Carbon-Supported Pt-Ni Alloys Prepared by the Borohydride Method as Electrocatalysts for DMFCs

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Carbon-supported Pt-Ni electrocatalysts in the Pt: Ni atomic ratio 90:10 and 70:30 were prepared by reduction at room temperature of Pt and Ni salts with sodium borohydride and tested for the first time in direct methanol fuel cells (DMFCs) both as anode and as cathode materials. The performance of Pt-Ni as cathode in DMFC was higher than that of Pt-Ni as anode. Pt-Ni as anode showed better performance than Pt both in terms of mass activity and specific activity. When used as an anode material, the cell performance increased with increasing nickel content in the material. The enhanced performance of Pt-Ni as a cathode is ascribed both to a better activity for the oxygen reduction (electrocatalytic effect) and a better methanol-tolerance (ensemble effect) than the metal related mainly to the alloyed nickel, while the improvement of Pt-Ni as anode for methanol oxidation is attributed to the presence of nonalloyed NiO species.

Direct methanol fuel cells (DMFCs) have been receiving increasing attention because of the advantages in transportation and storage of the fuel, the high-energy efficiency, simplicity, and convenience. However, DMFCs also present serious concerns, such as the slow kinetics of the anodic and cathodic reactions and methanol crossover.1,2

The anode electrocatalyst that can be used in DMFCs with proton exchange membranes (PEMs) as electrolyte has to be stable in acid media, should oxidize methanol at low overpotentials, and be stable over time. Methanol oxidation is a slow reaction that requires multiple active sites for the adsorption of methanol and sites that can donate OH species for the oxidative desorption of the adsorbed methanol residues. One of the best known and currently the most efficient anode electrocatalysts for DMFCs is Pt-Ru.3-5 But even using Pt-Ru in the anode the power density of a DMFC is about an order of magnitude lower than that of a polymer electrolyte membrane fuel cell operated on hydrogen if the same Pt loading is used. Therefore, a number of alternative elements to Ru, as W, Os, Co, Sn, and Mo, showing a cocatalytic activity for the anodic oxidation of methanol, if used either as platinum alloys or as adsorbate layers on platinum, have been investigated.6-11 Two models have been proposed to explain the effect of the second metal: M is the first is the bifunctional mechanism,12,13 according to which Pt sites are adsorption and dehydrogenation centers producing carbonaceous species, while on M sites the OH species are adsorbed at a less positive potential than on pure Pt; the second is the ligand model,12,13 which proposes the modification of the Pt electronic structure by the presence of M rendering Pt atoms more susceptible for OH adsorption and for the dissociative adsorption of methanol.

On the other hand, to overcome the problem of the methanol crossover, attempts are directed to the development of new cathode electrocatalysts with higher methanol tolerance than Pt. The current direction is to test the activity of some alloys of the first-row transition metals, which present a higher activity for the ORR than platinum in low-temperature fuel cells operated on hydrogen.15-18

The atomic ratios of the Pt-Ni/C electrocatalysts were determined by the EDX technique coupled to a scanning electron microscopy (SEM) LEO model 440 with a silicon detector with Be window and applying 20 keV.

Experimental

Carbon supported Pt-Ni electrocatalysts with nominal Pt: Ni atomic ratio 90:10 and 70:30 were prepared by a low-temperature method, using sodium borohydride as the reducing agent. High surface area carbon (Vulcan XC-72, Cabot, 240 m² g⁻¹) was impregnated with a solution of chloroplatinic acid (H₂PtCl₆·6H₂O, Johnson Matthey) and sodium nitrate (Na₂SO₄)·7H₂O, Aldrich). The metals were then reduced at room temperature with a sodium borohydride solution, which was slowly added to the precursors under sonication. The complete reduction of Pt and Ni precursors was followed by KI and dimethylglyoxime tests, respectively. The catalysts were washed with distilled water. The materials were 20 wt % metal on carbon. The flow chart of the synthesis of Pt-Ni/C electrocatalysts by the borohydride method is shown in Fig. 1.

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X-ray diffractograms (XRDs) of the electrocatalysts 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 20 values between 20 and 100°.

Cyclic voltammograms (CVs) were recorded in a single cell in 0.5 mol L⁻¹ H₂SO₄ solution. Argon (White Martins) was passed for 30 min to eliminate oxygen. A thin porous coating electrode containing Pt/C or Pt-Ni/C electrocatalysts was used as working electrode. A hydrogen electrode was used as reference and a platinum electrode as auxiliary. The CVs were recorded in the range 0.075-1.200 V vs. a RHE at a scan rate of 10 mV s⁻¹. These experiments were done at room temperature with a 1285A Solartron Potentiostat connected to a personal computer and using the software Corware for Windows (Solartron).

To test the electrochemical behavior in a single DMFC fed with methanol/oxygen, these 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 Pt-Ni/C, or Pt/C. Nation solution (5%, Aldrich) and isopropanol (Merck). All electrodes were made to contain 1 mg Pt cm⁻². After drying, the electrodes were hot pressed on both sides of a Nafion 117 membrane at 125°C and 5 MPa for 2 min. Before using them,
the Nafion 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. When the Pt-Ni/C electrocatalysts were used as anode material, the cathode material was 20% Pt/C E-TEK. In the same way, when the Pt-Ni/C electrocatalysts were used as cathode material, the anode material was 20% Pt/C E-TEK. The cell polarization data at 90°C were obtained by circulating a 2 mol L⁻¹ aqueous methanol solution at the anode and oxygen pressurized at 0.3 MPa at the cathode.

Results and Discussion

The EDX composition of the carbon supported Pt-Ni electrocatalysts is reported in Table I. The values of the actual composition were near to the nominal compositions attempted in the preparation. Figure 2a shows the XRD patterns of the carbon supported Pt-Ni alloy electrocatalysts with a metal loading of 20 wt % and different Pt:Ni atomic ratios. For the sake of comparison, the commercial Pt/C electrocatalyst with 20 wt % metal loading is also shown in this figure. Detailed Pt (220) peaks of these electrocatalysts are shown in Fig. 2b. As indicated in Fig. 2a, in all the samples, only the reflections corresponding to the planes (111), (200), (220), (311), and (222), characteristic of the face-centered cubic (fcc) structure of Pt were present. In the binary Pt-Ni electrocatalysts, these five diffraction peaks were shifted to higher values of 2θ, which is indicative of a contraction of the lattice. These shifts of the Pt peaks, which are clearly seen in Fig. 2b, reveal the alloy formation between Pt and Ni, caused by the incorporation of Ni in the fcc structure of Pt. No characteristic peaks of metallic Ni or Ni oxides were detected, but their presence cannot be discarded because they may be present in a small amount or even in an amorphous form. The peaks of as-prepared Pt-Ni electrocatalysts were sharper than those of Pt E-TEK, indicating that they have larger particle sizes than the commercial platinum. The average size of the Pt and Pt-Ni nanoparticles was estimated by using Sherrer’s equation.²⁷ Table I shows the values of the lattice parameter and mean particle size determined from the XRD analysis for all the electrocatalysts. The dependence of the lattice parameter of unsupported Pt-Ni alloys on Ni contents according to Vegard’s law is reported in Ref. ²⁸. On the basis of the values for unsupported alloys, the amount of alloyed Ni was estimated to be about 8 atom % for the Pt₉₀Ni₁₀/C electrocatalyst (near to the nominal composition) and about 6 atom % for the Pt₇₀Ni₃₀/C sample (poor degree of alloying). From these results, it can be inferred that in the Pt₉₀Ni₁₀/C electrocatalyst most of the nickel is in a nonalloyed form (as metal or as NiO species). Briefly, the two Pt-Ni electrocatalysts contain about the same amount of Ni alloyed, but have a markedly different amount of non-alloyed Ni. The particle size of carbon supported Pt-Ni alloy electrocatalysts prepared by different methods is reported in Table II. As shown in Table II, the low-temperature preparation method used allows one to obtain Pt-Ni particles with relatively small size as compared to the carbon supported Pt-Ni prepared by other methods.²⁹,³¹

Figure 3 shows CVs performed with a thin porous coating elec-

Table I. Physical parameters of the Pt and Pt-Ni electrocatalysts.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>EDX composition</th>
<th>Lattice parameter (nm)</th>
<th>Particle size by XRD (nm)</th>
<th>Pt surface area by CV (m² g⁻¹)</th>
<th>Roughness factor (cm² cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₉₀Ni₁₀/C</td>
<td>71:29</td>
<td>0.38977</td>
<td>4.8</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>Pt₇₀Ni₃₀/C</td>
<td>87:13</td>
<td>0.38874</td>
<td>4.1</td>
<td>65</td>
<td>650</td>
</tr>
<tr>
<td>Pt/C</td>
<td>(100)</td>
<td>0.39041</td>
<td>2.8</td>
<td>95</td>
<td>950</td>
</tr>
</tbody>
</table>
trode containing Pt and Pt-Ni electrocatalysts. The active areas were calculated from the CVs using the charge associated to hydrogen desorption on the electrode surface. However, the contribution of the alloying element to the roughness factor was difficult to discern and thus, following Mukerjee et al.,29 it will be assumed to be negligible. For the sake of comparison with the surface area of pure Pt, and then to normalize the current density with respect to the Pt surface area, it is more important to know the Pt surface area in the alloy than the total surface area.

As shown in Table I, the electrochemical surface area of Pt/C is about twice that of the binary electrocatalysts.

The polarization curves in single DMFC with Pt/C and Pt-Ni/C both as cathode (Pt/C as anode) and as anode (Pt/C as cathode) electrocatalysts operating with 2 mol L−1 methanol solution and a cathode pressure of 0.3 MPa at 90°C are shown in Fig. 4 (with the current density expressed in terms of mass activity, MA). It has to be remarked that, with Pt loading of 1 mg cm−2 in all cases, the current density in terms of electrode geometric area (A cm−2) is the same as the current density normalised by the Pt loading (A mg−1 Pt). The best performance was obtained with the cell employing the Pt90Ni10/C electrocatalyst as the cathode material. The performance of the cells with Pt-Ni/C as the anode material was lower than that of cells operating with Pt/C. The polarization curves with the current density expressed in terms of specific activity (SA) are shown in Fig. 5a (different cathodes, Pt/C as anode electrocatalyst) and Fig. 5b (different anodes, Pt/C as cathode electrocatalyst). When used as a cathode material, the cell performance with Pt-Ni electrocatalysts was remarkably better than that of the cell with Pt, and was nearly independent of the nickel content in the electrocatalyst. When used as an anode material, the cell performance increased with increasing nickel content in the material, and the performance of Pt90Ni10/C was higher than pure Pt/C. The improvement in cell performance when Pt-Ni is used as cathode electrocatalyst can be explained by two additive effects of the nickel presence. First, the presence of Ni enhances the activity for the ORR of these electrocatalysts, as discussed above. Second, because the dissociative chemisorption of methanol requires the existence of several adjacent Pt ensembles, the presence of Ni around Pt active sites could hinder methanol adsorption on Pt sites due to the dilution effect. Indeed, it is well established that for methanol oxidation at least three adjacent Pt sites in the proper crystallographic arrangement are necessary to activate the chemisorption of methanol.6,29 For the Pt-Ni alloy electrocatalysts, the probability of finding three neighboring Pt atoms on the surface is lower if no Pt enrichment on the surface takes place. Both these effects depend on the amount of alloyed Ni, which explains the similar performance of the two Ni-containing electrocatalysts prepared here.

Regarding the improvement of the cell performance with Pt-Ni as anode catalyst, according to Choi et al.,23 the enhancement in methanol oxidation by Ni in Pt-Ni can be attributed to the electronic effect, that is, the modification of electronic properties of Pt, and to the contribution of the various oxidation states of Ni present. By X-ray photoelectron spectroscopy (XPS) measurements the authors found that in Pt-Ni electrocatalysts Ni is present as NiO, Ni(OH)2, and NiOOH. From the higher catalytic activity of the alloy compared to pure Pt, the authors deduced that these oxidation states aid in improving methanol oxidation by providing Pt-bonded CO with oxygen species. According to Mathiyarasu et al.,23 Ni oxide/hydroxide layers within the Pt matrix which are relatively stable in the acidic medium, exhibit protonic/electronic conductivity and the oxide/hydroxide layer in the Pt-Ni alloy matrix displays high catalytic activity with respect to methanol. On these bases, the improvement of the performance of the cell with Pt-Ni as anode material with increasing Ni content can be mainly ascribed to the increasing presence of unalloyed NiO species.

Table II. Average particle size of carbon supported Pt-Ni alloys prepared by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Metal particle size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloying at 900°C and annealing for 12 h in Ar (E-TEK)</td>
<td>5.6</td>
<td>29</td>
</tr>
<tr>
<td>Alloying at 950°C and annealing for 15 h in Ar (Johnson Matthey)</td>
<td>5.8</td>
<td>29</td>
</tr>
<tr>
<td>Alloying at 900°C for 2.5 h in a reducing atmosphere (10% H2, 90% N2)</td>
<td>6.4</td>
<td>30</td>
</tr>
<tr>
<td>Reduction of Pt and Ni salt precursors with hydrazine at 60°C</td>
<td>12.5-50</td>
<td>31</td>
</tr>
<tr>
<td>Reduction of Pt and Ni salt precursors with hydrazine at room temperature for 12 h</td>
<td>13-25</td>
<td>31</td>
</tr>
<tr>
<td>Microwave assisted reduction of Pt and Ni precursors with hydrazine</td>
<td>2.9-3.6</td>
<td>31</td>
</tr>
<tr>
<td>Reduction of Pt and Ni precursors with NaBH4 at room temperature</td>
<td>4.1 and 4.8</td>
<td>This paper</td>
</tr>
</tbody>
</table>

Figure 3. CVs of Pt-Ni/C (BM) and Pt/C E-TEK electrocatalysts in 0.5 mol L−1 H2SO4 at a scan rate of 10 mV s−1.

Figure 4. Polarization curves in single DMFC with (△) Pt/C, (●) Pt90Ni10/C, and (■) Pt90Ni10/C, both as cathodes and (○) Pt90Ni10/C and (□) Pt90Ni10/C, both as anodes at 90°C and 0.3 MPa O2 pressure using a 2 mol L−1 methanol solution. Current densities normalized with respect to the geometric surface area (MA). Pt-Ni/C materials were paired with Pt/C.
effective methanol-resistant oxygen-reduction electrocatalyst, and the lower is the possibility that it can be used advantageously in both electrodes of the cell. As can be seen in Fig. 6, the Pt$_{90}$Ni$_{10}$/C electrocatalyst presented a higher “cathode quality factor” than the Pt$_{70}$Ni$_{30}$/C sample. Additionally, the presence of NiO species in the electrocatalyst increased the activity of the bimetallic alloy when used as anode material.

Conclusions

The experiments described in the present paper confirm not only that Pt-Ni is a good catalyst for the ORR, but also that Pt-Ni is a good methanol-tolerant material.

The findings in this investigation can be summarized as follows:

By reduction with NaBH$_4$, the particle size of the obtained carbon supported Pt-Ni alloys is smaller than that of Pt-Ni/C prepared by other methods.

In DMFC tests, Pt-Ni/C electrocatalysts performed better as cathode than as anode materials.

The performance of DMFCs with Pt-Ni electrocatalysts as cathode material depends on the amount of effectively alloyed Ni and does not depend on the total amount of Ni in the material.

The performance of DMFCs with Pt-Ni electrocatalysts as anode material increased with increasing amounts of NiO species.

The Pt$_{90}$Ni$_{10}$/C electrocatalyst showed a higher “cathode quality factor” than the Pt$_{70}$Ni$_{30}$/C electrocatalyst.

On these bases, the degree of alloying of a Pt-Ni electrocatalyst determines its use in the DMFC. If the electrocatalyst is used as cathode material, a high degree of alloying is preferable. If, on the other hand, the material is used as anode material, a low degree of alloying leads to a better performance.

Acknowledgments

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, proc. 140205/2001-2) and the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP, proc. 99/06430-8 and proc. 03/04334-9) for financial assistance to the project.

CNPq assisted in meeting the publication costs of this article.

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