Pt-Co/C Electrocatalysts for Oxygen Reduction in H₂/O₂ PEMFCs Synthesized by Borohydride Method

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A Pt-Co/C electrocatalyst with Pt:Co atomic ratio 85:15, prepared by a low-temperature chemical reduction with sodium borohydride, was studied as possible cathode material for polymer electrolyte membrane fuel cells (PEMFCs). The physical characterization of this electrocatalyst was performed by energy-dispersive X-ray analysis, X-ray diffraction, and transmission electron microscopy. The performance of the catalytic material was evaluated by cyclic voltammetry and polarization experiments in a single PEMFC and compared with those of an unalloyed Pt/C catalyst prepared by the same method and a commercial Pt-Co/C catalyst. Both the Pt-Co/C catalysts were also submitted to a thermal treatment in a reducing atmosphere.

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Platinum catalysts still serve as state-of-the-art electrocatalysts in low-temperature polymer electrolyte membrane fuel cells (PEMFCs). However, due to kinetic limitations of the oxygen reduction reaction (ORR), the cathodic overpotential losses amount to 0.3-0.4 V under typical PEMFC operating conditions. The increased Pt catalytic activity observed for Pt alloys, particularly the intermetallic Pt₃Co, Pt and Co form a substitutional alloying component. Mukerjee et al. attributed the catalytic activity of Pt alloys to surface roughening, caused by the dissolution of the more oxidizable alloying metal, i.e., Pt alone, in phosphoric acid or alkaline medium, and in the proton exchange membrane fuel cell environment. The improvement in the ORR electrocatalysis of Pt alloys has been ascribed to different structural changes caused by alloying. Jalan and Taylor claimed that the increased Pt catalytic activity observed for Pt alloys is related to the shortening of the Pt-Pt interatomic distance. Paffett et al. attributed the enhancement of ORR activity on the alloys to surface roughening, caused by the dissolution of the more oxidizable alloying component. Mukerjee et al. and Min et al. attributed the enhancement of Pt catalytic activity to combined electronic (Pt d-band vacancy) and geometric (Pt—Pt bond distance) effects. Recently, Stamenkovic et al. attributed the enhancement of the catalytic activity for ORR on Pt₃Ni and Pt₃Co alloy surfaces to the inhibition of Pt-OHₐd formation on Pt sites surrounded by “oxide”-covered Ni and Co atoms beyond 0.8 V. By a critical examination of X-ray photoelectron spectroscopic (XPS) data, Arico et al. and Shukla et al. observed that the amount of platinum oxide in Pt-Co/C alloy electrocatalysts decreases with increasing content of Co. According to the authors, this is primarily due to the oxide-cleansing action of the transition metals from the Pt surface.

Among these Pt catalysts, Pt-Co alloys were extensively studied, particularly the intermetallic Pt₃Co. Pt and Co form a substitutional continuous solid solution in the whole range of composition and two ordered phases. In the region of 75% Pt, there is a face-centered cubic (fcc) superlattice Pt₃Co of the Cu₃Au (Li₃) type. Regular termination of the bulk Li₃ structure normal to the three major zone axes produces a variety of surface compositions, from the pure Pt [(200) and (220) planes], 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, i.e., surface enrichment without surface segregation. Mukerjee and Srinivasan rationalized the enhanced electrochemical performance in PEMFCs with commercial Pt-Co/C catalysts by E-TEK on the basis of the existence of an ordered Pt₃Co structure.

Generally, the main problems regarding the preparation of carbon-supported Pt-M alloys are the poor content of the nonprecious metal in the alloy, i.e., the true alloy composition has less of this metal than the nominal catalyst composition, and the increase of the particle size with respect to pure Pt. Also, the electrocatalytic activity increases, up to a certain value, with increasing particle size. This is attributed to a change in the distribution of surface atoms at the (100) and (111) crystal faces or to the Pt d-band occupancy; however, Pt agglomeration causes a decay in the catalyst performance owing to the decrease of platinum surface area per Pt unit mass. A common method of preparation of carbon-supported Pt-M alloys is deposition of the nonprecious metal on a previously formed carbon-supported platinum, followed by alloying at high temperatures. This thermal treatment at high temperatures (>900°C) gives rise to an undesired metal particle growth by sintering and coalescence of platinum particles. Using this method, Beard and Ross prepared Pt-Co/C catalysts in the atomic ratio 3:1 starting from commercial Pt/C in two ways. One way (series A) consisted in the preparation of an acidic (pH 2) CO(OH)₂ solution, followed by Pt/C addition into this solution. In the other way (series B), Pt/C was added into a basic (pH 11) solution of the cobalt precursor. Thermal treatments at 700, 900, and 1200°C under inert atmosphere were performed on each catalyst. In both series, Pt-Co alloy was not formed in the absence of thermal treatment. Following thermal treatment in series A, the lattice parameter decreased with increasing heating temperature, indicative of alloy formation. In series B, the lattice parameter decreased after heating but to a lesser extent than in series A. In all cases, the value of the lattice parameter was higher than the value of carbon-supported Pt₃Co (0.3854 nm). The particle size for series A at each thermal treatment temperature was larger than the corresponding catalyst in series B. The final particle size of the series A material treated at 1200°C (12 nm) was about four times greater than that of the starting Pt catalyst.

Shukla et al. prepared Pt-Co/C with a Pt:Co atomic ratio 1:1 nominal composition starting from 16 wt % Pt/Vulcan XC-72, dispersed in distilled water. The pH of the solution was raised to 8 with dilute ammonium hydroxide. The required amount of Co(NO₃)₂•6H₂O salt solution was added to this solution. This was followed by the addition of dilute HCl until a pH of 5.5 was attained. The resulting powder was heat-treated at 900°C in a nitrogen atmosphere for 1 h. The lattice parameter of the alloy was not indicated. By XPS measurements, they found some surface enrichment of platinum metal.

Min et al. prepared Pt-Co/C catalysts starting from commercially available 10 w% Pt/C catalyst. The appropriate amount of CoCl₂ solution was slowly added to Pt/C. The atomic ratio of Pt to Co was adjusted to 3:1. These catalysts were subjected to heat-
treatment at 700, 900, or 1100°C for 2.5 h in a reducing atmosphere (10% \( \text{H}_2 \) and 90% \( \text{N}_2 \)). These alloy catalysts exhibit fcc structures. As the heat-treatment temperature increases, the particle size increases from 3.0 to 8.6 nm, and the lattice parameter of the platinum clusters decreases from 0.3923 to 0.3855 nm.

Xiong \textit{et al.}\textsuperscript{28} prepared Pt-Co alloy catalysts in the Pt:Co atomic ratio 27:73 (20 wt %) \textit{in situ} on a high surface area Vulcan XC-72R support by reducing a mixture of chloroplatinic acid and the respective metal salt solution with sodium formate. Typically, the reduction reaction was carried out at 70°C. The reduction was also carried out by first adding a few drops of sodium borohydride followed by further reduction with sodium formate. The particle size was 3.6 nm and 4.5 nm, without and with sodium borohydride, respectively. The amount of cobalt alloyed with platinum was not reported.

This work deals with the preparation of carbon-supported Pt-Co catalysts in the atomic percent ratio 85:15 using a simple method based on the reduction of Pt and Co precursors with sodium borohydride at room temperature. This method was previously used to prepare Pt/C\textsuperscript{29} and Pt-Re/C\textsuperscript{30} electrocatalysts. The material was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray analysis (EDX). Gas-diffusion electrodes built with the catalysts were examined by cyclic voltammetry (CV) and current-potential experiments in a single PEMFC. The performance of a PEMFC using this material as cathode catalyst was compared with that obtained using both Pt/C prepared with the same method and a commercial Pt-Co/C (E-TEK) electrocatalyst.

**Experimental**

**Catalyst preparation.**—Pt/C and Pt-Co/C electrocatalysts were prepared by the borohydride method (BM), by impregnating high surface area carbon (Vulcan XC-72, Cabot, 240 m\(^2\) g\(^{-1}\)) with a chloroplatinic acid (\( \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}, \text{Johnson Matthey} \)) solution and, in for the Pt-Co/C catalyst, a cobalt hydroxide (\( \text{Co(OH)}_2 \cdot 6\text{H}_2\text{O}, \text{Aldrich} \)) solution. The metals were then reduced with a sodium borohydride solution, which was slowly added to the precursors solution under sonication. The materials were 20% w/w metal on carbon.

Heat treatments were carried out at 500°C in an \( \text{H}_2/\text{Ar} \) (1:9) atmosphere for 1 h.

**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 gas-diffusion electrodes. A diffusion layer was made with carbon powder (Vulcan XC-72) and 15% w/poly(tetrafluoroethylene) and applied on a carbon cloth (PWB-3, Stackpole). On top of this layer, the catalyst was applied in the form of a homogenious dispersion of Pt-Co/C, or Pt/C, Nafion solution (5%, Aldrich), and isopropanol (Merck).\textsuperscript{31} All electrodes were made to contain 0.4 mg Pt cm\(^{-2}\). After drying, a prepared cathode and anode containing 20% Pt/C E-TEK 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 \( \text{H}_2\text{O}_2 \), washed, and then treated with a 0.5 mol L\(^{-1}\) \( \text{H}_2\text{SO}_4 \) solution. The geometric area of the electrodes was 4.62 cm\(^2\). 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.

**EDX.**—The atomic ratios of the Pt-Co/C catalysts were determined by using the EDX technique coupled to a scanning electron microscopy LEO Mod. 440 with a silicon detector with Be window and applying 20 keV.

**XRD.**—X-ray diffractograms of the catalysts were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu K\( \alpha \) radiation (\( \lambda = 0.15406 \) nm) generated at 40 kV and 20 mA.

Scans were done at 3° min\(^{-1}\) for 20 values between 30 and 100°. To estimate the particle size from XRD, Scherrer’s equation was used.\textsuperscript{32} For this purpose, the (220) peak of the Pt fcc structure around 2\( \theta = 70° \) was selected. To improve the fitting of the peak, recordings for 20 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.\textsuperscript{33}

**TEM and HRTEM.**—The samples for the TEM characterizations were prepared as follows: a carbon film was deposited on a mica sheet that was placed on the Cu grids (300 mesh and 3 mm diam). The material to be examined was dispersed in water by sonication, placed on the carbon film, and left to dry. Histograms of particle sizes were constructed using about 300 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.

**CV.**—The electroactive areas of the catalysts were determined through the oxidation of adsorbed CO at room temperature. After recording a CV in an \( \text{N}_2 \) purged system, CO was admitted to the cell and adsorbed at 0.075 V for 10 min. The excess CO was eliminated with \( \text{N}_2 \) gas and the stripping charges determined between 0.075 and 1.200 V vs. a reference hydrogen electrode using a scan rate of 10 mV s\(^{-1}\) and correcting the currents for the background. The experiments were done with a 1285A Solartron potentiostat connected to a personal computer and using the software Corrware for Windows (Solartron).

**Results and Discussion**

**EDX analysis.**—The metal compositions of the catalysts were determined by EDX. For the Pt-Co/C material prepared by the BM it was 85:15 in atoms. For the commercial material Pt-Co/C E-TEK it was 50:50 in atoms.

**XRD analysis.**—Figure 1 and 2 show the XRD patterns of Pt/C and Pt-Co/C, respectively. In all the samples, apart from the first peak related to carbon, only the reflections 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 reflections were shifted to higher values of 2θ, which is characteristic of a contraction of the lattice. No peaks characteristic of Co or Co oxides were detected, but their presence cannot be discounted because they may be present in very small amounts or even in an amorphous form. The peaks for the catalysts prepared by reduction with borohydride were sharper than those for the commercial materials, indicating that the former have larger particle sizes. Table I shows the values of the lattice parameter, Pt—Pt distance, mean particle size, and specific surface area determined from the XRD analysis for all the catalysts, and with and without thermal treatment. The values of the lattice parameter and the Pt—Pt distances were smaller for the Pt-Co materials than for Pt, corresponding to the contraction of the lattice due to the partial substitution of Pt by Co in the fcc structure. A further decrease in the lattice parameter was observed for the materials submitted to thermal treatment at 500°C. The results also indicated that the Pt-Co material with 15 atom % Co prepared by reduction with borohydride has almost the same lattice parameter than the E-TEK material with 50 atom % Co. From the local EDX analysis performed with the HR-TEM (as shown later), the composition of an individual Pt-Co alloy particle was 91:9. Thus, although the alloy composition of the catalyst prepared by the BM was not too far from the nominal composition (85:15), for the commercial catalyst most of the Co was unalloyed. The decrease of the lattice parameter following the thermal treatment attested the presence of unalloyed cobalt in both catalysts. Part of the oxidized materials is reduced and converted into alloys during heating. The value of the lattice parameter of thermally treated commercial samples corresponds to the value of carbon-supported Pt formed in the literature.11,13 Table I also shows that the mean particle size of the materials prepared by reduction with borohydride was larger than that of the E-TEK material for both pure Pt and Pt-Co catalysts. Also, the particle size of the prepared material increased with the thermal treatment, due to coalescence of the Pt particles, an effect that does not seem to happen with the E-TEK Pt-Co catalysts. The different tendencies to sintering and coalescence of the metal particles reflects the different preparation methods. The stability of the metal particles depends on the surface acid-base properties of the carbon support. The surface oxygen-containing functional groups may act as anchoring centers for the metal particle limiting their growth. The acidic-basic environment present on the surface of the carbon particles during the impregnation with the precursors may modify the number and the characteristics of these anchoring centers, thus affecting the surface diffusion of the Pt particles on the carbon during the thermal treatment.11,13

Table I. Structural characteristics of the Pt and Pt-Co electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice parameter (nm)</th>
<th>Distance Pt—Pt (nm)</th>
<th>Mean particle size by XRD (nm)</th>
<th>Surface area by XRD (m² g⁻¹)</th>
<th>Surface area by CV (m² g⁻¹)</th>
<th>SA CV /SA XRD</th>
<th>Roughness factor (cm² cm⁻²)</th>
</tr>
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<tbody>
<tr>
<td>Pt/C, BM</td>
<td>0.3901</td>
<td>0.2758</td>
<td>4.4</td>
<td>64</td>
<td>32</td>
<td>0.50</td>
<td>128</td>
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<tr>
<td>Pt-Co/C, BM</td>
<td>0.3874</td>
<td>0.2739</td>
<td>3.8</td>
<td>73</td>
<td>35</td>
<td>0.48</td>
<td>140</td>
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<tr>
<td>Pt-Co/C, BM, TT</td>
<td>0.3860</td>
<td>0.2729</td>
<td>5.4</td>
<td>51</td>
<td>30</td>
<td>0.59</td>
<td>120</td>
</tr>
<tr>
<td>Pt/C, E-TEK</td>
<td>0.3904</td>
<td>0.2761</td>
<td>2.8</td>
<td>100</td>
<td>61</td>
<td>0.61</td>
<td>244</td>
</tr>
<tr>
<td>Pt-Co/C, E-TEK</td>
<td>0.3874</td>
<td>0.2739</td>
<td>2.9</td>
<td>95</td>
<td>53</td>
<td>0.66</td>
<td>252</td>
</tr>
<tr>
<td>Pt-Co/C, E-TEK, TT</td>
<td>0.3854</td>
<td>0.2726</td>
<td>3.3</td>
<td>83</td>
<td>61</td>
<td>0.73</td>
<td>244</td>
</tr>
</tbody>
</table>

* TT: thermally treated.

The HRTEM image of the catalyst, shown in Fig. 4, reveals the asymmetric faceted shape, typically cuboctahedral, of Pt-Co particles, in agreement with the HRTEM measurements on carbon-supported platinum by Sattler and Ross.35 Combined HRTEM/EDX analysis of the sample indicated a Pt:C atomic ratio of 91:9 for the alloy particle.

The histograms with the distribution of particle sizes of Pt/C and Pt-Co/C catalysts from BM and E-TEK before thermal treatment are shown in Fig. 5(a-d). The Pt-Co/C catalyst by BM show a particle size distribution broader than that of Pt-Co/C by E-TEK. Moreover, the Pt particle size distribution of Pt-Co/C by BM exhibits a tail in the larger particle size region. For Pt/C by BM, 77% of the particles have diam between 2.5 and 3.5 nm, with an average particle size of 3.7 nm, whereas for Pt/C by E-TEK, 65% of the particles have diam between 2.0 and 3.5 nm, with an average particle size of 3.0 nm. For the Pt-Co/C catalysts prepared by BM, 76% of the particles have diameters between 2.5 and 4.5 nm with a mean particle size of 3.7 nm, whereas for the Pt-Co/C catalysts by E-TEK, 55% of the particles have diameters between 3 and 4 nm with a mean particle size of 3.4 nm.

CV analysis.—CV stripping experiments were carried out with adsorbed CO, and the oxidation currents, corrected by the currents in the absence of CO, were used to determine the electroactive areas.37 Figure 6 shows the CO stripping voltammograms of the commercial, as-prepared, and thermally treated electrocatalysts. The electroactive areas for Pt/C and Pt-Co/C electrocatalysts, as prepared and submitted to thermal treatment at 500°C, are reported in Table I. These values reflect only the Pt surface atoms. As seen in Table I, the ratio of the specific surface area from CV (SA CV ) and from XRD (SA XRD ) indicated that without thermal treatment the amount of Pt active sites depends on the preparation method but is nearly independent of cobalt presence in the catalyst. It means that either cobalt is not present on the alloy surface or the presence of cobalt increases the Pt active sites. Following thermal treatment of the binary catalysts, this ratio increased, perhaps due to the formation of a “Pt-skin structure” and the inhibition of Pt-OH ad formation of Pt sites surrounded by “oxide”−covered Co atoms17 or to the oxide-cleansing action of the transition metal from the Pt surface.19

Steady-state current-potential analysis.—The current-potential curves were analyzed using the semiempiirical equation37,39

\[ E = E_o - b \log j - Rj \]  

where \( E_o \) is a constant given by

\[ E_o = E_i - b \log j_o \]

Here, \( E_i \) is the reversible potential of the cell, \( b \) is 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 catalyst. Because Eq. 1 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, only the region for \(E > 0.8\) V was considered in these analyses. The parameters \(E_\circ\), \(b\), and \(R\) were obtained using a least-squares Levenberg-Marquardt fitting procedure.

Figure 7 shows the current-potential curves for a single PEMFC using as cathodes the Pt/C and Pt-Co/C catalysts investigated here. The electrode kinetic parameters obtained from the experimental results reported in Fig. 6 are presented in Table II. Within the fitting error, the Tafel slope \(b\) did not show any dependence on the catalyst composition. An increasing tendency to reach limiting diffusional currents for the electrode with Pt-Co/C by E-TEK is observed in Fig. 7. As reported in Table II, this catalyst shows an increase in the value of \(R\) due to an increase in the linear diffusion components. These results are a consequence of the presence of a high amount of unalloyed Co (in the oxide form), as revealed by XRD analysis, causing diffusion limitations in the reactant gas inside the catalyst particles.

Using the \(R\) values, \(jR\)-corrected Tafel plots (\(E + jR\) vs. \(\log j\)) were constructed, and the results are presented in Fig. 8 for all the catalysts. The electrocatalytic activity of Pt-Co catalysts for the ORR, based on the geometric areas of the electrodes, is higher than that of the homologous Pt/C materials. An increased activity in terms of the geometric surface area of the electrodes with these catalysts is also indicated by the values of the current density at 900
mV reported in Table II. A similar trend is observed for the values of $E_0$ and the potential at 10 mA cm$^{-2}$. Based on the geometric area, the ORR on the Pt-Co/C catalyst by BM is slower than on Pt-Co/C by E-TEK. However, the value of the current density at 900 mV, calculated on the basis of the electrochemical active surface area, as obtained from CV measurements (see Table 1), indicates that the activity of the Pt-Co/C catalyst by BM for the ORR is higher than that of Pt-Co/C by E-TEK. For $E < 0.8$ V, the Tafel slope was about 130 mV dec$^{-1}$ for both Pt and Pt-Co electrocatalysts. This change of $b$ is a consequence of a change of the degree of coverage of the Pt surface by chemisorbed oxygenated species, which follows the Temkin isotherm (high coverage) at low reaction overpotentials ($E > 0.85$ V) and the Langmuir isotherm (low coverage) at high reaction overpotentials ($E < 0.85$ V).$^{42-45}$ The reduction of overpo-
tential for ORR by alloying is obtained with a Tafel slope similar to that of pure Pt potential 0.8 V. Consequently, the enhancement on Pt-Co alloys is probably brought about by enhancing the same rate-determining step of the first electron-transfer step as on pure Pt.

In this work, we have obtained catalysts with the same chemical composition (Pt and Pt-Co in the alloy atomic ratio Pt:Co about 90:10) and different particle sizes, and electrocatalysts with roughly the same particle size and different chemical composition. Thus, we can evaluate separately the effect of each of these parameters on the specific activity. As can be inferred from the data reported in Tables I and II, electrocatalysts with the same chemical composition show a better electrocatalytic activity for larger Pt particle sizes. As shown in Fig. 9, the specific activity for the ORR increases with increasing Pt particle size. The increased catalytic activity with increasing Pt particle size was ascribed to the less strong adsorption of OH on Pt particle size. The increased catalytic activity with increasing Pt particle size by XRD and TEM.

In the same way, catalysts with about the same particle size show a better electrocatalytic activity for larger Pt particle sizes. As shown in Fig. 9, the specific activity for the ORR increases with increasing Pt particle size. The increased catalytic activity with increasing Pt particle size by XRD and TEM.

In the same way, catalysts with the same particle size show a better activity, to a lesser extent, in the presence of cobalt. Summarizing, a significant effect of Pt particle size (independent of the presence of Co) on the electrocatalytic activity of these catalysts for the ORR has been revealed, and a not negligible positive effect of the presence of Co, due to either the inhibition of Pt-OH adsorption on Pt sites surrounded by “oxide”-covered Co atoms, the cleansing action of cobalt, or the decrease of the Pt—Pt bond distance, is also present.

Following a thermal treatment at 500°C, a decay of the electrochemical performance at low current density was noted for both Pt-Co/C catalysts, as seen in Table II and Fig. 7. A decrease of electrocatalytic activity after thermal treatment at 500°C was previously observed, to a lesser extent, in a Pt-V/C catalyst. This behavior can be explained considering that, unlike other systems formed by unsupported single phase Pt-Co, the electrocatalyst prepared in the present work is formed by carbon-supported Pt-Co alloy and nonalloyed Co and/or Co oxide. Being in the presence of different catalysts, the effect of the thermal treatment is also different. In the former case, only the formation of a “Pt-skin structure” takes place, but in the latter, the presence of nonalloyed Co, which enters the solid solution during annealing, could give rise to the formation of a Co-rich Pt-Co solid solution on the outer layers of the metal particle. We remark that 500°C is a temperature not high enough to form a homogeneous alloy. On this basis, due to the formation of the Pt-skin structure, the amount of Co in the second layer is very high. It is known that some catalytic properties of the Pt-skin structure are different from the pure Pt surface. This was attributed to the electronic effect of intermetallic bonding of the alloying component-rich second layer with the topmost Pt atoms. The decrease in the activity of the electrocatalysts following the thermal treatment can be explained by the model of Toda et al.,51 based on an increase of d-electron vacancies of the thin Pt surface layer caused by underlying alloy. On the basis of their model, such an increase of 5d vacancies led to an increased 2electron donation from O2 to the surface Pt, resulting in an increased O2 adsorption and a weakening of the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_0$ (mV)</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$R$ (Ω cm$^2$)</th>
<th>$J_{990}$ (mA cm$^{-2}$)</th>
<th>$E_{10}$ (mV)</th>
<th>$J_{900}$ (µA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C, BM</td>
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<td>6.3</td>
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<tr>
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<td>8.0</td>
<td>894</td>
<td>57</td>
</tr>
<tr>
<td>Pt-Co/C, BM TT$^b$</td>
<td>945</td>
<td>66</td>
<td>0.23</td>
<td>4.7</td>
<td>878</td>
<td>39</td>
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<tr>
<td>PtCo/C, E-TEK</td>
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<td>65</td>
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<td>29</td>
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<tr>
<td>Pt-Co/C, E-TEK TT</td>
<td>960</td>
<td>64</td>
<td>0.24</td>
<td>9.0</td>
<td>897</td>
<td>34</td>
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<tr>
<td>Pt-Co/C, E-TEK</td>
<td>951</td>
<td>65</td>
<td>0.25</td>
<td>5.6</td>
<td>883</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$ Normalized with respect to the electrochemically active surface area.

$^b$ TT: thermally treated.

Figure 8. Ohmic drop corrected Tafel plots for ORR in PEMFC at 80°C and 1 atm for Pt and Pt-Co electrocatalysts.

Figure 9. Specific activity vs. Pt particle size by XRD (○) and TEM (▲) for Pt/C and Pt-Co/C at 80°C and 1 atm in PEMFC.
O—O bond. When the 5d vacancy increases more or the Fermi level further lowers by addition of the second element beyond each optimum content (the present case), the Pt—O bonding becomes stronger and the back donation becomes difficult, resulting in a lowered O₂ reaction rate. When the content of the second element too large, the resulting large d vacancy may contribute to the enhancement of O—O bond scission energy, decreasing the ORR activity. The formation of such a Co-rich alloy on the Pt particle surface cannot be detected by XRD, so further investigations are needed to better understand this behavior.

As seen in Fig. 10, at high current densities, the thermal treatment at 500°C produced different effects on the performance of cells with different Pt-Co/C catalysts. The cell performance using a thermally treated Pt-Co/C catalyst by E-TEK was higher than that of the cell with the as-received catalyst. This improvement is related to the decreased amount of cobalt oxide present on the surface of the catalyst following the thermal treatment in the presence of hydrogen. However, the cell performance at high current densities of thermally treated Pt-Co/C by BM was lower than that of the cell with the untreated catalyst. This can be ascribed to the increased Pt particle size, which increases the tendency to reach limiting diffusional currents.

Conclusions

Pt₅₃Co₁₅/C electrocatalysts prepared by reduction with sodium borohydride in solution presented a good performance for the ORR in single PEMFC fed with H₂/O₂. Based on the geometric area, the electrocatalytic activity for the ORR of Pt-Co/C by BM was higher than that of the homologous Pt/C, but lower than that of Pt₅₃Co₁₅/C by E-TEK, due to the larger alloy particle size. However, based on the electrochemically active surface area, the ORR activity of Pt-Co/C by BM was higher than that of the commercial Pt-Co/C catalyst.

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