

# CO-CATALYTIC EFFECT OF NICKEL IN Pt-Ru/C AND Pt-Sn/C ELECTROCATALYSTS FOR ETHANOL ELECTROOXIDATION

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**Abstract**--In the present study, we examined the effect of adding nickel to Pt-Ru and Pt-Sn catalysts for ethanol electrooxidation. The alcohol-reduction process with ethylene glycol was used to prepare ten electrocatalysts. These were microchemically and physically characterized by EDX and XRD analysis. The electrocatalysts were evaluated at mini-electrodes with cyclic voltammetry at 25 and 50 °C in sulfuric acid and ethanol solutions, and as anodes in fuel cell tests. Nickel addition to Pt-Ru mixtures significantly increased the catalytic activity toward ethanol electrooxidation. For Pt-Ru-Ni catalysts, the current density was around five times greater than all other investigated mixtures. Nickel also duplicated the catalytic activity of the Pt-Sn catalyst. Furthermore ethanol electrooxidation increased with temperature for most catalytic mixtures, and the electrocatalytic activity of mixtures containing nickel, demonstrate a considerable increase with temperature. Pt-Ru-Ni catalytic activity was higher than that of all other investigated mixtures. The fuel cell test demonstrated that the addition of nickel to Pt-Ru and Pt-Sn catalysts enhances the performance of the DEFC.

**Keywords**-- Ethanol; Electrooxidation; PtRuNi; PtSnNi; Fuel cell.

## I. INTRODUCTION

The development of direct ethanol fuel cells (DEFCs) is important for obtaining an alternative and efficient energy converter. Within this objective, there is an interesting topic that is considered fundamental to the development of these devices: the preparation of electrocatalysts and their evaluation in the ethanol electrooxidation process (Lamy *et al.*, 2004; Léger *et al.*, 2005; Song and Tsikaras, 2006).

Numerous groups have investigated the preparation of different electrocatalytic mixtures. Currently, the most commonly investigated electrocatalysts are Pt-Ru, Pt-Sn, and Pt-Ru-Sn mixtures (Antolini, 2007a; Antolini, 2007b; Antolini *et al.*, 2007; Jiang *et al.*, 2007; Jiang *et al.* 2005; Simoes *et al.*, 2007; Spinacé *et al.*, 2004) and two electrocatalytic mixtures that contain nickel, Pt-Ru-Ni (Wang *et al.*, 2006) and Pt-Sn-Ni (Spinacé *et al.*, 2005; Ribadeneira and Hoyos, 2008).

In these works, the results obtained for Pt-Ru-Ni and Pt-Sn-Ni mixtures show that nickel could be an excellent co-catalyst for ethanol electrooxidation. However, it

remains difficult to make a fair comparison and establish if there is a real increase in catalytic activity because these mixtures have not been compared under the same experimental and evaluation conditions.

As a consequence, we conducted a direct comparison of ten electrocatalytic mixtures using the same reduction process, electrocatalytic preparation, atomic relations, metal load, cyclic voltammetry (CV), and single fuel cells, evaluation conditions. In this study, we determined if the addition of nickel to Pt-Ru and Pt-Sn catalysts really increases their catalytic activity toward ethanol oxidation.

## II. EXPERIMENTAL PROCEDURES

### A. Electrocatalyst preparation

Six different catalytic mixtures were prepared without nickel: Pt:Ru (85:15 and 75:25), Pt:Sn (85:15 and 75:25) and Pt:Ru:Sn (75:15:10 and 75:10:15). In order to establish the effect of nickel addition, four additional catalytic mixtures were prepared: Pt:Ru:Ni (75:15:10 and 75:10:15) and Pt:Sn:Ni (75:15:10 and 75:10:15). All electrocatalysts were prepared with a metal load of 20 wt% using the alcohol reduction process (Oliveira *et al.*, 2007; Jiang *et al.*, 2006), with H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Merck), RuCl<sub>3</sub>·3H<sub>2</sub>O (Merck), SnCl<sub>4</sub>·5H<sub>2</sub>O (Erbo) and NiCl<sub>2</sub> (Erbo) as metal sources.

During the reduction process, ethylene glycol was used as a solvent and reduction agent. Vulcan Carbon<sup>®</sup> XC-72 was used as a support for all electrocatalysts. All mixed solutions were prepared with a 75/25 v/v ethylene glycol/water ratio throughout the alcohol reduction process. For each electrocatalytic mixture the precursor solutions were ultrasonically scattered for 30 min, and the pH was then adjusted to 11.5. The metal reduction process was conducted at 140°C for 3h. All mixtures were filtered for 2 hours and dried at 70°C for an additional 2 hours. In the reduction process there is not any type of unexpected precipitate.

Each electrocatalytic powder was added to a Nafion<sup>®</sup> suspension to produce an ink with a 5:2 catalyst: Nafion weight ratio (Lister and McLean, 2004), which was ultrasonicated overnight (12 hours). The electrocatalytic ink was supported at the top of a vitreous carbon rod (the working electrode) for evaluation by cyclic voltammetry (CV). The covered electrocatalyst area in the working electrode was geometrically determined using an optical microscope, and the area-values ranged between 0.22 and 0.36 cm<sup>2</sup>.

## B. Micro-chemical and physical characterization

For all electrocatalytic mixtures, the micro-chemical characterization was performed by energy-dispersive X-ray analysis (EDX) for atomic ratio determination. After the alcohol (ethylene glycol) reduction process, micro-chemical analysis was made for each electrocatalytic mixture and compared with the nominal atomic ratio. EDX analysis was made for a  $3600 \mu\text{m}^2$  catalyst area.

This analysis was accomplished with a scanning electron microscope (SEM) JEOL JSM – 5910LV. Incident electron beam energies from 3 to 30 keV were used. In all cases, the beam was set at a normal incidence relative to the sample surface. The physical characterization was made by XRD analysis, which was performed using a PANanalytical X'Pert PRO diffractometer with a Cu K $\alpha$  radiation source.

## C. Electrochemical characterization

In the cyclic voltammetry experiments, a typical three-electrode system with a pure-platinum-wire counter electrode was used. The Ag/AgCl (3.0M) system was used as the reference electrode. However, all values are reported with respect to the normal hydrogen electrode (NHE). The working electrode was the transferred catalytic ink over the vitreous carbon rod.

Electrochemical characterization was performed in a Bio Analytical System (B.A.S. 100 b/w) work station coupled to a personal computer. For each CV, N<sub>2</sub> (99.998% pure) was circulated for 15 min to remove the oxygen in the electrolyte. The nitrogen atmosphere was preserved during each test. The experiments were conducted in two different electrolytic means: H<sub>2</sub>SO<sub>4</sub> (0.5M) and ethanol (1.0M) in H<sub>2</sub>SO<sub>4</sub> (0.5M) at 25 and 50°C. The scan ranged from -13 to 807 mV vs. NHE and the scan rate was 50 mV/s. All catalytic mixtures, even Ni mixtures, were stable with temperature in this electrolyte in the range of -15 to 810 mV vs. NHE.

## D. MEA preparation and single fuel cell evaluation

After the catalytic powder EDX analysis and ink elaboration, each catalytic mixture was brush painted onto a decal surface of fiberglass coated with Teflon®. The decal was heated in an oven at 140°C for 30 min. The process of painting and heating was repeated until catalyst loading of  $2.0 \text{ mg/cm}^2$  was reached in the anode and  $1.0 \text{ mg/cm}^2$  was reached in the cathode (Pt E-Tek).

The catalyst layer formed on the decal was hot pressed onto a Nafion® 117 membrane (sodium form) at 150°C and 800 kg/cm<sup>2</sup> for five minutes to produce the membrane electrode assembly (MEA) (Lister and McLean, 2004). After hot pressing, the decal was removed to form the MEA. The MEA was maintained at 80°C for 2 h in 0.5 M sulfuric acid, followed by immersion in 80°C deionized water for an additional 2 hours. The MEA was then dried on a heated table at 60°C for 30 min. Each fabricated MEA was placed in a housing block with a gas diffusion area of  $5 \text{ cm}^2$  and evaluated in a fuel cell test station (Electrochem Inc®). The experimental conditions for the fuel cell are reported in Table 1.

Table 1. Single fuel cell experimental conditions.

| Parameter             | Values                            |
|-----------------------|-----------------------------------|
| Temperature           | $80 \pm 1 \text{ }^\circ\text{C}$ |
| Ethanol flow          | $2,0 \pm 0,1 \text{ mL/min}$      |
| Ethanol concentration | 1,0 mol/L                         |
| Oxygen flow           | 20 mL/min                         |
| Oxygen purity         | 98%                               |
| Oxygen backpressure   | $15 \pm 2 \text{ psi}$            |
| Relative humidity     | >90%                              |

## III. RESULTS AND DISCUSSION

Figure 1 depicts the EDX analysis for Pt<sub>75</sub>Ru<sub>10</sub>Sn<sub>15</sub>. Modifications of the EDX pattern when ruthenium and tin are replaced with nickel are also depicted in Fig. 2 and 3, respectively. The EDX patterns demonstrate the appearance of typical peaks for the metals in the mixture.

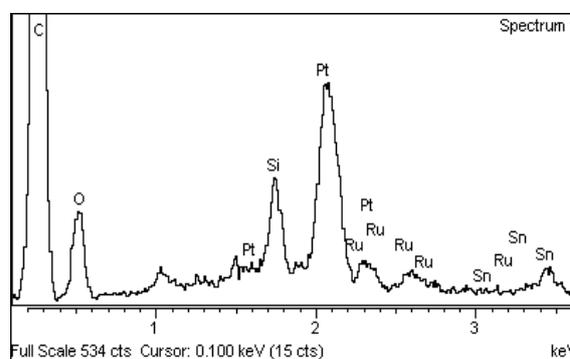


Figure 1. EDX spectrum for Pt<sub>75</sub>Ru<sub>10</sub>Sn<sub>15</sub>/C.

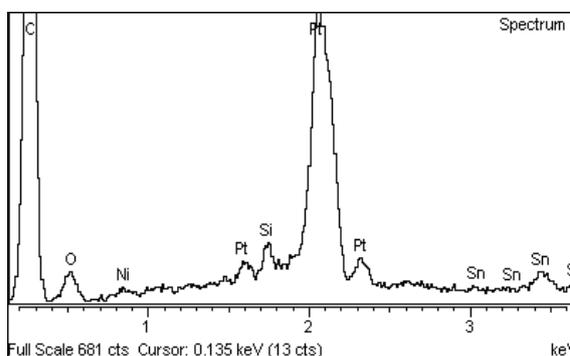


Figure 2. EDX spectrum for Pt<sub>75</sub>Sn<sub>15</sub>Ni<sub>10</sub>/C.

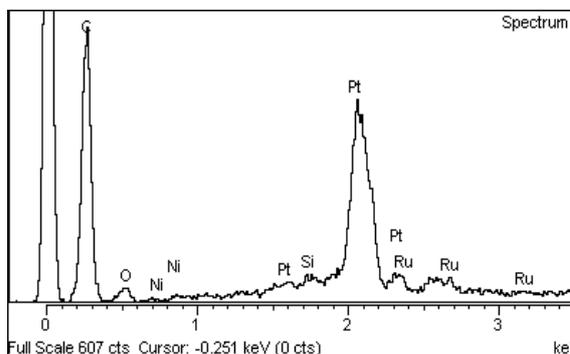


Figure 3. EDX spectrum for Pt<sub>75</sub>Ru<sub>15</sub>Ni<sub>10</sub>/C.

Table 2 provides a summary of the EDX analyses for the prepared electrocatalysts. The measured atomic ratios of bi-metallic mixtures were close to the nominal atomic ratios, which is indicative of the accuracy of the ethylene-glycol-method in reducing all metals present in the precursor solutions. In the case of tri-metallic mixtures, the atomic ratios were less concordant with the nominal ratios. Despite this fact, all EDX analysis reports demonstrate an acceptable agreement between the nominal and obtained atomic ratios, which is why the ethylene-glycol method is considered a versatile and efficient technique for reducing different types of metals over the support employed. In tri-metallic mixtures in particular, supports that contain nickel (like Pt<sub>75</sub>Ru<sub>15</sub>Ni<sub>10</sub>/C) show very good agreement between nominal and measured atomic ratios.

The XRD results and the corresponding peaks values for the different electrocatalysts are shown in Fig. 4 and the Table 3, respectively. For all catalytic mixtures, there was a broad peak at 25°, which is associated with the amorphous structure of graphite associated with the catalytic support (Vulcan XC72). Within this peak, different metallic compounds were detected that, in each case, compose the different catalytic mixtures. In particular, the diffractogram of the Pt-Ru and Pt-Sn mixtures (85:15 and 75:25 atomic ratios) shows peaks at approximately 2θ = 40°, 46°, 67°, and 81°, which are related to the [1 1 1], [2 0 0], [2 2 0], [3 1 1] planes, respectively. These planes belong to the fcc structure of platinum and platinum alloys like. Figure 4 demonstrates how these peaks disappear in the tri-metallic mixtures, with the exception of the 2θ = 40°. This is due

to structure modification of the electrocatalyst, depending on the different metals and compositions used for each catalytic mixture. The Fig. 4 shows the loss of crystallinity in the tri-metallic mixtures toward a more amorphous structure of the catalysts, trend also observed in lesser degree in other investigation works (Song and Tsiakaras, 2006.; Wang *et al.* 2006; Oliveira *et al.* 2007).

In the XRD analysis, the following compounds were detected: metallic ruthenium at 2θ = 44°, with a [1 0 1] plane in the hexagonal crystal system and ruthenium oxide (RuO<sub>2</sub>) at 2θ = 54°, with a [2 1 1] plane in the tetragonal system, for the Pt-Ru mixtures. The latter was also detected at 2θ = 55° with an amorphous structure in the four tri-metallic mixtures that contain ruthenium. For the Pt-Sn bi- and tri-metallic catalysts, tin oxides (SnO and SnO<sub>2</sub>) were detected with an amorphous structure at 2θ = 26° for SnO and with the [2 1 1] plane in the tetragonal system at 2θ = 52° for SnO<sub>2</sub>. Nickel was detected as metallic nickel at 2θ = 45° with the [1 1 1] plane of the cubic crystal system, and also as nickel oxide (NiO) at 2θ = 43° with the [2 0 0] plane of the cubic crystal system.

The on-set reaction potentials in sulfuric acid and ethanol solutions were assigned at the potential value for which the derivative of current obtained in the CV curve equals zero (Fig. 5), this is the point in which the corresponding reaction occurs. The results show that the on-set reaction potentials in sulfuric acid (associated with oxide formation) are higher than the on-set potentials obtained for ethanol electrooxidation (Fig. 6). The current density reached at potentials below 400 mV

Table 2. Nominal and EDX atomic ratios of prepared electrocatalysts.

| Electrocatalyst | Nominal atomic ratio % |          |          | EDX atomic ratio % |          |          |
|-----------------|------------------------|----------|----------|--------------------|----------|----------|
|                 | Pt                     | 2° Metal | 3° Metal | Pt                 | 2° Metal | 3° Metal |
| PtRu/C          | 85                     | 15       | -        | 84,6               | 15,4     | -        |
| PtSn/C          | 85                     | 15       | -        | 85,0               | 15,0     | -        |
| PtRu/C          | 75                     | 25       | -        | 76,1               | 23,9     | -        |
| PtSn/C          | 75                     | 25       | -        | 75,2               | 24,8     | -        |
| PtRuSn/C        | 75                     | 15       | 10       | 80,6               | 7,1      | 12,2     |
| PtSnRu/C        | 75                     | 15       | 10       | 70,8               | 17,7     | 11,5     |
| PtRuNi/C        | 75                     | 15       | 10       | 74,3               | 15,2     | 10,5     |
| PtNiRu/C        | 75                     | 15       | 10       | 78,6               | 11,1     | 10,3     |
| PtSnNi/C        | 75                     | 15       | 10       | 78,2               | 11,2     | 10,6     |
| PtNiSn/C        | 75                     | 15       | 10       | 73,5               | 15,3     | 11,2     |

Table 3. XRD detected peaks for all electrocatalytic mixtures.

| Electrocatalyst | XRD Peaks (2θ) |      |      |      |      |      |
|-----------------|----------------|------|------|------|------|------|
|                 | 1              | 2    | 3    | 4    | 5    | 6    |
| Pt85Ru15/C      | 25.6           | 40.1 | 46.5 | 67.9 | 81.6 | 86.3 |
| Pt85Sn15/C      | 24.9           | 39.9 | 46.2 | 67.7 | 81.6 | -    |
| Pt75Ru25/C      | 25.4           | 39.9 | 46.3 | 67.6 | 81.5 | -    |
| Pt75Sn25/C      | -              | -    | -    | -    | -    | -    |
| Pt75Ru15Sn10/C  | 25.6           | 39.3 | -    | -    | -    | -    |
| Pt75Sn15Ru10/C  | 25.2           | 38.8 | -    | -    | -    | -    |
| Pt75Ru15Ni10/C  | 25.5           | 39.9 | -    | -    | -    | -    |
| Pt75Ni15Ru10/C  | 25.4           | 39.9 | -    | -    | -    | -    |
| Pt75Sn15Ni10/C  | 25.4           | 39.6 | -    | -    | -    | -    |
| Pt75Ni15Sn10/C  | 25.0           | 40.1 | -    | -    | -    | -    |

vs. NHE is due to ethanol dissociative adsorption over the catalytic surface. In addition, the results show that the on-set reaction potentials in sulfuric acid and in ethanol demonstrate significant changes with increasing temperature for the ten electrocatalytic mixtures.

The on-set reaction potentials for ethanol oxidation using Pt-Ru catalysts demonstrated little change when nickel was added. The addition of nickel raised the on-set potential for oxide formation in Pt-Sn mixtures, as well as for ethanol oxidation. This last response was reflected in the lower voltage output observed when Pt-Sn-Ni mixtures were used in the anodes of direct ethanol fuel cells.

The catalytic activity was determined by comparing the current reached in the positive sweep at 700 mV vs. NHE. These values were determined for oxide formation and ethanol electrooxidation from the CV curves. It is clear that the catalytic mixtures containing nickel showed a higher current density for oxide formation than all other electrocatalysts investigated (Fig. 7). The Pt-Sn electrocatalysts also demonstrated a relatively high current density during oxide formation. In addition, the Pt-Ru-Ni mixtures showed the highest increase in catalytic activity with increasing temperature.

For ethanol electrooxidation, Fig. 8 and 9 demonstrate that the bi-metallic and the Pt-Ru-Sn mixtures had lower catalytic activity than tri-metallic mixture containing nickel, with the exception of the Pt<sub>75</sub>Sn<sub>15</sub>Ni<sub>10</sub>/C

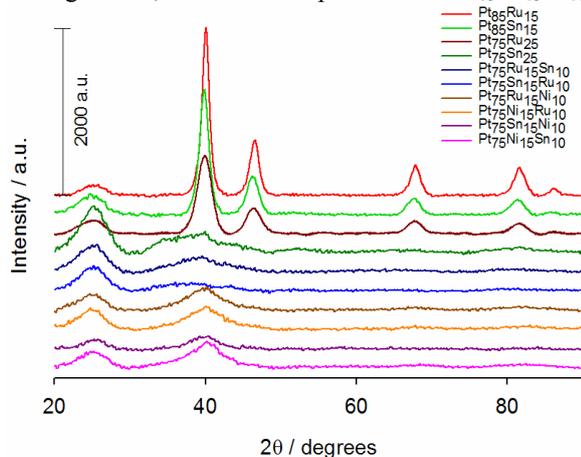


Figure 4. XRD spectrum for all catalytic mixtures.

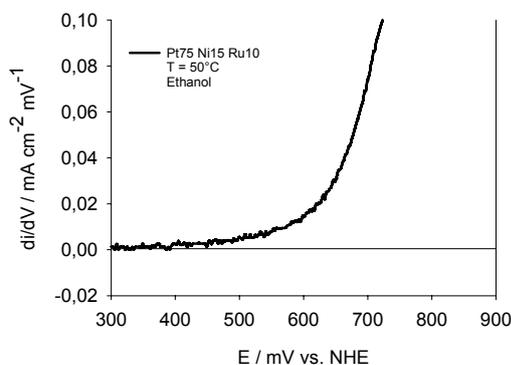


Figure 5. Cyclic voltammetry derivative for Pt<sub>75</sub>Ni<sub>15</sub>Ru<sub>10</sub> at 50 mV/s, T<sub>2</sub>=50°C in ethanol (1.0M).

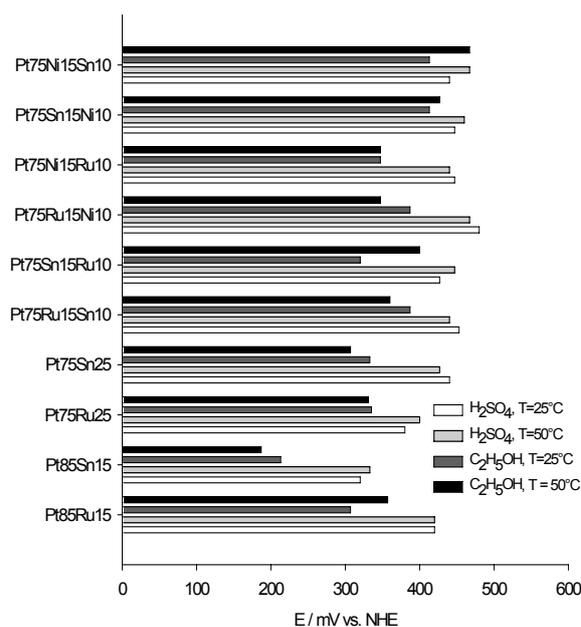


Figure 6. On-set reaction potentials in H<sub>2</sub>SO<sub>4</sub> (0.5M) and ethanol (1.0M) at 25 and 50°C.

mixture. The Pt<sub>75</sub>Ni<sub>15</sub>Sn<sub>10</sub>/C electrocatalyst showed a higher current density than the Pt<sub>75</sub>Sn<sub>15</sub>Ni<sub>10</sub>/C catalytic mixture, as well as a greater catalytic activity with increasing temperature. Furthermore, the addition of nickel to the Pt-Ru mixtures significantly increased their catalytic activity toward ethanol electrooxidation. The current reached in the Pt-Ru-Ni catalysts was around five times higher than that obtained with other mixtures. The Pt<sub>75</sub>Ni<sub>15</sub>Sn<sub>10</sub> electrocatalyst also increased the catalytic activity by a factor of around two compared with the Pt-Sn mixtures.

These facts demonstrate a similar improvement in catalytic activity by nickel during oxide formation and ethanol electrooxidation. The temperature increase destabilizes the C-(Pt) bond, with the release of CO molecules which avoid the adsorption and complete reaction processes of the ethanol molecules. These facts indicate that nickel facilitates the ethanol electrooxidation

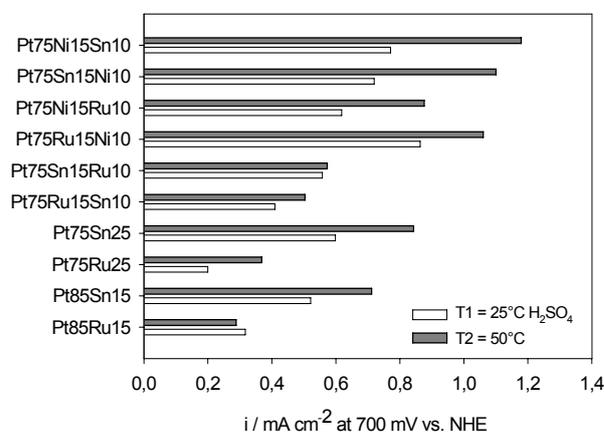


Figure 7. Catalytic activity for oxide formation in H<sub>2</sub>SO<sub>4</sub> (0.5M) at 25 and 50°C.

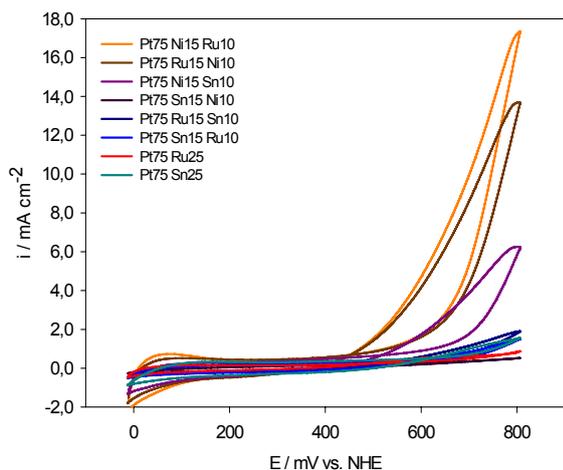


Figure 8. Cyclic voltammeteries for ethanol (1.0M) at 50°C.

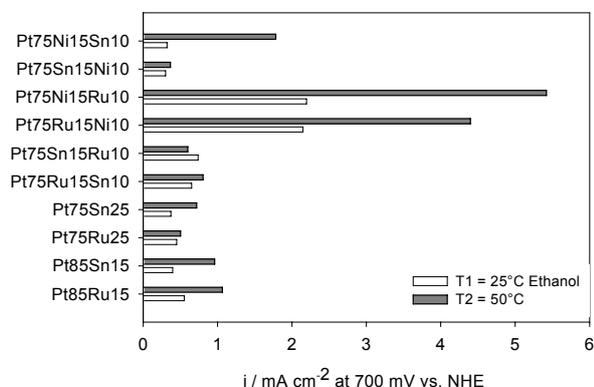


Figure 9. Catalytic activity for ethanol (1.0M) electrooxidation at 50°C.

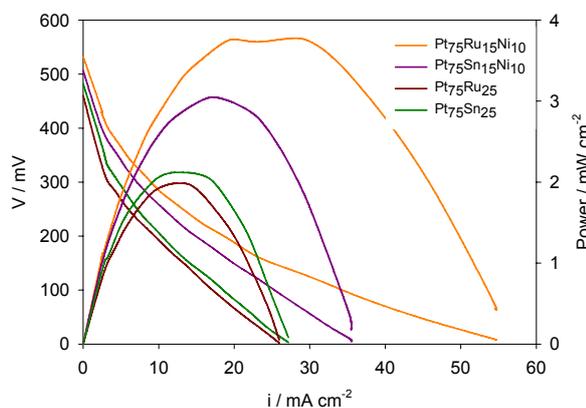


Figure 10. Effect of nickel addition on single fuel cell performance.

process by means of the diminution of adsorbed CO. The Pt-Ru-Ni electrocatalysts allow for the generation of a better catalytic surface than all other investigated electrocatalysts at 25°C and 50°C.

Finally, the results obtained using direct ethanol fuel cells in terms of potential–current density curves and power density–current density curves are shown in Fig. 10. When Pt-Ru-Ni catalysts were used in the anode, remarkable enhancement in cell performance was ob-

served. Pt-Ru-Ni performed better than all other catalysts. These results are in agreement with CV results that demonstrate a higher activity of Pt-Ru-Ni at higher potentials. Also, with Ni addition to Pt-Sn mixtures, the current density increased. All these results demonstrate that the Ni addition enhances the ethanol electrooxidation and the fuel cell performance in DEFCs, how it is evidenced in similar investigations (Oliveira *et al.*, 2007; Wang *et al.*, 2006; Spinacé *et al.*, 2005), including a previous work which this investigation is an extension (Ribadeneira and Hoyos, 2008).

#### IV. CONCLUSIONS

The previous results demonstrate that preparation of catalysts using ethylene glycol - reduction method is appropriate for the reduction of metals contained in the precursors, producing an acceptable agreement between the nominal and measured atomic ratios. In addition, the increase in catalytic activity was higher in Pt-Ru than in Pt-Sn mixtures when nickel is added. Furthermore, the electrochemical studies demonstrate that the temperature increase raised the catalytic activity: the electrocatalytic activities of mixtures containing nickel were increased considerably with increasing temperature, whereas the increase in catalytic activity with increasing temperature was slight when tin was present in the electrocatalytic mixture. In summary, the addition of nickel to Pt-Ru and Pt-Sn mixtures significantly increased their catalytic activity toward oxide formation and ethanol electrooxidation. The single fuel cell test demonstrated that nickel addition affects Pt-Ru and Pt-Sn catalysts by enhancing the performance of the DEFC. It is pertinent to mention that our results are in agreement with other investigations of the literature qualitatively, likewise our results are 30% lower than those reported in the literature. Particularly these results are in qualitatively agreement with the Antolini, Oliveira *et al.* and Wang *et al.* recent investigations.

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