

Short communication

Preparation of Pt-Co/C electrocatalysts by reduction with borohydride in acid and alkaline media: the effect on the performance of the catalyst

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Abstract

Carbon supported Pt₈₅Co₁₅ electrocatalysts for the oxygen reduction reaction (ORR) in PEM fuel cells were prepared by reduction of Pt and Co precursors with sodium borohydride in acid and alkaline media at room temperature. The electrocatalyst prepared in the acidic conditions showed better kinetic parameters for the ORR than the electrocatalyst prepared in basic conditions. This result was ascribed to a higher degree of alloying, with a shortening of the Pt-Pt bond distance, of the sample prepared in acid medium. At high current densities, instead, the performance in PEM fuel cells of the carbon supported alloy prepared in acid medium was lower than that prepared in basic medium, due to the larger metal particle size.

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1. Introduction

Proton-exchange membrane (PEM) fuel cells have received considerable attention for transportation applications, distributed generation and portable applications due to the high energy density, relatively low operating temperature, zero or low emission of pollutants, and minimal corrosion problems. However, the commercial viability of PEM fuel cells is still hindered by several problems, including the poor kinetics of the cathodic reaction. It is well known that most of the performance losses in PEM fuel cells working with hydrogen and to some extent in those working directly with methanol come from the cathodic reaction, that is, the oxygen reduction reaction (ORR). Thus, many efforts are addressed to the improvement in oxygen reduction kinetics in PEM fuel cells.

Many investigations have shown that Pt-based alloy electrocatalysts [1–13], such as Pt-M, (where M = Co, Ni, Fe, V, Mn, and Cr), have significantly higher electrocatalytic activity for the oxygen reduction reaction than platinum for both phosphoric acid and PEM fuel cells. The improvement in

the ORR on Pt alloy electrocatalysts has been explained by considering several factors such as structural and electronic effects [2,6].

Usually, carbon supported Pt binary alloy electrocatalysts are prepared by impregnation of the second metal on platinum supported on carbon (Pt/C) and then by alloying at temperatures above 700 °C in an inert gas or hydrogen atmosphere [2,3,14]. This heat treatment at high temperatures can facilitate the growing of the alloy nanoparticles due to sintering and coalescence, which is undesirable because it may result in the decrease of the Pt mass activity for the ORR. Also, the control of the particle size distribution with this preparation method is quite limited. Recently, some groups have reported that Pt alloy electrocatalysts could be prepared by the co-reduction of the metallic salt precursors at low temperatures and that the obtained Pt alloy particle sizes are relatively small [15,16].

In this work, carbon supported Pt-Co electrocatalysts in the Pt:Co atomic composition ratio 85:15 were prepared by simultaneous reduction of Pt and Co ionic precursors with NaBH₄ at room temperature. Considering that minor changes in the preparation procedure may result in different characteristics and properties of the electrocatalysts the reduction process was carried out in acid and basic media. This allowed to determine the influence of the conditions on the metal particle size and the degree of alloying, as well as

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in the resulting performance as cathode materials in PEM fuel cells.

2. Experimental

2.1. Electrocatalysts preparation

2.1.1. Method A

Pt₈₅Co₁₅/C electrocatalysts were prepared by the borohydride method (BM), by impregnating high surface area carbon (Vulcan XC-72, Cabot, 240 m² g⁻¹) with a chloroplatinic acid (H₂PtCl₆·6H₂O, Johnson Matthey) and a cobalt hydroxide (Co(OH)₂·6H₂O, Aldrich) solutions. The cobalt hydroxide precursor was soluble in water:methanol 1:1 and a few drops of HCl were added until the pH of the solution was 2. The metals were then reduced with a sodium borohydride solution, which was slowly added to the precursors solution under sonication.

2.1.2. Method B

In this method, a cobalt hydroxide solution was prepared in water:methanol at pH = 2 and then the pH was increased with addition of NH₄OH solution until pH = 9. Then, the metals were reduced with a sodium borohydride solution, which was slowly added to the precursors solution under sonication.

Previous works with commercial materials were done using Pt₇₅Co₂₅/C electrocatalysts [4,5]. In the reduction with borohydride used here the concentration of the precursors was adjusted to give that atomic ratio. However, the resulting electrocatalysts prepared with both methods were found to be Pt₈₅Co₁₅/C. The materials used in this work were then prepared with this nominal composition. The materials were 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 PEM fuel cell fed with hydrogen/oxygen, the electrocatalysts 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). On top of this layer, the electrocatalyst was applied in the form of an homogeneous dispersion of Pt₈₅Co₁₅/C, or Pt/C, Nafion[®] solution (5%, Aldrich) and isopropanol (Merck) [17]. All electrodes were made to contain 0.4 mg Pt cm⁻². 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 PEM fuel cell was pre-conditioned 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 electrocatalysts 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 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 2 θ values between 20 and 100°. In order to estimate the particle size from XRD Scherrer's equation was used [18]. For this purpose, the (2 2 0) peak of the Pt face centered cubic (fcc) structure around 2 $\theta = 70^\circ$ was selected. In order to improve the fitting of the peak, recordings for 2 θ values from 60 to 80° were done at 0.02° min⁻¹. The lattice parameters were obtained by refining the unit cell dimensions by the least squares method [19].

3. Results and discussion

The composition of the Pt-Co/C prepared electrocatalysts was determined by EDX analysis. Fig. 1 shows the typical EDX spectrum of the as prepared Pt-Co sample by method B. It was found that the EDX atomic Pt:Co composition of that sample in various regions of the powders was 84:16, which is very close to the nominal value. A similar result was obtained for the sample prepared by method A.

The XRD patterns of Pt/C and Pt-Co/C electrocatalysts are given in Fig. 2(a). Details of the Pt (2 2 0) peaks of the binary electrocatalysts are shown in Fig. 2(b). In all the

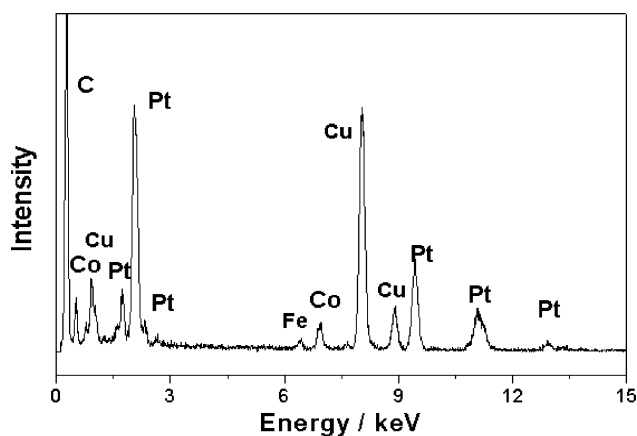


Fig. 1. EDX spectrum of the Pt-Co/C alloy electrocatalyst obtained by method B.

samples, apart from the first peak, related to carbon, only the reflexions corresponding to the planes (111), (200), (220), (311) and (222), characteristic of the fcc structure of Pt were present. With the introduction of Co into the fcc structure of Pt, the Pt reflexions were shifted to higher values of 2θ , which is indicative of a contraction of the lattice. No characteristic peaks of metallic Co or Co oxides were detected, but their presence cannot be discarded because they may be present in a very small amount or even in an amorphous form. Considering the (220) peak of the Pt fcc structure, Fig. 2(b) shows that the incorporation of Co promotes a shift to higher angles of the electrocatalyst obtained with method A as compared with the sample obtained with method B. This is indicative of the incorporation of a higher amount of Co atoms in the fcc structure of Pt in the catalyst prepared with method A. As a consequence, a slightly larger decrease of the lattice parameter was observed for the electrocatalyst prepared by method A compared to that obtained by method B, as shown in Table 1. Assuming that the dependence of the lattice parameter on Co content is the same for supported and unsupported Pt-Co alloys, the Co atomic fraction of carbon supported Pt-Co, x_{Co} , can be obtained from Vegard's law

$$x_{\text{Co}} = \frac{(a_o - a)}{k} \quad (1)$$

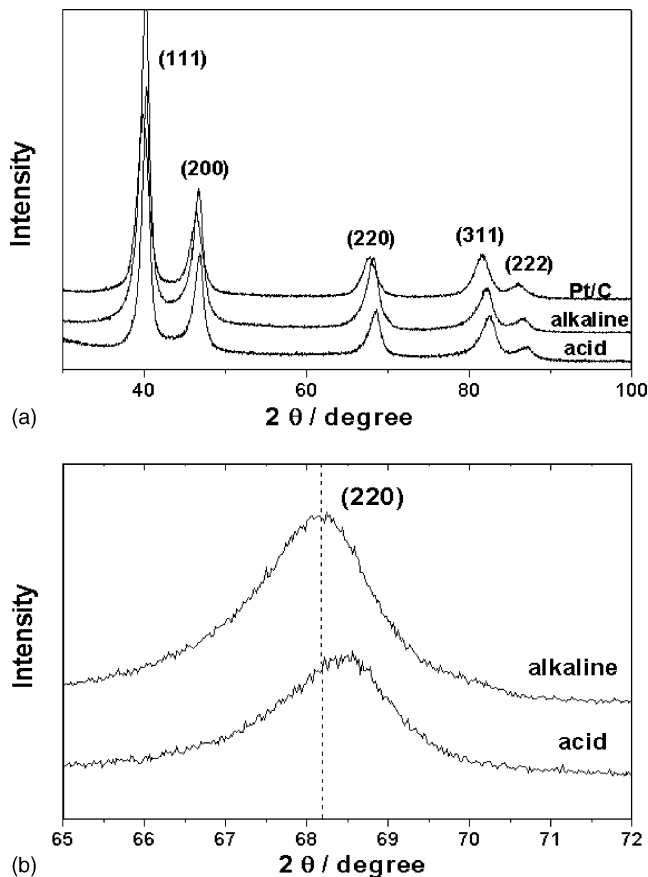


Fig. 2. (a) XRD diffractograms of carbon supported Pt and Pt-Co electrocatalysts. (b) Detailed fcc (220) peaks of Co containing alloys.

Table 1
Structural characteristics of the Pt-Co/C and Pt/C electrocatalysts

Electrocatalyst	Lattice parameter (nm)	Pt-Pt distance (nm)	Particle size (nm)
Pt/C	0.3901	0.2758	4.4
Pt-Co/C, method A	0.3871	0.2737	4.9
Pt-Co/C, method B	0.3874	0.2739	3.8

where a_o is the lattice parameter of pure carbon supported Pt, 0.3901 nm, and $k = 0.0368$ nm is a constant, obtained from the lattice parameters of unsupported Pt (0.3923 nm) and Pt₃Co alloy (0.3831 nm), assuming a linear dependence on Co atomic fraction. The values of x_{Co} for Pt-Co/C electrocatalysts obtained in acid and basic media were 0.08 and 0.07, respectively. This means that the degree of alloying was only about 43% of the total Co present in the electrocatalyst prepared by method B, and 49% for the sample prepared by method A. Table 1 also shows that the mean particle size of the materials prepared in acid medium is larger than that of the Pt-Co/C prepared in basic medium.

A similar effect of Co precursor solution pH on the physical characteristics of Pt-Co/C electrocatalysts was found by Beard and Ross [20] for Pt-Co electrocatalysts prepared by a different route. They prepared carbon supported Pt-Co (3:1 atomic ratio) electrocatalysts by impregnation of a Co precursor in both acid and alkaline aqueous media on previously formed Pt/C, followed by heat treatment to promote alloy formation. Significantly greater alloying and greatly increased particle size were observed in the electrocatalyst prepared in acid medium. Electrocatalysts prepared in alkaline medium, instead, were alloyed to a lesser extent and the particle size increased moderately.

According to the Pourbaix diagram [21], Pt is slightly soluble in chloride solutions at pH 2. So, it can be speculated that in acid conditions a process of dissolution/precipitation of metal particles takes place, promoting in this way the mixing of Pt and Co atoms and the growth of the carbon supported metal particles. Indeed, in basic medium Pt-Co crystallites nucleate and grow on the same site of the carbon

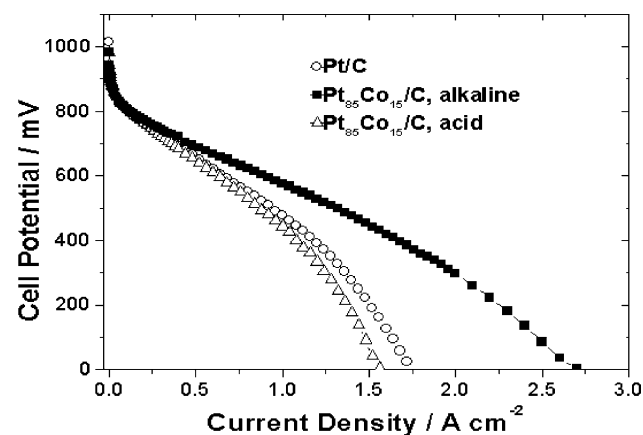


Fig. 3. H₂/O₂ PEM fuel cell polarization curves with Pt-Co/C and Pt/C electrocatalysts for oxygen reduction at 80 °C and 1 atm.

Table 2

Kinetic parameters for the ORR on Pt-Co/C and Pt/C electrocatalysts in PEM fuel cells at 80 °C and 1 atm pressure

Electrocatalyst	E_o (mV)	b (mV dec ⁻¹)	R (Ω cm ²)	$J_{900\text{mV}}$ (mA cm ⁻²)	$E_{10\text{mA cm}^{-2}}$ (mV)
Pt/C	955	65	0.22	6.3	887
Pt-Co/C, method A	962	62	0.27	9.3	898
Pt-Co/C, method B	961	65	0.18	8.8	894

Pt load: 0.4 mg cm⁻².

support up to the final particle size [20]. In acid medium, instead, smaller alloy particles dissolve before reaching the final size so, following the saturation of the solution, Pt and Co re-deposition occurs on pre-existing alloy particles.

The current–potential curves obtained in the single cell were analysed using the semi-empirical equation [22–24]

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

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 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 [23,24]. Since Eq. (2) does not include diffusion limitations other than linear contributions, and because a change in Tafel slope from 60 to 120 mV dec⁻¹ is expected for the ORR at potentials around 0.8 V [22,25], only the region for $E > 0.8$ V was considered in these analyses. The parameters E_o , b and R were obtained using a least squares Levenberg–Marquardt fitting procedure [22].

Fig. 3 shows the current–potential curves for a single PEM fuel cell using as cathodes the as prepared Pt/C and

Pt-Co/C electrocatalysts. The electrode kinetic parameters obtained from the experimental results reported in Fig. 3 are presented in Table 2. Within the fitting error, the Tafel slope b is not influenced by the electrocatalyst composition. Using the R values, jR -corrected Tafel plots ($E + jR$ versus $\log j$) were constructed and the results are presented in Fig. 4 for all the electrocatalysts studied. As it is evident from Fig. 4, both the Pt-Co/C electrocatalysts show a higher electrocatalytic activity for the ORR, as compared to that on the Pt/C electrocatalyst. An increase in the activity of the binary electrocatalysts in terms of the geometric surface area of the electrode is also indicated by the values of E_o , the current density at 900 mV and the potential at 10 mA cm⁻² (activation controlled region). As can be seen in Fig. 4 and Table 2, the activity for the ORR of the electrocatalyst prepared by method A is higher than that of the electrocatalyst obtained with method B. These results can be ascribed to the shortening of the Pt–Pt bond distance. A linear relation of the activity for the ORR ($j_{900\text{mV}}$) and the Pt–Pt bond distance of the electrocatalysts here investigated was obtained, as shown in Fig. 5. As shown by Mukerjee et al. up to the maximum value of the basic volcano plot (about 0.272 nm) [5], the lattice contractions due to alloying result in a more favourable Pt–Pt spacing for the dissociative adsorption of O₂.

As shown in Fig. 6, the cell resistance (R) in Eq. (2) increases with increasing the metal particle size, i.e. $R_{\text{PtCo}}^A > R_{\text{Pt}} > R_{\text{PtCo}}^B$, as a consequence of the decrease in the electrochemical active area. The difference in particle size is also responsible for the larger activity in the PEM fuel cells with

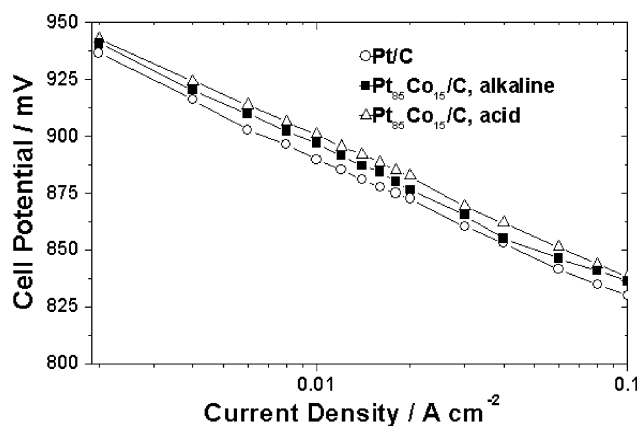


Fig. 4. Ohmic drop corrected Tafel plots for the oxygen reduction reaction in PEM fuel cells at 80 °C and 1 atm for Pt-Co/C and Pt/C electrocatalysts.

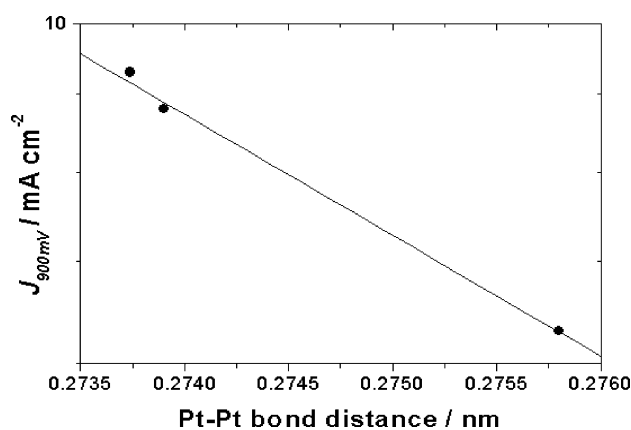


Fig. 5. Log of specific activity at 900 mV in PEM fuel cells vs. Pt–Pt neighbour distance for Pt-Co/C and Pt/C electrocatalysts.

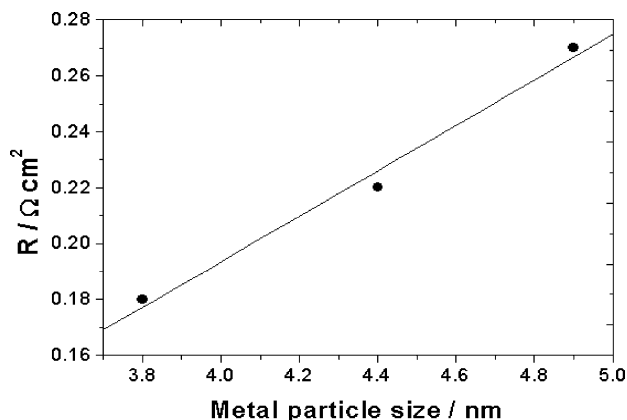


Fig. 6. Dependence of the R value (see Table 2) on metal particle size.

the material prepared in alkaline medium. The ratio of the current densities at 400 mV for the cells with the acid and alkaline materials is 0.70 (Fig. 3). This value compares well with the value of 0.77 obtained for the ratio of the particle sizes of the two materials (Table 1).

4. Conclusions

The results of this work show the importance of the control of the preparation conditions of Pt₈₅Co₁₅/C electrocatalysts on the performance in PEM fuel cells. Indeed, the physical characteristics of the electrocatalysts depend upon the solution chemistry under which they are prepared. As a consequence, their electrochemical properties also depend on the conditions used in the synthesis. When a Pt₈₅Co₁₅/C electrocatalyst is prepared from an acidic solution, the formation of a binary alloy with higher Co content and larger particle size is observed. This material presents an enhanced activity for the ORR in PEM fuel cells except at high current densities where the performance is lower due to the reduced electrochemically active area.

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