Structure and Activity of Carbon-Supported Pt–Co Electro catalysts for Oxygen Reduction

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Carbon-supported Pt–Co electro catalysts in the Pt:Co atomic ratio 85:15, mainly for application in polymer electrolyte fuel cells, have been prepared by different methods. The materials were tested in single cells with respect to the oxygen reduction reaction and their performances were compared. Of the several methods considered, the preparation of the electro catalyst via the deposition and reduction of a Co precursor on previously formed carbon-supported platinum gave the best results. By increasing the Co content, a decrease of metal particle size and an improvement in the activity for the ORR of these catalysts was observed. For the electro catalysts with a Pt:Co atomic ratio of 75:25, a good stability upon cycling was also found.

1. Introduction

The alloys of transition metals, such as V, Cr, Co, Ti, and Ni, with platinum exhibit significantly higher electrocatalytic activities toward the oxygen reduction reaction (ORR) than platinum alone in low-temperature fuel cells.1–19 These Pt–alloy electro catalysts improve both the performance and the resistance to sintering and coalescence of the nanoparticles under the operating conditions of the phosphoric acid fuel cell (PAFC) and polymer electrolyte fuel cell (PEMFC). The improvement in the ORR electro catalysis has been ascribed to different factors such as the Pt–Pt interatomic distance,1 the surface area,3 the d-orbital vacancy,19 and the distribution of surface atoms.15

Conflicting results on electrocatalytic activity1,20 and dissolution of non-noble metal components in the PAFC environment1,21 suggested the possibility of differences in the electrochemical properties of bulk versus supported alloy electro catalysts.9 Thus, the improvement for the ORR activity observed in gas diffusion electrodes for several Pt–alloy electro catalysts could be attributed to factors specific of small particle size catalysts or related to the structural factors of the cell geometry. In light of this outline, the preparation method of these catalysts, affecting their chemical and morphological characteristics, becomes very important. Several methods have been described for the preparation of carbon-supported Pt and Pt alloys, most of which involve chemical or electrochemical reduction in solutions containing the desired precursor ions. Results obtained with different methods vary because the properties of the material, as the degree of alloying and metal particle size, depend on the preparation procedure.

An alternative way to tailor the nanosized Pt-based alloys is the use of organometallic compounds as precursors.22–25 By the thermal decomposition or reducing treatment of organometallic precursors, small nanoparticles of metal or alloy with narrow size distribution could be obtained. For example, Sun et al.22 obtained Pt–Co nanoparticles of about 2 nm with very narrow size distribution from the organometallic precursors. Similarly, nearly monodisperse Pt–Co,23 Pt–Fe,24 and Pt–Mn25 nanoparticles were prepared by the decomposition of organic precursors. Among the various organometallic precursors used, metal–carbonyl complexes are often employed for preparing carbon-supported metal or alloy catalysts. Recently, Boucher et al. successfully synthesized carbon-supported Pt–Sn alloy catalysts through the carbonyl chemical route.26 The obtained Pt–Sn alloy catalysts with very small particle size, narrow size distribution, and disordered structure exhibited good performances for electrocatalytic reactions. Carbon-supported Pt–Cr alloy catalysts with different PtCr atomic ratios were prepared via a Pt-carbonyl route by Yang et al.27 The obtained Pt–Cr alloy nanoparticles are well dispersed on the surface of carbon with a relatively narrow size distribution.

Furthermore, to get insight into the relationship between the surface composition and the catalytic activity, it is very important to determine if the surface segregation takes place during the preparation of bimetallic surfaces, that is, enrichment of one element at the surface relative to the bulk. For this purpose, Toda et al.19 prepared unsupported PtM (M = Fe, Co, Ni) alloys by radio frequency magnetron sputtering and evaluated the alloy surface states with X-ray photoelectron spectroscopy (XPS). They found that after the oxygen reduction reaction in perchloric acid solution the active surfaces of the catalysts were covered by a few monolayers of Pt. Recently, Stamenkovic et al.28,29 prepared bulk PtCo and PtNi alloys by conventional metallurgy, followed by sputtering or annealing. Clearly defined surface composition was determined via low-energy ion-scattering (LEIS) spectroscopy. The data by LEIS showed that the first layer of a clean annealed PtNi(Co) surface contains only Pt atoms, implying that the “Pt-skin” structure can also be created on a polycrystalline PtNi(Co) alloy. They attributed the enhancement of the catalytic activity for ORR on PtNi and PtCo alloy surface to the inhibition of Pt–OH adsorption on Pt sites surrounded by “oxide”–covered Ni and Co atoms beyond 0.8 V.

By a critical examination of X-ray photoelectron spectroscopic data, Arico et al.30 and Shukla et al.31 observed that the amount of platinum oxide in PtCo alloy electro catalysts decreases with the increase of the content of Co. According to the authors, this is primarily due to the oxide-cleansing action of the transition metals from the Pt surface.

Pt and Co form a substitutational continuous solid solution in the whole range of composition and two ordered phases.32 The Pt–Co ordered phase with a Cu–Au (L10) type of structure is
stable from about 42 to 72% Pt. In the region of 75% Pt, there is an fcc superlattice Pt₃Co of the Cu₃Au (L₁₂) type. Regular termination of the bulk L₁₂ structure normal to the three major zone axes produces a variety of surface compositions, from the pure Pt ((200) and (220) planes) and 25% Co ((111) plane) to 50% Co ((100) and (110) planes). Thus, it is possible to have a surface with a higher concentration of Co than in the bulk, that is, surface enrichment without surface segregation. Mukerjee and Srinivasan rationalized the enhanced electrochemical performance in PEMFC with commercial Pt–Co/C catalysts on the basis of the existence of an ordered Pt₃Co structure. According to Watanabe et al., the ordered Pt–Co structure showed 1.35 times higher mass activity compared to that of the disordered alloy. The presence of a 25% contribution from the PtCo phase was also observed in the commercial carbon-supported Pt₃Co alloy by E-TEK.

Recent works on the effect of nonprecious metal on the catalytic activity of carbon-supported Pt–Co electrocatalysts produced conflicting results. Oliveira Neto et al. found that the electroactive area of the material decreases with increasing Co content in the samples, while Xiong et al. observed an increase in the activity for the ORR with Co content in the catalyst with a maximum for a Pt:Co atomic ratio 1:7. In both of these studies, the effect of the degree of alloying was not taken into account.

The main problems affecting carbon-supported Pt–M alloys are the poor degree of alloying, that is, the alloy composition is less than the nominal catalyst composition, and the increase of the particle size with respect to pure Pt. Usually, the carbon-supported Pt alloy electrocatalysts for the ORR were prepared by the impregnation of the second metal on Pt/C and then by alloying at temperatures above 700 °C under an inert gas or a hydrogen atmosphere. This heat treatment at high temperatures gives rise to an undesired alloy particle growth, which may result in the decrease in Pt mass activity for the ORR. Recently, some groups have reported that such Pt alloy electrocatalysts could be prepared by the coreduction of the metallic salt precursors at low temperatures and that the obtained Pt alloy particle sizes are relatively small.

In this work, we have prepared carbon-supported Pt–Co by three different methods. One is the common method consisting in the deposition of the nonprecious metal on a previously formed carbon-supported platinum, followed by alloying at high temperatures. The other two methods tested in this work are the formation of the carbon-supported Pt–Co alloy by simultaneous deposition of Pt and Co precursors on the carbon particles, followed by reduction with (a) a strong reducing agent (NaBH₄) at room temperature and (b) H₂ gas at 550/900 °C. Pt–Co alloy formation in the first case occurs via the diffusion of Co atoms into the Pt lattice, while the other two methods lead to the direct formation of Pt–Co crystallites.

2. Experimental Section

2.1 Preparation of the Electro catalysts. Carbon-supported Pt–Co electrocatalysts were prepared using the following methods.

(1) Alloying Method (AM). The required amount of E-TEK 20 wt % Pt/Vulcan XC-72 (particle size 2.8 nm) was dispersed in distilled water followed by ultrasonic blending for 15 min. The pH of the solution was raised to 8 with dilute ammonium hydroxide. Stirring was continued during and after the pH adjustment. The required amount of a solution of cobalt chloride (CoCl₂ 6H₂O, Aldrich) was added to this solution. This was followed by the addition of dilute HCl to the solution until a pH of 5.5 was attained. Stirring was continued for 1 h and then the resultant mass was filtered and dried at 90 °C in an air oven for 2 h. Subsequently, the solid was well ground and the powder was heat-treated at 900 °C in a hydrogen/argon atmosphere for 1 h to form the respective binary alloy catalyst.

(2) Reduction with H₂. The electrocatalyst was prepared by impregnating high surface area carbon (Vulcan XC-72, Cabot, 240 m² g⁻¹) with a chloroplatinic acid (H₂PtCl₆·6H₂O, Johnson Matthey) solution and a cobalt hydroxide (Co(OH)₂·6H₂O, Aldrich) solution under sonication for 3 h. The impregnated carbon was dried and then thermally treated at 550 °C (H5) and 900 °C (H9) for 3 h in a hydrogen atmosphere.

(3) Reduction with NaBH₄ (BM). In this case, the electrocatalyst was prepared by impregnating high surface area carbon with a chloroplatinic acid solution and a cobalt hydroxide (Co(OH)₂·6H₂O, Aldrich) solution. The metals were then reduced with a sodium borohydride solution, which was slowly added to the precursor solution under sonication. The materials prepared by methods 2 and 3 were 20 wt % metal on carbon, while those from the method 1 were (20 + X) wt % metal on carbon, where X is the weight % of the cobalt.

2.2 Electrode Preparation and Test in Single PEMFC. To test the electrochemical behavior in a single PEMFC fed with hydrogen/oxygen, these catalysts were used to make two-layer gas diffusion electrodes. A diffusion layer was made with carbon powder (Vulcan XC-72) and 15% w/w PTFE and applied over a carbon cloth (PWB-3, Stackpole). A homogeneous water suspension of carbon powder and PTFE was filtered under vacuum onto both faces of the carbon cloth to form the gas diffusion layer of the electrode. On top of this layer, the catalyst was applied in the form of a homogeneous dispersion of Pt–Co/C, or Pt/C, Nafion solution (5%, Aldrich) and 2-propanol (Merck) by a painting procedure. All electrodes were made to contain 0.4 mg Pt cm⁻². The Pt loading was determined by weight. The experimental error in the catalyst loading was ±2 wt %. It was noted that during the painting procedure the platinum loss was about 10 wt %. To decrease Pt loss, an excess of Pt (10 wt %) was used in the catalytic ink. After drying, the electrodes were hot-pressed on both sides of a Nafion 115 membrane at 125 °C and 50 kg cm⁻² for 2 min. Before use, the Nafion 115 membranes were treated with a 3% solution of H₂O₂, washed, and then treated with a 0.5 mol L⁻¹ solution of H₂SO₄. The geometric area of the electrodes was 4.62 cm², and the anode material was 20% Pt/C E-TEK. The cell temperature was 80 °C and the reagent gases were humidified at 85 (oxygen) and 95 °C (hydrogen) and fed to the cell at atmospheric pressure. Before recording the current–potential curves, the single PEMFC was stabilized by operating it at 500 mA cm⁻² for 2 h.

2.3 Energy Dispersive X-ray Analyses (EDX). The atomic ratios of the Pt–Co/C catalysts were determined by the EDX technique coupled to a scanning electron microscopy LEO Mod. 440 with a silicon detector with Be window and applying 20 keV.

2.4 X-ray Diffraction (XRD). X-ray diffractograms of the catalysts were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu kα radiation (λ = 0.15406 nm) generated at 40 kV and 20 mA. Scans were done at 3° min⁻¹ for 2θ values between 20 and 100°. To estimate the particle size from XRD, Scherrer’s equation was used. For this purpose, the (220) peak of the Pt fcc structure around 2θ =
3. Results and Discussion

The EDX compositions of the various carbon-supported Pt–Co electrocatalysts are given in Table 1, which shows that the EDX results are very near the nominal 85:15 atomic ratio of Pt:Co.

The results of XRD analysis of Pt$_{85}$Co$_{15}$/C and Pt/C electrocatalysts are shown in Figure 1 and Table 1. The reflections of the Pt$_{85}$Co$_{15}$ samples shifted to higher angles compared to those of Pt indicating a contraction of the lattice and alloy formation. On the basis of the results reported in Table 1, the catalyst prepared by BM presented the highest degree of Co alloying and the lowest metal particle size. The catalyst prepared by AM revealed a good degree of Co alloying and also the highest metal particle size. The catalysts prepared by H5 and H9 were characterized by poor alloying.

The degree of alloying ($x_a$) in the supported Pt–Co materials was calculated with the expression

$$x_a = (a - a_o)/(a_C - a_o) \quad (1)$$

where $a$ is the experimental lattice parameter, $a_C$ is the lattice parameter assuming that all the cobalt is alloyed, and $a_o$ is the lattice parameter of supported platinum (Pt/C).

2.5 Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM).

The samples for the TEM characterizations were prepared as follows: a carbon film was deposited onto a mica sheet that was placed onto the Cu grids (300 mesh and 3 mm diameter). The material to be examined was dispersed in water by sonication, placed onto the carbon film, and left to dry. Combined HRTEM/EDX analysis was performed using a 10 nm electron beam. Histograms of particle sizes were constructed using about 700 particles. This technique was implemented in the Microscopy Laboratory of the National Synchrotron Radiation Laboratory using a HRTEM microscope JEOL, JEM 3010, URP, operating at 300 kV and having a resolution of 0.17 nm.

2.6 Cyclic Voltammetry (CV).

Cyclic voltammograms were recorded in a single compartment cell in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution. Argon (White Martins) was passed for 30 min to eliminate oxygen. As working electrode, a thin porous coating solution. Argon (White Martins) was passed for 30 min to eliminate oxygen. As working electrode, a thin porous coating. The EDX compositions of the various carbon-supported Pt–Co electrocatalysts by BM (a), AM (b), H5 (c), H9 (d), and Pt/C (e).

The polarization curves obtained in the single fuel cell were analyzed using the semiempirical equation$^{41–43}$

$$E = E_o - b \log j - R/j \quad (2)$$

where $E_o$ is a constant given by

$$E_o = E_r - b \log j_o \quad (3)$$

Here, $E_r$ is the reversible potential of the cell, $b$ the Tafel slope, $j_o$ is the exchange current density for the ORR, and $R$ represents the total contribution of resistive components to the polarization. This includes the charge-transfer resistance of the hydrogen oxidation reaction, the ionic resistance of the electrolyte, which predominates, the electronic resistance, and the linear diffusional terms due to transport limitations of the reactant gas in the diffusion layer of the electrode and in the thin film of electrolyte on the catalyst.$^{42,43}$

Since eq 2 does not include diffusion limitations other than linear contributions and because a change in the Tafel slope from 60 to 120 mV dec$^{-1}$ is expected for the ORR at potentials around 0.8 V,$^{43,44}$ only the region for $E > 0.8$ V was considered in these analyses. The parameters $E_o$, $b$, and $R$ were obtained by using a least-squares Levenberg–Marquardt fitting procedure.$^{43}$

Figure 2 shows the H$_2$/O$_2$ PEMFC performance with Pt/C and Pt$_{85}$Co$_{15}$/C electrocatalysts prepared by different methods. The kinetic parameters obtained from the experimental results reported in Figure 2 are presented in Table 2. Within the fitting error, the Tafel slope $b$ was not influenced by the method used to prepare the catalyst. The best results of the kinetic analysis in terms of the values of $E_o$, the current density at 900 mV in terms of the geometric surface area, and the potential at 10 mA cm$^{-2}$ were obtained with the AM and H5 electrocatalysts. To take into account the true catalyst surface area, the current density at 900 mV (ORR activity) was calculated in terms of the metal surface area. The surface area (SA) of Pt and PtCo alloys was estimated, assuming homogeneously distributed and spherical particles, using the relationship $SA = 6/(\rho d)^{3/2}$, where

![Figure 1. XRD patterns of Pt$_{85}$Co$_{15}$/C electrocatalysts by BM (a), AM (b), H5 (c), H9 (d), and Pt/C (e).](image-url)

![Figure 2. H$_2$/O$_2$ PEMFC performance with Pt/C and Pt$_{85}$Co$_{15}$/C electrocatalysts.](image-url)
Correlation of oxygen electrode performance (log \( j_{900mv} \)) of Pt and Pt–Co electrocatalysts in PEMFC with the mean interatomic distance.

\( \rho \) is the alloy density, and \( d \) is the particle size. The roughness factors are reported in Table 1, and the current densities at 900 mV, normalized with respect to the metal surface area, are reported in Table 2. As can be seen in Table 2, the highest activity for ORR based on the metal surface area was shown by the AM catalyst.

Figure 3 shows the logarithm of the electrocatalytic activity for the ORR (\( j_{900mv} \)) obtained from the polarization curves for BM, H5, and H9 electrocatalysts with Pt–Co atomic ratio 85:15 and AM electrocatalysts with different Pt–Co atomic ratios (see Tables 3 and 4) versus the Pt–Pt bond distance. As can be seen in Figure 3, the values of the electrocatalytic activity for ORR on BM and H5 catalysts are too low and too high, respectively, with respect to the curve describing the dependence of the ORR activity on the mean interatomic distance.

![Figure 2](image-url)

**Figure 2.** \( \text{H}_2/\text{O}_2 \) PEMFC polarization curves with \( \text{Pt}_{90}\text{Co}_{10}/\text{C} \) and \( \text{Pt}/\text{C} \) electrocatalysts for oxygen reduction at \( 80 \degree \text{C} \) and 1 atm. Catalyst layer with Pt loading 0.4 mg cm\(^{-2}\) and Nafion loading 1.1 mg cm\(^{-2}\). Diffusion layer with 15 wt % PTFE and C loading 3 mg cm\(^{-2}\).

**TABLE 2: Kinetic Parameters for Oxygen Reduction on Carbon-Supported Pt and Pt\(_{85}\)Co\(_{15}\) Electrocatalysts by Different Preparation Methods in PEMFC at 80 \degree \text{C} and 1 atm Pressure\(^a\)**

<table>
<thead>
<tr>
<th>preparation method</th>
<th>( E_o ) (mV)</th>
<th>( b ) (mV dec(^{-1}))</th>
<th>( R ) (( \Omega ) cm(^2))</th>
<th>( j_{900mv} ) (( \mu )A cm(^{-2}))</th>
<th>( E_{10mA/cm2} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>961</td>
<td>65</td>
<td>0.18</td>
<td>8.0</td>
<td>27</td>
</tr>
<tr>
<td>AM</td>
<td>975</td>
<td>68</td>
<td>0.27</td>
<td>12.0</td>
<td>91</td>
</tr>
<tr>
<td>H5</td>
<td>970</td>
<td>60</td>
<td>0.32</td>
<td>12.8</td>
<td>45</td>
</tr>
<tr>
<td>H9</td>
<td>961</td>
<td>61</td>
<td>0.23</td>
<td>10.7</td>
<td>65</td>
</tr>
<tr>
<td>Pt/C</td>
<td>957</td>
<td>65</td>
<td>0.17</td>
<td>7.0</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\)Pt loading 0.4 mg cm\(^{-2}\). \(^b\)Normalized with respect to metal surface area.

**TABLE 3: Structural Characteristics by XRD Analysis of Pt–Co/C Electrocatalysts with Various Cobalt Contents**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( \text{lattice parameter} ) (nm)</th>
<th>mean interatomic distance (nm)</th>
<th>particle size (nm)</th>
<th>degree of alloying (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pt}<em>{90}\text{Co}</em>{10}/\text{C} )</td>
<td>0.3923</td>
<td>0.2774</td>
<td>17.4</td>
<td>0</td>
</tr>
<tr>
<td>( \text{Pt}<em>{95}\text{Co}</em>{5}/\text{C} )</td>
<td>0.3880</td>
<td>0.2743</td>
<td>8.5</td>
<td>63</td>
</tr>
<tr>
<td>( \text{Pt}<em>{85}\text{Co}</em>{15}/\text{C} )</td>
<td>0.3868</td>
<td>0.2735</td>
<td>6.7</td>
<td>64</td>
</tr>
<tr>
<td>( \text{Pt}<em>{75}\text{Co}</em>{25}/\text{C} )</td>
<td>0.3841</td>
<td>0.2716</td>
<td>4.6</td>
<td>80</td>
</tr>
</tbody>
</table>

\(^*\)Calculated as shown in section 2.4.

**TABLE 4: Kinetic Parameters for Oxygen Reduction on Pt–Co/C Electrocatalysts with Various Cobalt Contents in PEMFC at 80 \degree \text{C} and 1 atm Pressure\(^a\)**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( E_o ) (mV)</th>
<th>( b ) (mV dec(^{-1}))</th>
<th>( R ) (( \Omega ) cm(^2))</th>
<th>( j_{900mv} ) (( \mu )A cm(^{-2}))</th>
<th>( E_{10mA/cm2} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pt}<em>{90}\text{Co}</em>{10}/\text{C} )</td>
<td>952</td>
<td>62</td>
<td>0.36</td>
<td>6.5</td>
<td>888</td>
</tr>
<tr>
<td>( \text{Pt}<em>{95}\text{Co}</em>{5}/\text{C} )</td>
<td>975</td>
<td>68</td>
<td>0.27</td>
<td>12.0</td>
<td>905</td>
</tr>
<tr>
<td>( \text{Pt}<em>{85}\text{Co}</em>{15}/\text{C} )</td>
<td>978</td>
<td>67</td>
<td>0.21</td>
<td>13.36</td>
<td>910</td>
</tr>
<tr>
<td>( \text{Pt}<em>{75}\text{Co}</em>{25}/\text{C} )</td>
<td>975</td>
<td>65</td>
<td>0.21</td>
<td>13.68</td>
<td>911</td>
</tr>
</tbody>
</table>

\(^*\)Pt loading 0.4 mg cm\(^{-2}\).

In the first case, notwithstanding the mean interatomic distance near to the optimum value and the small particle size, the activity was low, which may be due to the synthesis at room temperature. The beneficial effect of the thermal treatment in hydrogen during the synthesis is probably related to the elimination of impurities in the catalyst surface that block the active sites for the reaction, combined with the reduction of high oxidation states of Pt (Pt oxides) originally present.

In the latter case, the good activity of the H5 catalyst, despite the poor alloying, may be due to the interaction between platinum and the unalloyed cobalt at the surface of Pt particles. The ratio of unalloyed Co and Pt atoms on the surface of the metal particle (Co/Pt), of this catalyst was calculated. From the lattice parameters of carbon-supported Pt (0.3915 nm), as obtained in the present work and in ref 46, Pt bulk (0.3923 nm) and Pt-3Co bulk (0.3831 nm), and assuming the same dependence of the lattice parameter on Co atomic fraction, as the Vegard’s law, of supported and unsupported alloys (see later), the alloy composition Co/Pt of the H5 catalyst was 0.012. The ratio between unalloyed Co and total Pt atoms Co/Pt, is given by

\[ \text{Co}/\text{Pt} = (\text{Co/Pt})_n - \text{Co}/\text{Pt} \]  

(4)

where (Co/Pt)_n is the nominal Co/Pt atomic ratio (0.176). The resulting value of Co/Pt was 0.166. (Co/Pt)_n is given by

\[ \text{Co}/\text{Pt} = \text{Co}/\text{Pt} \]  

(5)

where \( D \) is the platinum dispersion, that is, the ratio of platinum atoms at the particle surface and the total number of platinum atoms. The relation between platinum dispersion and particle size, for particles with large size (\( d > 24 \) \( d_\text{at} \)) is given by

\[ D = 5.01 \frac{d_\text{at}}{d} \]  

(6)

where \( d_\text{at} \) is the Pt atomic size (0.139 nm). The calculated value of \( D \) was 0.175, which resulted in a value for (Co/Pt)_n of 0.93, in the region of the formation of Pt–Co ordered phase. On this basis, the presence of some degree of ordering in the distribution of unalloyed Co (or CoO) atoms on the Pt surface can be predicted, and this should improve the activity of the catalyst.

At high current densities, the best cell performance was predicted, and this should improve the activity of the catalyst.
and AM can be observed in Figure 2. These results are related to the presence of a high amount of unalloyed Co (in the oxide form) in the H5 sample and to the large metal particle sizes for Pt/C and the AM Pt85Co15/C electrocatalysts, causing diffusion limitations in the gas phase at the catalyst particles.

Considering the good kinetic parameters and the acceptable degree of alloying, a study of the effect of the nominal Co amount on the PEMFC performance was carried out with the catalysts prepared by the alloying method. The results of XRD analysis on the carbon-supported Pt–Co electrocatalysts with various Co contents are reported in Figure 4 and Table 3. The value of the lattice parameter of the Pt80Co20/C electrocatalyst was higher than that of Pt alone, because of the larger Pt particle size of the binary electrocatalyst. It is known that the lattice parameter of supported Pt is smaller than that of bulk Pt and, as expected, this value grows toward the bulk value (0.39231 nm) with increasing Pt particle size. In addition to the five main characteristic peaks of the Pt fcc structure, other four weak reflections (represented by an asterisk in Figure 4) were found for the Pt75Co25/C electrocatalyst, which are assigned to a superlattice structure, showing the formation of the ordered Pt3Co alloy phase in this electrocatalyst. As shown in Figure 5, the metal particle size decreases with the nominal Co/Pt atomic ratio. This means that the sintering rate of the Pt particles decreases with increasing Co amount in the electrocatalyst. The growth of Pt–M metal particles following alloy preparation by AM is higher for Co than for other metals, such as Cr, Fe, and Ni. Then, it can be assumed that the presence of a small amount of Co enhances the sintering of Pt particles, but an excess of Co may hinder the motion of Pt atoms on the carbon surface. Figure 6 shows the dependence of the Pt lattice constant on the nominal Co atomic fraction $x_{Co} = Co/Pt/(1 + Co/Pt)$. Assuming that the dependence of the lattice parameter on Co content is the same for supported and unsupported Pt–Co alloys, the lattice parameter of carbon-supported Pt–Co, $a_c$, results

$$a_c = a_o - k x_{Co}$$

where $a_o$ is the lattice parameter of pure carbon-supported Pt, and $k$ is a constant obtained from the lattice parameters of
unsupported Pt and PtCo alloys, applying the Vegard’s law (0.0368 nm). The dotted line in Figure 6 represents the theoretical dependence of the lattice parameter on $x_{\text{Co}}$, calculated on the basis of eq 7, assuming that all the cobalt present in the catalyst is alloyed with Pt. As can be seen in Figure 6, with increasing Co content, the difference between the experimental and the theoretical value of the lattice parameter decreases, indicating a higher degree of Co alloying (see Table 3). Considering that the particle size decreases with increasing Co content, we can infer that Co alloying occurs more readily in the presence of smaller Pt particles. To confirm this hypothesis, a linear dependence of the degree of alloying on metal particle size can be observed in Figure 7.

Figure 8 shows the H$_2$/O$_2$ PEMFC performance with Pt–Co/C electrocatalysts with various metal compositions. The kinetic parameters obtained from the experimental results reported in Figure 8 are presented in Table 4. Within the fitting error, the Tafel slope $b$ is the same for all catalyst compositions. The Pt$_{75}$Co$_{25}$/C electrocatalyst exhibits the best performance both at low and high current densities.

According to Mukerjee et al., a plot of electrocatalytic activity ($j_{900mv}$) versus the mean interatomic distance exhibits a volcano type behavior. They obtained different mean interatomic distances by alloying different metals with Pt, with Pt–Cr lying at the top of the curve, at about 0.273 nm. As shown in Figure 3, the results of this work are in good agreement with those of Mukerjee et al., with the maximum value of activity at the same mean interatomic distance. The mean interatomic distance of the Pt$_{75}$Co$_{25}$/C electrocatalyst is near the top of this curve, thus showing the best activity for the ORR. Also, at high current densities the Pt$_{75}$Co$_{25}$/C electrocatalyst presented the best performance, because of both the low amount of unalloyed Co and the relatively small metal particle size, resulting in an increased limiting current.

A morphological and electrochemical analysis of the Pt$_{75}$Co$_{25}$/C electrocatalyst prepared by alloying at 900 °C was carried out. Figures 9 and 10 show, respectively, the TEM image of the carbon-supported Pt$_{75}$Co$_{25}$ alloy catalyst and the corresponding particle size distribution histogram constituted with the data collected from more than 700 nanoparticles. As can be seen, the Pt–Co alloy nanoparticles tend to form aggregates, because of the thermal treatment at high temperature. The mean particle size is about 3.9 ± 1.2 nm in diameter with a tail in the larger particle size region.

A low magnification HRTEM image of the electrocatalyst is shown in Figure 11a. Two-dimensional projections give the impression of spherical or elliptical shapes, as opposed to faceted shapes such as cuboocahedral. However, apparent rounding of particles can be caused by two effects: (i) the inclination of the particles from the low index zone axis make the faceted corners appear to be slightly curved and (ii) even when particles are aligned along low index zone axis they can appear to be spherical because of interference from the carbon substrate that obscures sharp edges and corners. However, a detailed image of a single particle at high magnification, Figure 11b, does show the faceted shape characteristic of fcc asymmetric or symmetric cuboocahedral nanocrystals. Combined HRTEM/EDX analysis of the sample indicated that the Pt:Co atomic composition of the alloy particle is 81:19, in good agreement to that calculated from the XRD measurements (bulk composition Pt:Co = 80:20).

Figure 9. TEM micrograph of the electrocatalyst Pt$_{75}$Co$_{25}$/C. Magnification 150 000.

Figure 10. Histogram of Pt particle size distribution in the Pt$_{75}$Co$_{25}$/C electrocatalyst.

Figure 11. HRTEM micrograph of the electrocatalyst Pt$_{75}$Co$_{25}$/C, (a) low magnification and (b) high magnification.
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Figure 12. Cyclic voltammograms for (a) Pt/C E-TEK and (b) as prepared Pt_{75}Co_{25}/C electrodes upon various cycles.

The cyclic voltammograms of a commercial 20% Pt/C (E-TEK) and the Pt_{75}Co_{25}/C electrocatalysts for several consecutive cycles are presented in Figure 12a and 12b, respectively. As can be seen, the alloyed electrocatalyst exhibits a high stability upon cycling. This result explains the high stability found for the PtCo electrocatalyst in PEMFC, which shows only negligible losses in performance over a period of 400 h.

To evaluate further the stability of the Pt_{75}Co_{25}/C electrocatalyst, SEM/EDX analysis was carried out following 24 h of cell operation. The Pt:Co atomic ratio increased to 82:18, from the value of the alloy composition (75:25). XRD analyses before and after cell operation and the performance of electrode kinetic parameters after the short duration test confirmed that the amount of alloyed cobalt did not change. So, the amount of cobalt lost was ascribed to the loss of nonalloyed cobalt.

4. Conclusions

Of the three preparation methods of carbon-supported Pt_{75}Co_{15} electrocatalysts tested, the best result in terms of activity for the ORR and degree of alloying was obtained by preparing the electrocatalyst with the alloying method. Using this method to prepare Pt–Co/C in different ratios, it was found that the best composition was Pt:Co = 75:25 (with degree of alloying 80%). The Pt_{75}Co_{25}/C electrocatalyst showed good alloying, almost the ideal mean interatomic distance and relatively small particle size, good performance both at low and high current densities, and good stability upon cycling.

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References and Notes

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