetics in the DAFC is one of the targets for the implementation of this technology in portable devices, because it would allow increasing the noble metal utilization and reducing the overall cost [7, 8]. The current highly performance solid electrolytes based in sulfonated polymers entails the electrooxidation of alcohols in acidic media, which needs the use of expensive noble metallic alloys based on platinum, being the pair platinum-ruthenium widely recognized [11-14].

One of the possible strategies is the optimization of the carbon support. Carbon supports (commonly carbon blacks) are used to maximize the noble metal utilization and reduce costs. The catalyst support is not a mere inert material to disperse the active phase and maximize the metal utilization, but it can also interact electronically with the metal and modify its intrinsic activity [15, 16]. During the last decade, carbon nanofibers (CNFs) have been studied as catalytic supports giving place to improved performance in the oxidation of methanol compared to the classical carbon blacks [17, 18]. This improved catalytic activity has been attributed to their good compromise between the external porosity and structural features, derived from the nanosized diameter of the filaments, the orientation of the graphenes with respect to the fiber axis, as well as the high ratio of edge atoms to basal atoms on the surface [19]. Their peculiar filamentous structure leads to a negligible micropore content, which favors mass
transport through the electrocatalytic layers [20]. Additionally, the well-developed graphite-like structure of CNF can provide a high conductivity and a high resistance to corrosion. The edge-rich surface is expected to provide suitable sites for the stabilization of catalyst nanoparticles. Furthermore, regular arrangement of such sites can provide a more uniform distribution of catalyst particles on the surface [21]. Therefore, the high content of the edge surface is expected to interact with the nanosized metal and to contribute to the stabilization of the nanoparticles on the surface.

Carbon nanofibers properties can also be adjusted to favor certain processes. In a previous work we observed that a high graphitization degree of functionalized CNFs favors the electrooxidation of methanol on Pt electrocatalysts [19]. In a recent work [22] the effect of support properties has been studied for the reduction of oxygen (cathodic half-reaction) in platinum electrocatalysts, concluding that an optimum activity is found when using carbon nanofibers with a compromise between properties. CNFs also show an enhanced behavior in terms of activity and stabilization of metal particles when compared to the commercial carbon black. Nevertheless, the reaction mechanism is different for every electrocatalytic process and the results are not extrapolable to the anodic process, as we will demonstrate along this paper. This work is aimed to analyze the effect of different characteristics (diameter, graphitization, etc.) of as-grown herringbone type carbon nanofibers on the electrochemical oxidation of methanol and ethanol at low temperature.
2. Experimental details

2.1 Synthesis of PtRu nanoparticles and deposition on carbon nanofibers

In-house synthesized carbon nanofibers with diverse physical properties were used to evaluate their influence on the PtRu catalysts electrochemical behavior. Their synthesis procedure is reported elsewhere [23, 24]. Basically, the carbon nanofiber growth was carried out at five synthesis temperatures between 550ºC and 750ºC (supports will be labeled as ‘CNF’ followed by the synthesis temperature in Celsius degrees) at low weight hourly space velocity (WHSV) of 4 L g\(^{-1}\) h\(^{-1}\), to achieve different graphitization degrees and different porosity features according to previous works [23, 24]. Moreover, two additional CNFs were synthesized at higher WHSV (2.5 times higher, 10 L g\(^{-1}\) h\(^{-1}\)) at 550ºC and 750ºC, labeled as CNF550HV and CNF750HV (HV refers to high velocity). These samples are characterized by a higher pore volume with respect to those obtained at lower space velocity, which will be shown to have an important effect on the catalytic activity. The growth of nanofibers was carried out for enough reaction duration to obtain a high volumetric carbon content of 99%, monitoring the conversion of methane into carbon by gas chromatography. It is known that the synthesis at lower temperatures than 550ºC leads to very low methane conversion, and consequently very low CNF growth rate for practical purposes, whereas synthesis at higher temperatures than 700ºC do not significantly improve crystallinity neither porosity of the nanofilaments, so the selected interval seems to be ideal in terms of the study of the support.

Platinum-ruthenium nanoparticles were synthesized by the water in oil microemulsion route [25, 26]. The composition of the microemulsion and the preparation methodology have been adapted and optimized, taking into consideration the peculiar low surface area of carbon nanofibers, in order to obtain high electrochemical surface areas according to previous works with platinum [22]. Briefly, it consist of preparing a microemulsion composed by 16.5 % surfactant (polyethylene glycol dodecyl ether, Brij®30, Sigma-Aldrich), 3.9% aqueous solution containing the metal precursors (0.05 M H\(_2\)PtCl\(_6\) and 0.05 M RuCl\(_3\)) and 79.6% n-heptane as the hydrophobic phase. Subsequently, the appropriate amount of carbon support is dispersed in the microemulsion under sonication for at least one hour to achieve a metal
concentration in the catalyst of 20 wt.%. The reduction step involves the slow addition of sodium borohydride in excess at room temperature and under vigorous stirring, left overnight under continuous stirring, and finally the catalyst is thoroughly washed with ethanol and water to remove the chemicals used during the synthesis, and dried overnight at 60°C.

2.2 Solid-state characterization techniques

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

The crystallinity of platinum-ruthenium crystallites and carbon was studied by X-Ray Diffraction. XRD patterns were performed using a Bruker AXS D8 Advance diffractometer, using Cu-Kα radiation. Crystallite sizes were calculated from the Scherrer’s equation applied to the (002) peak for carbon and (220) peak for platinum related reflections.

Raman spectra were employed to evaluate the ordering degree of CNFs. The spectra were obtained using a Horiba Jobin Yvon HR800 UV, using the green line of an argon laser (λ = 514.53 nm) as excitation source. The carbon ordering degree was evaluated by means of the relative intensities of D (ca. 1350 cm⁻¹) and G (ca. 1590 cm⁻¹) peaks.

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

Electrical conductivity measurements were also performed pressing the carbonaceous powder at 10 MPa as described elsewhere [24]. The electrical resistance was measured by the four-point probe method applying electrical currents up to 0.02 A.
Energy dispersive X-ray (EDX) analyses and thermogravimetric analyses (TGA) in air were performed to quantify the metal loading in the PtRu/CNF electrocatalysts. EDX measurements were also used to determine the Pt:Ru atomic ratio. An EDX analyzer Röntec XFlash Si(Li) coupled to a Hitachi S-3400N scanning electron microscope (SEM) was used for that purpose. For TGA experiments in air, a Setaram Setsys Evolution thermogravimetric analyzer was used at atmospheric pressure, and the temperature was varied from room temperature to 950°C with a constant rate of 5 °C min⁻¹.

2.3 Electrochemical experiments

All the electrochemical experiments were carried out in a half-cell using a three-electrode assembly and an Autolab Potentiostat-Galvanostat. A large area pyrolitic graphite rod served as the counter electrode and a reversible hydrogen electrode (RHE) system was used as the reference electrode. All potentials in the text are referred to the latter. The working electrodes were composed of the electrocatalysts deposited as a thin layer over a pyrolitic graphite disk (7 mm diameter). An aqueous suspension of the catalyst under study was prepared by ultrasonically dispersing it in ultrapure water (Milli-Q) and Nafion. An aliquot of 40 µL of the well-dispersed suspension was pipetted on the top of the pyrolitic carbon disk substrate surface and dried at 80°C under nitrogen atmosphere, resulting in a metal loading of ca. 0.15 mg cm⁻². After preparation, the electrode was immersed into the deaerated 0.5 M H₂SO₄ electrolyte, prepared from high purity reagents (Merck) and water purified in a Milli-Q system. The electrolyte was saturated with pure N₂ or CO gases (99.997%, Air Liquide), depending on the experiments.

To characterize the PtRu/CNF electrocatalysts, cyclic voltammograms were recorded in the supporting electrolyte solution (0.5 M H₂SO₄) between 0.05 V and 0.85 V vs. RHE at a scan rate of 0.02 V s⁻¹. CO stripping voltammograms were obtained after bubbling this gas in the cell for 10 min at 0.20 V vs. RHE, followed by electrolyte exchange and nitrogen purging to remove the excess of CO. The admission potential was selected considering that for this value maximum adsorbate coverage is achieved for CO adsorption [27, 28]. Electrochemical surface active areas were determined from
the integration of the CO oxidation region, after correction for double layer capacitance, and assuming 420 µC cm$^{-2}$ involved in the process. Methanol and ethanol electrochemical oxidation reactions were studied by cyclic voltammetry, with a scan rate of 0.02 V s$^{-1}$, substituting the base electrolyte for a deaerated solution of the corresponding alcohol (2 M) in the base electrolyte (0.5 M H$_2$SO$_4$). The stability of the catalysts was evaluated by chronoamperometry from room temperature to 60ºC, using a jacketed glass cell to which water from a thermostated bath was pumped, at a potential value of 0.5 V vs. RHE (this is, in the activation controlled region).
3. Results and discussion

Physical properties of the CNFs have been varied by means of different synthesis temperatures from 550ºC to 750ºC and two values of weight hourly space velocity, as indicated in the experimental section. Table 1 summarizes the most important properties of the selected CNF samples, including the average nanofiber diameter from TEM images (D), together with its standard deviation (σD), the BET specific surface area (SBET), the pore volume (vpore), the relative intensities ratio between disordered and graphitic Raman peaks (ID/IG), the carbon crystal size (Lc) along the c-axis from the broadening of C (002) peak in XRD patterns, and the electrical conductivity of the compressed powder at 10 MPa (EC10MPa).

CNF synthesis temperature influences their properties in two different ways. As a general rule, increasing CNF synthesis temperature leads to the thickening of CNFs by the effect of catalyst sintering (Ni based), which results in the decrease of the BET specific surface area, also the decrease of pore volume, and maintaining a negligible percentage of micropores in all cases (ca. 1%). On the other hand, the graphitization degree increases with temperature up to 700ºC, both in terms of the ID/IG ratio and crystal size from Raman and XRD analyses respectively, favoring also the electrical conductivity as compiled in Table 1. Moreover, the density of surface defects diminishes with the increase of temperature, as exemplified in the TEM micrographs of Fig. 1. The variation of space velocity, on the other hand, leads to a significant variation of the pore volume with slight changes in crystallinity, which will result of interest along this paper to evaluate the effect of pore volume on the activity towards the oxidation of alcohols.

Alloyed PtRu nanoparticles of about 2 nm size and a narrow size distribution are well dispersed on the surface of the four carbon nanofiber samples, as can be observed in the representative TEM captions of Fig. 1. The increase of both nanofiber diameter and surface ordering degree with synthesis temperature can also be observed in these micrographs, as commented previously.

Table 2 compiles some of the main physical-chemical characteristics of PtRu (1:1 at.) catalysts supported on the different carbon nanofibers. The metal concentration is close to nominal in all cases (20 wt.%), as confirmed by EDX and TGA experiments,
with an atomic Pt:Ru ratio close to 50:50. X-ray diffractograms (Fig. 2) correspond to the face centered cubic (fcc) structure of platinum together with the graphitic carbon reflection at ca. 26°. The reflections attributed to metal particles are slightly shifted towards wider angles than the corresponding supported Pt, as a result of the alloy with ruthenium. The lattice parameter, calculated from the Bragg equation, is slightly lower than that of pure platinum supported on carbon (ca. 0.392 nm) and no reflections associated to Ru, or metal oxides are present, indicating that Ru is alloyed in the platinum structure. PtRu crystal sizes, calculated from the broadening of the (220) reflection and the Scherrer's equation, were found between 1.8 and 2.5 nm. It is to be noted that the average crystal size slightly and progressively increases with the decrease of the CNF surface area, as a result of the slightly higher degree of agglomeration during either the growth or deposition of metal particles, influenced by the surface area of the support. It is also noticeable that the relative intensity of carbon related peak (at ca. 26°) with respect to platinum related peaks increases with the CNF synthesis temperature, as well as the (002) carbon reflection becomes narrower and slightly shifted to higher angles, agreeing to the previous discussion of support graphicity variation with temperature.

Regarding the electrochemical characterization, Fig. 3 shows the cyclic voltammograms in the oxidation of a CO monolayer, formed at 0.2 V vs. RHE, as well as the second cycle corresponding to the voltammogram of the clean metal surface in the base electrolyte (0.5 M H₂SO₄). The oxidation of CO occurs in a single peak starting at a potential of ca. 0.5 V vs. RHE. The peak potential for each sample is indicated in the figure. It is well known that the electrochemical oxidation of CO and alcohols is a surface structure sensitive reaction [1, 29, 30]. From the CO stripping voltammograms, slight differences (ca. 60 mV) are related to the variation of CNF properties, as observed in Pt/CNF electrocatalysts [22], in which the introduction of different CNFs does not considerably change the CO oxidation profile. The minimum differences encountered could be related to the variation of surface structure derived from differences in particle size or to different metal-support interaction in which a higher graphitization degree of the support may favor the electrooxidation of CO at more negative potential values (0.61 V vs. RHE). Nevertheless, these results highlight the fact that PtRu nanoparticles with similar surface structures have been obtained independently of the support features
as a consequence of synthesizing metal nanoparticles by means of the microemulsion procedure, which allows the control of metal growth inside micelles. Similar metal surface structures result of key importance for the evaluation of the support properties influence on alcohol oxidation activity.

The electrochemical surface areas (ECSA) were calculated from CO stripping curves assuming a charge of 420 µC cm⁻² in the oxidation of a monolayer of linearly adsorbed CO normalized by the total amount of metal (PtRu) [30], and the values are summarized in Table 2. The values of ECSA correspond to highly dispersed PtRu catalysts, in agreement with the low particle size of PtRu nanoparticles (ca. 2 nm) [31] and their good distribution on the surface as demonstrated in TEM observations. The highest ECSA values, of ca. 140 m² g⁻¹, are obtained with the catalysts based on CNF600 and CNF650, those supports characterized by their intermediate properties. This can be attributed to their best compromise in terms of support surface area and dispersion as resulting from a moderate concentration of surface groups in the support, in a similar way that observed for platinum catalysts supported on CNFs [22].

The electrooxidation of methanol (2M CH₃OH in 0.5M H₂SO₄) was studied at room temperature by cyclic voltammetry as represented in Fig. 4. An anodic contribution starts at ca. 0.4 V vs. RHE, developing an anodic curve which reaches a certain maximum current density value. It is remarkable that the increase of the graphitization degree of the support from CNF550 to CNF650 leads to the increase of this maximum mass activity towards the oxidation of methanol from ca. 100 mA mg⁻¹ to ca. 260 mA mg⁻¹. This rise in activity must be attributed to an enhanced metal-support interaction in highly graphitic carbon nanofibers resulting in the improvement of specific activity, since the differences of electrochemical surface areas (ECSA) do not explain by itself such activity behavior. However, the catalysts based on the CNFs with higher graphicity, (CNF700 and CNF750), present lower maximum activities (ca. 205 mA mg⁻¹ and 225 mA mg⁻¹, respectively), in agreement with its lower ECSA compared to the catalyst based on CNF650.

A similar approach was carried out to study the electrooxidation of ethanol (2M CH₃CH₂OH in 0.5M H₂SO₄). Although it is well known that the catalytic system PtRu is not the optimum for the EOR, being PtSn considerably more active [32-34], the
analysis of CNF properties on the behavior of PtRu nanoparticles may be extended to the PtSn system. The corresponding cyclic voltammograms are represented in Fig. 5. It is worth to mention that the current density values obtained in the oxidation of ethanol are comparatively lower than those obtained in the oxidation of methanol (Fig. 4), as discussed in the introduction section, the oxidation of ethanol presents even slower kinetics than the oxidation of methanol. The most remarkable result is that the influence of the CNF properties on the activity does not follow the same trend as the observed for the oxidation of methanol. Notice that the best catalysts for MOR, these are, the ones based on highly graphitic supports, give place to considerably lower activity than the best catalyst for EOR, this is PtRu/CNF600. This decay of EOR activity becomes especially important in the case of PtRu/CNF700 and PtRu/CNF750, which activity is significantly low when compared to the catalysts based on the rest of CNFs. The same trends are found considering the activity at a potential of 0.5 V vs. RHE, this is, in the activation controlled region, as represented in Fig. 6 for the average values of MOR and EOR activity considering the standard deviation from the replication of the experiments. Again, whereas a minimum graphicity is mandatory to maximize the MOR activity with no significant improvement by increasing CNF synthesis temperature beyond 650ºC, the EOR activity presents a maximum value for CNF600.

A plausible explanation of the dramatic decay of EOR activity when using CNF700 or CNF750 may be found when considering their pore volume (0.21 and 0.22 cm$^3$ g$^{-1}$ respectively, Table 1). To clarify this phenomenon CNF550HV and CNF750HV, characterized by a higher pore volume than the respective CNF550 and CNF750 (34% and 45% higher respectively), where studied as PtRu support for the electrooxidation of methanol and ethanol. Fig. 7 shows the electrooxidation of (a) methanol and (b) ethanol voltammograms for the supports characterized by low pore volume (discontinuous lines) and high pore volume (continuous lines). It is noticeable that the activity towards the oxidation of methanol hardly changes with the use of high pore volume based catalysts, as well as the oxidation of ethanol on CNF550 and CNF550HV based catalysts, but it significantly increases about ten-fold when PtRu is supported on CNF750HV with respect to CNF750.

Stability tests were carried out registering chronoamperometric curves for the electrooxidation of methanol at temperature values between room temperature and
60°C. Fig. 8 compiles the behavior of two of the catalysts (PtRu/CNF600 and PtRu/CNF700) in terms of mass activity at a constant potential (0.5 V vs. RHE). In all cases the stationary current increases with temperature with a slight decrease of performance with time. Activation energy was calculated from the polarization curves obtained at different temperatures (30, 40, 50 and 60°C), considering the mass activity at 0.5 V vs. RHE and the Arrhenius plot as shown in the inset of Figures 8(a) and 8(b). Values in the order of 32-40 kJ mol\(^{-1}\) were obtained, very similar among catalysts, this is, no significant effect of support on the activation energy, and comparable to PtRu particles of similar size [35].

To sum up, highly crystalline carbon nanofibers are preferable to obtain a high electrochemical activity towards the oxidation of methanol, independently of fuel cell operation temperature, but a minimum BET surface area is needed to properly disperse nanoparticles and maximize the electrochemical active area. In contrast, highly graphitic CNFs are not preferable for the oxidation of ethanol since their worse porous structure hinders the access of such alcohol to the catalytic active sites, concluding that a minimum porosity development is mandatory to obtain a good performance. For the EOR, the pore volume of the support seems to play a very important role.
Conclusions

Carbon nanofibers, varying in terms of average diameter, ordering degree, surface structure and porosity, were synthesized and investigated as support for platinum-ruthenium nanoparticles. A microemulsion procedure was employed to synthesize small PtRu nanoparticles of ca. 2 nm with a high electrochemically active surface area and independently of the support features. The catalysts were tested for the anodic electrochemical reaction of direct alcohol fuel cells, analyzing the activity towards the oxidation of both methanol and ethanol. It was observed that the relation between support properties and the electrochemical activity is different for methanol and ethanol oxidation. Methanol oxidation is favored when supporting PtRu nanoparticles on highly graphitic CNFs, being necessary a minimum ordering degree which can be achieved synthesizing the support at 650ºC, despite the worse porous properties compared to the rest of CNFs. On the other hand, the highly graphitic nanofibers that improve the oxidation of ethanol show low activity towards the oxidation of ethanol. Further research has demonstrated that the pore volume may play an important role and consequently CNFs characterized by a more developed porosity maximize the EOR activity despite their lower graphicity.
Acknowledgements

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References


Captions to figures

Figure 1. TEM captions of (a) PtRu/CNF550; (b) PtRu/CNF600; (c) PtRu/CNF650; (d) PtRu/CNF700.

Figure 2. XRD patterns of 20% PtRu/CNF catalysts.

Figure 3. CO stripping voltammograms at 25°C and a scan rate of 20 mV s⁻¹.

Figure 4. Cyclic voltammograms for the oxidation of methanol (2M) in the base electrolyte at 25°C and a scan rate of 20 mV s⁻¹.

Figure 5. Cyclic voltammograms for the oxidation of ethanol (2M) in the base electrolyte at 25°C and a scan rate of 20 mV s⁻¹.

Figure 6. Comparative chart of the mass activity in the low potential region (0.5 V vs. RHE) for the oxidation of methanol and ethanol according to the CNF used as support for PtRu nanoparticles.

Figure 7. Effect of the pore volume on the electrocatalytic activity towards the oxidation of (a) methanol and (b) ethanol. The continuous lines (—) represent CNFs with lower pore volume compared to the discontinuous lines (…).

Figure 8. Stability tests by potential holding at different temperatures and at 0.5 V vs. RHE for the oxidation of methanol (2M) in the base electrolyte for (a) PtRu/CNF600 and (b) PtRu/CNF700. The inset graphics show the Arrhenius plots for the calculation of activation energy.
Table 1. Supports physical-chemical properties.

<table>
<thead>
<tr>
<th>Support</th>
<th>D ± σ_D (nm)</th>
<th>S_{BET} (m^2 g^{-1})</th>
<th>v_{pore} (cm^3 g^{-1})</th>
<th>Raman I_D/I_G</th>
<th>L_c (nm)</th>
<th>EC_{10MPa} (S cm^{-1})</th>
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<tr>
<td>CNF550</td>
<td>24 ± 11</td>
<td>174</td>
<td>0.53</td>
<td>2.39</td>
<td>6.4</td>
<td>2.7</td>
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<tr>
<td>CNF600</td>
<td>28 ± 13</td>
<td>150</td>
<td>0.43</td>
<td>1.87</td>
<td>7.8</td>
<td>3.5</td>
</tr>
<tr>
<td>CNF650</td>
<td>46 ± 22</td>
<td>124</td>
<td>0.32</td>
<td>1.53</td>
<td>8.6</td>
<td>4.4</td>
</tr>
<tr>
<td>CNF700</td>
<td>54 ± 18</td>
<td>94</td>
<td>0.21</td>
<td>0.87</td>
<td>10.2</td>
<td>13.0</td>
</tr>
<tr>
<td>CNF750</td>
<td>63 ± 17</td>
<td>99</td>
<td>0.22</td>
<td>1.03</td>
<td>9.4</td>
<td>17.3</td>
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<tr>
<td>CNF550HV</td>
<td>n.d.</td>
<td>185</td>
<td>0.71</td>
<td>1.76</td>
<td>5.2</td>
<td>1.7</td>
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<td>CNF750HV</td>
<td>n.d.</td>
<td>118</td>
<td>0.32</td>
<td>1.42</td>
<td>9.2</td>
<td>10.6</td>
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n.d.: not determined
Table 2. PtRu/CNF electrocatalysts properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PtRu crystal size (nm)</th>
<th>Pt:Ru at. ratio (at.% : at.%)</th>
<th>PtRu concentration (wt.%)</th>
<th>Lattice parameter (nm)</th>
<th>ECSA (m² g⁻¹)</th>
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<tr>
<td>PtRu/CNF550</td>
<td>1.8</td>
<td>45:55</td>
<td>22</td>
<td>0.388</td>
<td>122</td>
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<tr>
<td>PtRu/CNF600</td>
<td>1.9</td>
<td>46:54</td>
<td>18</td>
<td>0.387</td>
<td>142</td>
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<tr>
<td>PtRu/CNF650</td>
<td>2.0</td>
<td>43:57</td>
<td>21</td>
<td>0.389</td>
<td>142</td>
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<tr>
<td>PtRu/CNF700</td>
<td>2.3</td>
<td>47:53</td>
<td>21</td>
<td>0.388</td>
<td>113</td>
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<tr>
<td>PtRu/CNF750</td>
<td>2.7</td>
<td>46:54</td>
<td>22</td>
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<td>40:60</td>
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<td>48:52</td>
<td>22</td>
<td>0.386</td>
<td>101</td>
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</table>
Figure 1. (cont.)
Figure 1 (cont.)
Figure 2.

![X-ray diffraction patterns for different samples with labels: Pt, PtRu/CNF550, PtRu/CNF600, PtRu/CNF650, PtRu/CNF700, PtRu/CNF750, PtRu/CNF550HV, PtRu/CNF750HV. The peaks indicate the presence of carbon (C) and platinum (Pt).]
Figure 3.

![Graph of electrochemical data for PtRu/CNF electrodes.](image)

- **PtRu/CNF750**
  - Potential: 0.59 V

- **PtRu/CNF700**
  - Potential: 0.61 V

- **PtRu/CNF650**
  - Potential: 0.61 V

- **PtRu/CNF600**
  - Potential: 0.65 V

- **PtRu/CNF550**
  - Potential: 0.63 V

**Axes:**
- **Potential / V vs. RHE**
- **Current density / mA cm\(^{-2}\)**

The graph shows cyclic voltammograms for different PtRu/CNF electrodes, with peak potentials indicated for each.
Figure 4 (prepared for a width equivalent to two columns).

![Graphs showing mass activity vs. potential for PtRu/CNF at different temperatures.](image-url)
Figure 5 (prepared for a width equivalent to two columns).
Figure 6.

Mass activity at 0.5 V (vs. RHE) / mA mg$^{-1}$

- Methanol
- Ethanol

Support:
- CNF550
- CNF600
- CNF650
- CNF700
- CNF750
Figure 7.
Figure 8.

(a) Logarithmic plot of mass activity (mA mg\(^{-1}\) PtRu) against temperature (°C) with a slope of 39 kJ mol\(^{-1}\).

(b) Logarithmic plot of mass activity (mA mg\(^{-1}\) PtRu) against temperature (°C) with a slope of 32 kJ mol\(^{-1}\).
Graphical Abstract

**Methanol oxidation**

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

**Ethanol oxidation**

\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \]
Highlights

- Small PtRu nanoparticles (2 nm) were supported on different carbon nanofibers.
- The electrooxidation of methanol is favored on highly graphitic PtRu/CNF catalysts.
- The electrooxidation of ethanol is instead favored on highly porous PtRu/CNF.
- The CNF pore volume plays a determining role in the electrooxidation of ethanol.