

Short communication

Carbon supported Pt₇₀Co₃₀ electrocatalyst prepared by the formic acid method for the oxygen reduction reaction in polymer electrolyte fuel cells

José R.C. Salgado, Ermete Antolini, Ernesto R. Gonzalez*

Depto. de Fisico-Química, Instituto de Química de São Carlos, Universidade de São Paulo (USP), C.P. 780, Av. Dr. Carlos Botelho 1465, São Carlos, SP 13560-970, Brazil

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Abstract

Carbon supported Pt and Pt₇₀Co₃₀ electrocatalysts for the oxygen reduction reaction (ORR) were prepared by reduction with formic acid and tested in polymer electrolyte fuel cells. In the presence of Co an increase of the Pt particle size was observed in the as-prepared electrocatalyst and no evidence of Pt–Co alloy formation was detected from XRD measurements. Following thermal treatment (TT) at 900 °C of the Pt₇₀Co₃₀/C electrocatalyst, the presence in the XRD pattern of secondary Pt reflexions shifted to higher angles indicated partial alloy formation. The fuel cell performance with the as-prepared Pt₇₀Co₃₀/C electrocatalyst was inferior than that with Pt/C. The electrocatalytic activity increased with a TT of the binary electrocatalyst, and the value of the mass activity of the Pt₇₀Co₃₀/C electrocatalyst thermally treated at 900 °C was only slightly lower than that of Pt/C, notwithstanding the larger metal particle size, about five times that of pure Pt. On the other hand, there was a remarkable increase of the specific activity for the ORR of the Co-containing catalyst after TT at 900 °C with respect to Pt alone, which was ascribed to both the increased metal particle size and alloy formation. At high current densities the performance of PEMFC electrodes decreased with increasing Pt particle size.

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1. Introduction

It has been observed that the use of Pt–Co electrocatalysts for the oxygen reduction reaction (ORR) may improve the cell performance with respect to Pt alone in phosphoric acid (PAFC) [1,2] and in polymer electrolyte (PEMFC) [3–5] fuel cells. The activity enhancement using supported Pt alloy electrocatalysts was ascribed to geometric factors (decrease of the Pt–Pt bond distance) [6], electronic factors (increase of Pt d-electron vacancy) [7], change in surface structure [1]

or dissolution of the more oxidisable alloying component [8]. On the basis of the ORR activity versus Pt–Pt bond distance volcano plot and the dependence of the Pt–Pt distance on Co content in the alloy, the optimum Pt:Co atomic ratio was about 3:1 [9]. On the other hand, according to Xiong et al. [10], who prepared various carbon supported Pt–M electrocatalysts by a low temperature reduction procedure with sodium formate, the Pt–Co electrocatalyst showed the best performance with the maximum catalytic activity and minimum polarization at a Pt:Co atomic ratio of around 1:7.

By a critical examination of X-ray photoelectron spectroscopic data, Arico et al. [11], observed that the amount of platinum oxide in the alloy electrocatalysts decreases with the increase of the content of Co and Cr metals. According

* Corresponding author. Tel.: +55 16 3373 9899; fax: +55 16 3373 9952.
E-mail addresses: salgado@iqsc.usp.br (J.R.C. Salgado),
ermete@iqsc.usp.br (E. Antolini), ernesto@iqsc.usp.br (E.R. Gonzalez).

to the authors, this is primarily due to the oxide-cleansing action of the transition metals from the Pt surface. It is worth noting that Cr and Co are electropositive elements in relation to Pt and, hence, Pt atoms could induce an electron withdrawing effect from the neighbouring Cr and Co atoms in the alloy bringing about the oxide-cleansing action. The authors believe that the primary factor which makes the alloy electrocatalysts exhibit a higher electrocatalytic activity towards the ORR than Pt is the lower oxidation state of Pt in the alloy as compared to pure Pt. In a similar study on Pt binary and ternary alloys, Shukla et al. [12] found that Pt–Co/C electrocatalysts have a low amount of Pt oxides.

Recently, Stamenkovic et al. [13,14] attributed the enhancement of the catalytic activity of Pt₃Ni and Pt₃Co alloy surfaces for the ORR to the inhibition of Pt–OH_{ad} formation on Pt sites surrounded by “oxide”-covered Ni and Co atoms beyond 0.8 V.

Conflicting results on electrocatalytic activity [6,15] and dissolution of the non-noble metal components in the PAFC environment [8,16] suggested the possibility of differences in the electrochemical properties of bulk versus supported alloy electrocatalysts [4]. Thus, the improvement in ORR activity observed in gas diffusion electrodes for several Pt-alloy electrocatalysts could be attributed to factors specific of small particle size electrocatalysts or related to the structural factors of the cell geometry. In the light of this, the preparation method of these electrocatalysts, affecting their chemical and morphological characteristics, becomes very important. Results obtained with different methods vary because the properties of the material, as well as the degree of alloying and metal particle size, depend on the preparation procedure.

The method commonly used to prepare Pt–Co/C electrocatalysts consists in the deposition and reduction of the Co precursor on previously formed Pt/C, followed by alloying at high temperature [1,2,12]. Recently, low temperature Pt–Co/C preparation methods by simultaneous deposition and reduction of Pt and Co have been tested [5,10,17].

This work deals with the preparation of carbon supported Pt–Co electrocatalysts using a method developed in this laboratory for the preparation of Pt/C [18], which starts with the treatment of carbon powder with formic acid. In contact with a H₂PtCl₆ solution the treated carbon reduces Pt(IV) on its surface. This method produced good results for the preparation of Pt/C. In a work comparing different preparation methods of carbon supported platinum (Pt/C) the material obtained with the formic acid method (FAM) presented the best performance [19].

On the other hand, the performance of Pt–Ru/C prepared by the FAM as CO-tolerant anodic material for PEMFC was lower than that of Pt–Ru/C electrocatalysts prepared by other synthetic routes, owing to the difficulty in obtaining electrocatalysts with a Ru:Pt atomic ratio higher than 16:84 [20]. But, in recent work, Pt–Ru/C electrocatalysts with a Ru:Pt atomic ratio of 25:75, were obtained by a slightly modified FAM. These electrocatalysts showed a good performance as CO-tolerant anode materials in PEMFCs [21].

2. Experimental

2.1. Preparation of the electrocatalysts

Pt/C and Pt₇₀Co₃₀/C (nominal composition) electrocatalysts were prepared by the formic acid method (FAM) [18], by addition of a formic acid solution to high surface area carbon (Vulcan XC-72, Cabot, 240 m² g⁻¹) at 80 °C. Chloroplatinic acid (H₂PtCl₆·6H₂O, Johnson Matthey) solution was slowly added to the dispersion to obtain Pt/C, and, in the case of the Pt₇₀Co₃₀/C electrocatalyst, a cobalt hydroxide (Co(OH)₂·6H₂O, Aldrich) solution was also added. Heat treatments (TT) were carried out at 500 and 900 °C in an H₂/Ar (1:9) atmosphere for 1 h. The materials were made 20% (w/w) metal on carbon.

2.2. Electrode preparation and test in single PEMFC

In order to test the electrochemical behaviour in a single PEMFC fed with hydrogen/oxygen, the Pt–Co/C electrocatalyst was 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). On top of this layer, the electrocatalyst was applied in the form of an homogeneous dispersion of Pt₇₀Co₃₀/C, or Pt/C, Nafion[®] solution (5%, Aldrich) and isopropanol (Merck) [22]. All electrodes were made to contain 0.4 mg Pt cm⁻² (geometric area). 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 using them, 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 °C (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 ratio of the Pt₇₀Co₃₀/C electrocatalyst was 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 electrocatalysts were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu K α radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 20 mA. Scans were done at 3° min⁻¹ for 2θ values between 20° and 100°. In order to estimate the particle size from XRD, Scherrer's equation was used [23]. For this purpose, the (2 2 0) peak of the Pt face centered cubic (f.c.c.)

structure around $2\theta = 70^\circ$ was selected, to avoid the influence of a broad band of the carbon substrate. In order to improve the fitting of the peak, recordings for 2θ values from 60° to 80° were done at $0.02^\circ \text{ min}^{-1}$. The lattice parameters were obtained by refining the unit cell dimensions by the least squares method [24].

3. Results and discussion

The actual composition of the $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalyst was evaluated by EDX analysis. It was found that the EDX composition in different parts of the as-prepared $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalyst goes from 60:40 to 80:20, indicative of a non-homogeneous distribution of Co in the electrocatalyst. Following thermal treatment (TT) at 900°C , instead, the EDX composition in different parts of the electrocatalyst was very close to the nominal value, i.e. a homogeneous dispersion of Co atoms was observed.

Fig. 1(a) shows the XRD diffractograms of the as-prepared Pt/C and the as-prepared and TT $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalysts. No shift of Pt reflexions towards higher angles, typical of Pt–Co alloy formation, was detected. The absence of alloying may be due to the fact that the reducing power of formic acid is not strong enough to allow the formation of Pt–Co

crystallites. The presence of secondary Pt reflexions shifted to higher angles, as shown in Fig. 1(b) for the (3 1 1) Pt peak, was observed in the XRD pattern of the Co-containing electrocatalyst when thermally treated at 900°C in a reducing atmosphere. These reflexions were ascribed to Pt–Co alloy formation in the bulk of the smaller Pt particles and/or in the external part of the larger Pt particles. The presence of CoO or Co_3O_4 reflexions was not observed in the diffractograms. It is highly probable that particles of cobalt oxide that may be present are very fine nanocrystals or have an amorphous structure, so they are not detected.

The incorporation of cobalt in the electrocatalyst gives rise to the formation of abnormally big particles during the preparation of the electrocatalysts. As can be seen in Table 1, the Pt particle size of $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalyst is about twice that of Pt/C. During the TT coalescence and sintering lead to the formation of Pt particles up to 21.3 nm for $\text{Pt}_{70}\text{Co}_{30}/\text{C}$.

The current–potential curves obtained in single fuel cells were analysed using the semi-empirical equation [25–27]:

$$E = E_0 - b \log j - Rj \quad (1)$$

where E_0 is a constant given by

$$E = E_r - b \log j_0 \quad (2)$$

Here, E_r is the reversible potential of the cell, b the Tafel slope, j_0 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, electronic resistances 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 electrocatalyst [26,27]. Since Eq. (1) does not include diffusion limitations other than linear contributions, and because a change in the Tafel slope from 60 to $120 \text{ mV decade}^{-1}$ is expected for the ORR at potentials around 0.8 V [25,28], only the region for $E > 0.8 \text{ V}$ was considered in these analyses. The parameters E_0 , b and R were obtained using a least squares Levenberg–Marquardt fitting procedure [25].

Fig. 2 shows the current–potential curves for a single PEMFC using as cathodes the as-prepared Pt/C and as-prepared and TT $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalysts. The kinetic parameters obtained from the experimental results reported in Fig. 2 are presented in Table 2. Using the R values, jR -corrected Tafel plots ($E + jR$ versus $\log j$), obtained with the raw experimental results reported in Fig. 2, were constructed and the results are presented in Fig. 3. As it is evident from Fig. 3, in this restricted potential region the as-prepared $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalyst presents a lower electrocatalytic activity for the ORR, as compared to that on the Pt/C electrocatalyst. A lower activity in terms of the geometric surface area of the electrode is indicated by the values of E_0 , the current density at 900 mV and the potential at 10 mA cm^{-2} (activation controlled region). This result is due to the larger

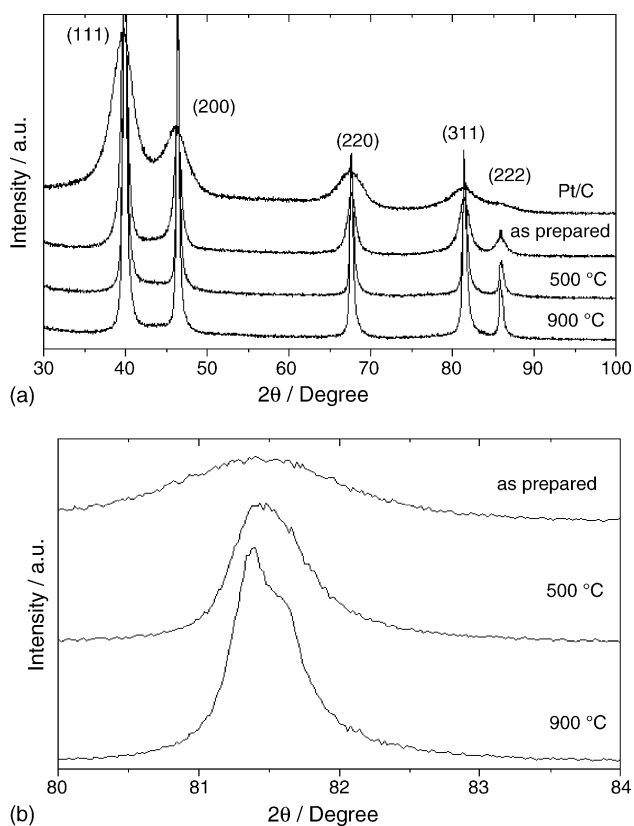
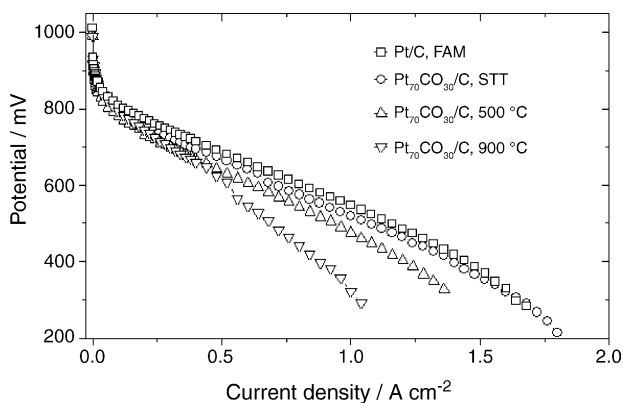


Fig. 1. (a) XRD diffractograms of as-prepared Pt/C and as-prepared and thermally treated $\text{Pt}_{70}\text{Co}_{30}/\text{C}$ electrocatalysts; (b) detailed f.c.c. (3 1 1) peaks of Co containing electrocatalysts.

Table 1

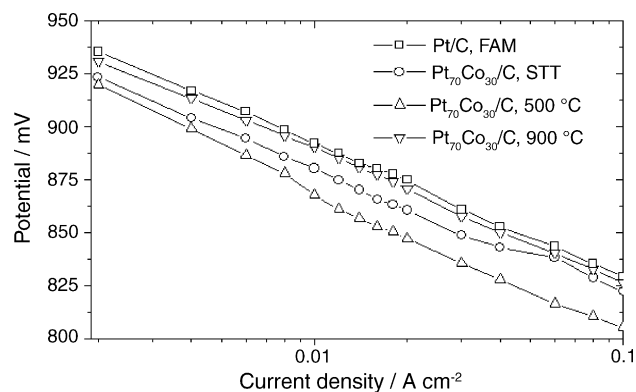
EDX composition and structural characteristics by XRD analysis of the carbon supported Pt and Pt₇₀Co₃₀ electrocatalysts prepared by the formic acid method

Catalyst	EDX Pt:Co	Thermal treatment (°C)	Pt lattice parameter (nm)	Pt particle size (nm)
Pt/C	100:0	None	0.39075	4.5
Pt ₇₀ Co ₃₀ /C	71:29	None	0.39159	7.9
		500	0.39143	13.2
		900	0.39172	21.3

Fig. 2. H₂/O₂ PEM fuel cell polarization curves with Pt₇₀Co₃₀/C and Pt/C electrocatalysts for oxygen reduction at 80 °C and 1 atm.

Pt particle size and/or the presence of CoO_x in the binary electrocatalysts, causing a decrease of the electrochemically active area. The increase in the value of R is due to an increase in the linear diffusion component, as a consequence of the decrease in the electrochemically active area. Following the TT at 500 °C, in terms of mass activity the binary electrocatalyst showed a lower electrocatalytic activity for the ORR, as compared to that of the untreated sample, due to the increase of Pt particle size. Indeed, according to Kinoshita [29], the mass activity versus Pt particle size plots for oxygen reduction exhibit a maximum at $d=3.5$ nm, and then a decrease with increasing Pt particle size.

An enhancement of the activity of Pt–Co/C electrocatalysts for the ORR was observed by increasing the TT temperature from 500 to 900 °C, as attested by the values of E_0 , $j_{900\text{mV}}$ and $E_{10\text{mAcm}^{-2}}$ (Table 3), attaining values near to those for pure Pt, notwithstanding a Pt particle size about five times larger. In particular, the values of E_0 for the electrode with the Pt₇₀Co₃₀/C electrocatalyst thermally treated at 900 °C (Pt particle size = 21.3 nm) and of the electrode with pure Pt (Pt particle size = 4.5 nm) were comparable, 951 and 955 mV, respectively. In the case of Pt/C by ETEK, in-

Fig. 3. Ohmic drop corrected Tafel plots for the oxygen reduction reaction in PEM fuel cells at 80 °C and 1 atm for Pt₇₀Co₃₀/C and Pt/C electrocatalysts.

stead, going from a Pt/C ratio of 40 wt.% to a Pt/C ratio of 60 wt.%, corresponding to Pt particle sizes of 4 and 8.5 nm, respectively [30], E_0 presented a large decrease, from 960 to 915 mV [22].

The effect of Co on the specific activity (SA) was estimated considering that, in a first approximation, the electrochemically active surface area is proportional to the platinum surface area. On this basis, being the platinum surface area inversely proportional to the particle size d , the PtCo to Pt specific activity ratio is given by

$$\frac{SA_{\text{PtCo}}}{SA_{\text{Pt}}} = \left(\frac{MA_{\text{PtCo}}}{MA_{\text{Pt}}} \right) \left(\frac{d_{\text{PtCo}}}{d_{\text{Pt}}} \right) \quad (3)$$

where $MA = j_{900\text{mV}}$ is the mass activity.

As can be seen in Table 2, the $SA_{\text{PtCo}}/SA_{\text{Pt}}$ ratio increases following TT at 500 °C, and to a large degree, after TT at 900 °C. The increase following annealing at 500 °C is due to the particle size effect. Indeed, as reported in [31–33], the catalytic activity increases with increasing Pt particle size, due to the less strong adsorption of OH on larger particles. As the particle size increases the d-band vacancy decreases and this in turn suggests that the adsorption strength of adsorbed oxygen species decreases. So, the reduction of in-

Table 2

Kinetic parameters for the ORR obtained from the fitting of Eq. (1) to the experimental polarization results for the cathode made with the prepared electrocatalysts

Catalyst	E_0 (mV)	b (mV decade ⁻¹)	R (Ω cm ²)	$j_{900\text{mV}}^a$ (mA cm ⁻²)	$E_{10\text{mAcm}^{-2}}^b$ (mV)	$SA_{\text{PtCo}}/SA_{\text{Pt}}$
Pt/C	955	63	0.19	7.3	890	–
Pt ₇₀ Co ₃₀ /C	933	55	0.22	3.0	872	0.72
Pt ₇₀ Co ₃₀ /C (500 °C)	941	74	0.24	3.8	862	1.53
Pt ₇₀ Co ₃₀ /C (900 °C)	951	62	0.32	6.3	887	4.09

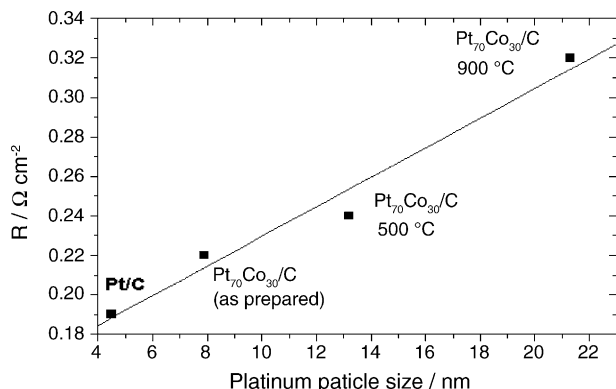
^a Current density at 900 mV.

^b Potential at 10 mA cm⁻².

Table 3

Kinetic parameters for the ORR of PEMFC cathodes made with carbon supported Pt–Co electrocatalysts obtained by different methods of preparation

Catalyst	E_0 (mV)	b (mV decade ⁻¹)	R (Ω cm ²)	$j_{900\text{mV}}^a$ (mA cm ⁻²)	$E_{10\text{mA cm}^{-2}}^b$ (mV)
Pt ₇₀ Co ₃₀ /C by the formic acid method	951	62	0.32	6.3	887
Pt ₈₅ Co ₁₅ /C by the borohydride method [5]	961	65	0.18	8.0	894
Pt ₇₅ Co ₂₅ /C by the alloying method [9]	975	65	0.21	13.7	911

^a Current density at 900 mV.^b Potential at 10 mA cm⁻².Fig. 4. Dependence of the R value (see text) on metal particle size.

intermediates containing oxygen on the Pt surface is more facile. As reported by Kinoshita [29], a large increase in specific activity occurs between 4.5 and 12 nm particles, which is less pronounced for Pt particle sizes larger than 12 nm. On this basis, the larger part of the difference in the specific activity between the catalyst thermally treated at 500 °C (Pt particle size = 12.4 nm) and that treated at 900 °C (Pt particle size = 21.3 nm) can be ascribed to alloy formation.

The increase of Pt particle size by the presence of Co and that following TT gives rise to an increasing tendency to reach limiting diffusional currents, as well as an increase of the R values for cathodes with the Pt₇₀Co₃₀/C electrocatalyst, as can be seen in Figs. 2 and 4.

In Table 3, the kinetic parameters for ORR of the PEFC cathode made with the Pt₇₀Co₃₀/C electrocatalyst thermally treated at 900 °C are compared with those of cathodes with carbon supported Pt–Co alloy catalysts prepared in our laboratory by other methods [5,9]. As can be seen, the values of the parameters for the catalyst prepared by the formic acid method are inferior to those of the catalysts prepared by the borohydride and the alloying methods. The lower ORR activity of Pt–Co/C prepared by the formic acid method is the result of poor alloying of the cobalt in the Pt f.c.c. lattice.

4. Conclusions

In the absence of thermal treatment carbon supported Pt₇₀Co₃₀ electrocatalysts prepared by the formic acid method are not alloyed, which may be due to the fact that the reducing power of formic acid is not strong enough to allow the for-

mation of Pt–Co crystallites. Following annealing at 900 °C in a reducing atmosphere the formation of a Pt–Co alloy in the external part of the metal particles takes place.

As-prepared Pt₇₀Co₃₀/C electrocatalysts show a reduced performance in PEMFC due to the increased Pt particle size. An improvement of the kinetic parameters was observed following thermal treatment, ascribed both to increased metal particle size and, after annealing at 900 °C, to alloy formation in the outer part of the metal particles.

It has to be remarked that the Pt₇₀Co₃₀/C electrocatalysts TT at 900 °C present a Tafel curve only slightly lower than that of pure Pt, notwithstanding a Pt particle size about five times larger than Pt/C. In the same way, the kinetic parameters E_0 , $j_{900\text{mV}}$ and $E_{10\text{mA cm}^{-2}}$ were only slightly lower than those of pure Pt.

Although the Pt₇₀Co₃₀/C catalysts prepared by reduction with formic acid cannot be considered good materials for PEMFCs, their preparation and study as presented in this work helped to identify important aspects of the chemical reduction methods to prepare supported catalysts and to understand the properties of the resulting materials, particularly with respect to the degree of alloying.

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