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Development of PtNi/C and PtSnNi/C Nanocatalysts for Energy Convertion from Ethanol Electrooxidation

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Abstract. Literature describes the importance in studying morphological and structural electrocatalysts features since they influence catalytic activity toward ethanol electrooxidation. Thus, this work consists in studying the relation between structural/composition features and catalytic activity toward ethanol electrooxidation from Pt, PtSn, PtNi and PtSnNi alloys nanoparticles supported on Vulcan Carbon XC72R. These nanoparticles were obtained by the impregnation reduction method at 130 ºC, employing a mixture of water/ethylene glycol (75/25 v/v) with different amounts of Pt, Sn and Ni. The nanostructured catalysts obtained were characterized by Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), High Resolution Transmission Electronic Microscopy (HRTEM) and Cyclic Voltammetry (CV). Preliminary results showed that the impregnation reduction is a reasonable method to obtain Pt-based nanoparticles with a composition control. XRD analysis showed that tin and nickel addition promoted a crystal lattice dilation and contraction, respectively. Besides, the simultaneous addition of Sn and Ni to Pt did not significantly affect the reticular lattice value. Moreover, crystallite size is diminished with Ni or Ni and Sn addition. PtSn, PtNi and PtSnNi/C nanoparticles have higher catalytic activity than Pt/C toward ethanol electrooxidation, which was verified by a significant current density values increase and an onset potential decrease. The best catalytic activity was observed to PtNi/C electrocatalyst.

Key words

Ethanol electrooxidation, nanoparticles, impregnation/reduction method.

1. Introduction

Methanol [1], have been widely proposed as a possible fuels for applications in mobile fuel cells employed in electric vehicles. However, methanol is considered toxic [2] and can cause environmental problems due to its high miscibility in water. Thus, ethanol (non-toxic) arises as an attractive alternative [3] as fuel for low temperature fuel cells, besides it can be produced in large scale from agricultural products and it is the biggest renewable source from biomass fermentation.

Nervertheless, ethanol used as fuel show some problems, which require research. Ethanol molecule has a C-C bond, hard to be broken [4], and its complete oxidation pass through a complex mechanism, involving 12 electrons and many adsorbed intermediates [2]. Moreover, DEFCs operate at low temperature ranges, which make ethanol oxidation slower. Thus, it is necessary to use electrocatalysts to accelerate this reaction.

Platinum-based electrocatalysts supported on carbon have been investigated to low temperature fuel cell [5]. Pure platinum is not efficient to ethanol electrooxidation, because its surface is poisoned by strongly adsorbed species coming from the dissociative adsorption of ethanol [5]. Thus, cocatalysts, as Sn and Ni [6], are added to platinum, facilitating ethanol electrooxidation according to two mechanisms: bifunctional and intrinsic [5]. The former postulates that the oxidation of strongly adsorbed species containing oxygen is facilitated in the presence of tin oxides by providing oxygen atoms in adjacent sites in a lowest potential than pure platinum. According to the intrinsic mechanism, the presence of tin modifies the electronic structure of platinum and, as a consequence, the adsorption of species containing oxygen [5]. Jiang et al [7] verified that catalysts containing Sn alloyed to Pt causes a favorable dilatation of crystal lattice, improving the ethanol electrooxidation.

Inside this context, the present work aims to study the relation between structural/composition characteristics and catalytic activity toward ethanol electrooxidation of Pt-based nanoparticles, supported on carbon, with different metals compositions. The electrocatalyst obtained were characterized by Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), High Resolution Transmission Electronic Microscopy (HRTEM) and Cyclic Voltammetry (CV).

2. Experimental Section

A. *Preparation of the electrocatalysts*

To obtain the PtSnNi alloys supported on carbon, the impregnation/reduction method was used [8]. Ethylene glycol was used as the reduction agent and carbon Vulcan XC72R as support. Initially, the solution containing the salts $H_2PtCl6.6H_2O$, $SnCl_2.2H_2O$ e $NiCl_2$ was prepared (with a metal charge of 40% wt) in ethylene glycol and water (75/25 v/v), followed by carbon addition. The composition of the alloys was modified, varying the atomic proportion among Pt, Sn and Ni, added as salts mentioned above. The compositions are described in Table I. The pH solution was adjusted in alkaline range (about pH 12) and heated at 130 °C, under agitation to enable the metals reduction. The samples passed through a centrifugation process and, after that, they were dried.

Table I. Composition of the synthesized alloys.

Electrocatalyst	**Nominal Composition (%)**	**RBS Composition (%)**
Pt:Sn:Ni/C	55:17:28	61:16:23
Pt/C	100	-
Pt:Ni/C	67:33	53:47
Pt:Sn/C	67:33	79:21

The electrocatalyst obtained were characterized by Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), High Resolution Transmission Electronic Microscopy (HRTEM) and Cyclic Voltammetry (CV).

B. *Rutherford Backscattering Spectrometry (RBS)*

The RBS analyses were performed using a He+ beam at 2 MeV produced by TANDEM accelerator of 3 MV. In all the cases, the incidence beam was perpendicular to the sample surface and the detection angle was 165° related to beam direction.

C. *X-ray diffraction (XRD)*

The X-Ray analyses were performed at a BRUKER-AXS-SIEMENS diffractometer, model D5000 with a Cu-Kα radiation generated at 40kV and 25 mA.

D. *High Resolution Transmission Electronic Microscopy (HRTEM)*

High-resolution TEM (HRTEM) images were recorded in a JEM 3000F microscope, operating at 300 kV with a point resolution of 1.7 Å. Specimens for TEM observations were prepared from ultrasonically dispersed suspensions of the sample in n-butanol. Several drops of the suspension were dropped on a copper grid covered with a holey carbon film.

E. *Cyclic Voltammetry*

Cyclic voltammetries were performed with the intent to determine the electrochemical behavior of the catalysts in a 1.0 M ethanol and 0.5 M H_2SO_4 solution. The measurements were carried out at 25 °C in deareated media by purging the electrolyte with nitrogen for 10 minutes before each measurement. Voltammetric curves were registered after 10 cycles in all experiments, to obtain identical and reproducible data without any appreciable changes, necessary to clean the electrode surface, at least in triplicate, by a PAR 273A potentiostat/galvanostat, with a scan rate of 50 $mV.s^{-1}$, in the -0.04 to 0.96 V potential range related to saturated calomelan electrode (SCE). A three-electrode cell was used to perform the analyses, with the platinum as counter electrode and SCE as reference. The work electrode was a graphite disc with an exposed area of 0.29 cm2 recovered by a mixture prepared as follows: 5 mg catalyst was mixed with 2 mL ethanol (Merck) and 25 µL of Nafion® (5%, Aldrich) solution. The mixture was ultrasonically suspended to obtain ink slurry. Then, 136 µL of the slurry was spread to the working electrode to form a thin layer.

3. Results and Discussion

A. *Rutherford Backscattering Spectrometry (RBS)*

PtSnNi/C – 5, PtSn and PtNi electrocatalysts were analyzed by RBS technique and the alloys composition are shown in Table I. It shows that the obtained alloy composition was very similar to the nominal composition (used in the synthesis). The result suggests that the impregnation/reduction process, using ethylene glycol as reducing agent, is a reasonable method to obtain PtSn, PtNi and PtSnNi alloy particles with the composition control.

B. *X-ray diffraction (XRD)*

X-ray diffractograms of the obtained electrocatalysts, described in Table 1, are shown in Figure 1.

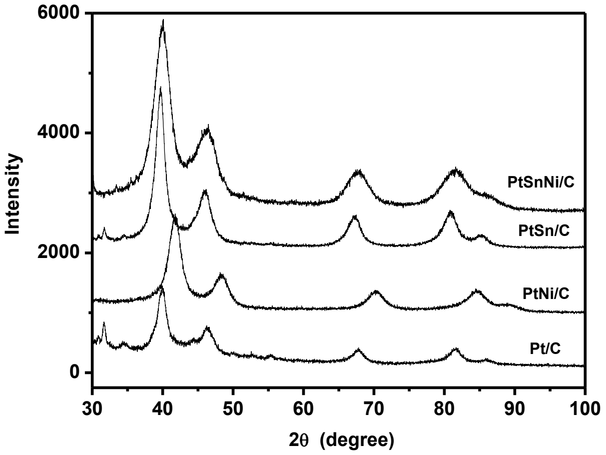

Figure 1. Diffractogram of the PtSnNi/C, PtSn/C, PtNi/C and Pt/C electrocatalysts.

In X-Ray diffraction analyses (Figure 1), it was observed peaks around 2θ = 40º, 47º, 68º, 80º, which are characteristic of a face centered cubic (fcc) Pt phase. Zhou et al [2] attributed the peaks located at 39º, 46º, 68º and 81º to the plans (1 1 1) (2 0 0) (2 2 0) and (3 1 1) of a fcc platinum phase. In other works, Kim et al [9] analyzed PtSn/C alloys by XRD and verified that there were no peaks of pure tin, indicating a good degree of alloying between Pt and Sn, although amorphous tin oxide could be involved. In this study, the peaks are very close of those mentioned in the literature, which indicates that in the electrocatalysts synthesized in the present work, the fcc Pt phase predominates. Spinacé et al [6] reported in their study, that PtSn/C and PtSnNi/C catalysts peaks around 2θ = 34º e 52º, which are consistent to cassiterite phase, SnO_2. In the present work, it was not found cassiterite peak, it means that these phase is not present in the synthesized catalysts, or it is present as amorphous phase.

The crystallite size, τ, was estimated from the half-height width of the diffraction peak (2 0 0) using the Scherrer formula (Eq.1) [10]:

$$\tau = \frac{(k.\lambda)}{(\beta.\cos\theta)}$$

Where τ is the crystallite size (in nanometers), λ is the wavelength (in nanometers), β is the full width at half-maximum (FWHM) (in radians), k is a constant (0.94 to spherical crystallites) and θ is the diffraction angle.

The calculated values to the crystallite size and lattice parameter of the obtained electrocatalysts are shown in Table II.

An estimative of lattice parameter was calculated from Equation 2:

$$n\lambda = 2\, d_{hkl}\, sen\, \theta$$

Where n represents the reflection order, λ is the wavelength (in nanometers), d_{hkl} is interplanar distance between two plans with Miller index h k l, and θ is the incident angle of X-rays.

The distance between the plans was determined from the equation 2, for each diffraction plan, (1 1 1) (2 0 0) (2 2 0) and (3 1 1), considering n = 1 (first order reflection), λ = 1.5418 (Cu-Kα radiation), and θ the half of 2θ of the diffraction peaks (Table II).

The distance magnitude between two adjacent and parallel atom plans is a function of Miller indices (h k l), as well as lattice parameter a. For the crystalline cubic symmetry, the Equation 3 is valid [11]:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

From each diffraction plan, it was determined a lattice parameter value estimated from Equation 3, and the average value is shown in Table II.

Table II. Crystallite size and lattice parameter calculated by XRD data.

Electrocatalyst	**Crystallite Size (nm)**	**Average Lattice Parameter (Å)**	**Interplanar distance(Å)**			
			(1 1 1)	**(2 0 0)**	**(2 2 0)**	**(3 1 1)**
Pt:Sn:Ni/C	3.73	3.913	2.254	1.963	1.381	1.181
Pt/C	7.47	3.917	2.260	1.962	1.384	1.180
Pt:Ni/C	4.61	3.775	2.165	1.880	1.341	1.145
Pt:Sn/C	7.56	3.943	2.277	1.978	1.392	1.187

According to a platinum diffraction pattern [12], lattice parameter is 3.92310 Å and interplanar distances for (1 1 1) (2 0 0) (2 2 0) and (3 1 1) diffraction plans are 2.26500, 1.96160, 1.38730, 1.18260 Å, respectively. XRD data are in good agreement with those data. Thus, comparing all XRD, it can be inferred that tin addition promote a dilatation of crystal lattice, whereas nickel addition promote a contraction of crystal lattice. These results are in agreement with literature [9, 13]. Besides, when Ni and Sn are added simultaneously, no significantly variation is observed in lattice values, because these elements promoted opposite effects in crystal lattice size.

C. High Resolution Transmission Electronic Microscopy (HRTEM)

Electrocatalysts were analyzed according them morphology by high resolution transmission electronic microscopy, and they are shown in Figure 2.

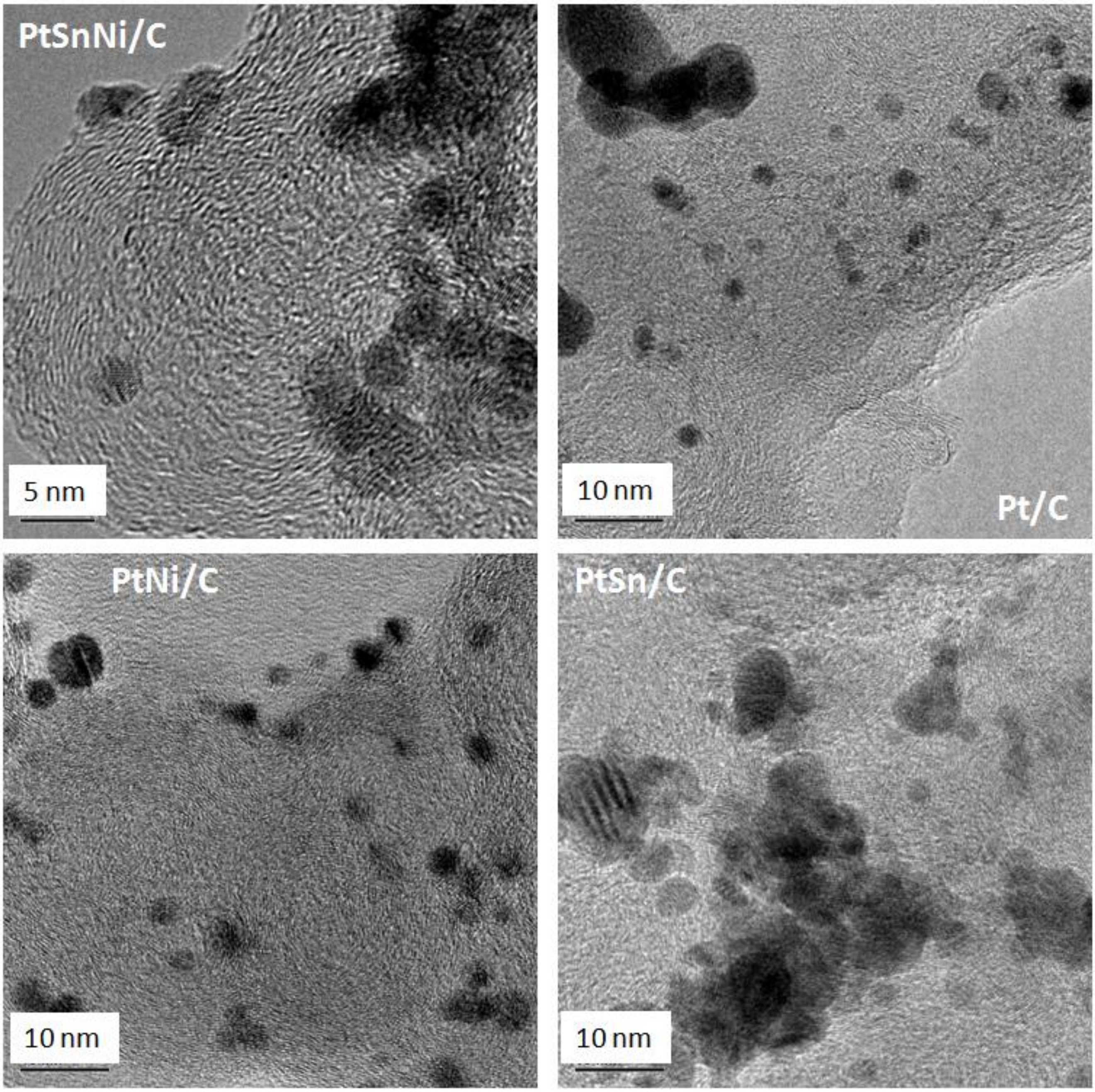

Figure 2. Images obtained from high resolution transmission electron microscopy of the synthesized electrocatalysts.

Figure 2 showed HRTEM images to Pt/C, PtSn/C, PtNi/C and PtSnNi/C synthesized electrocatalysts. It can be seen that these particles are in a nanometric scale with a good dispersion over carbon particle. However, for Pt/C, it is observed a significant difference of nanoparticles size. For others, the size distribution is more homogeneous. Nevertheless, PtSn particles are more agglomerated than others. When Ni is added, it is observed a better dispersion of particles on carbon..

From images showed in Figure 2, it was determined interplanar distance using *Image J* software. For this intent, it was chosen at least three particles randomly. Due to the founded distance values, it was concluded that the plan could be observed at HRTEM images was (2 0 0). The average interplanar distance was calculated and they are summarized in Table III.

Table III. Average (2 0 0) interplanar distance by HRTEM.

Electrocatalyst	**interplanar distance (Å)**
PtSnNi/C	2.2919
Pt/C	2.2712
PtNi/C	2.2813
PtSn/C	2.3091

Comparing these values with those obtained by XRD analysis, it is observed a good agreement between the two techniques. However, it was determined interplanar distance values a little higher by HRTEM than XRD. It is possible due to the imprecision associated to the determination method by HRTEM, which is based in measure of gray scale pixels in image.

D. *Cyclic Voltammetry*

The synthesized electrocatalysts were electrochemical characterized by cyclic voltammetry and they are shown in Figure 3.

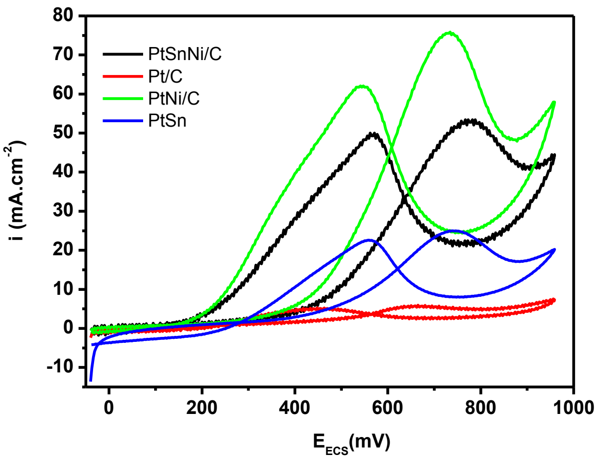

Figure 3. Cyclic voltammetry curves obtained in a 0.5 M H_2SO_4 and 1.0 M ethanol solution (scan rate of 50 $mV.s^{-1}$) for the synthesized electrocatalysts.

From the cyclic voltammetry curves (Figure 3), it is possible to observe the presence of one peak in the potential range of the positive sweep and another one in the negative sweep. Kim et al [9] found two oxidation peaks to PtSn/C catalyst in a 0.5 M H_2SO_4 and 2.0 M C_2H_5OH media. They state that the positive sweep is associated to the ethanol oxidation and the peak in the negative sweep is related to the oxidation of carbonaceous intermediates products from the incomplete ethanol oxidation. In the present work, the peaks observed (Figure 3) were associated to the phenomenon described by Kim et al [9].

The maximum current density values developed by the synthesized catalyst and their respective potential were determined from Figure 3. These data allow obtaining information about catalytic activity of synthesized catalysis. Another important parameter in this evaluation is the onset potential, the potential where currents starts to increase. All of these data are shown in Table IV.

Table IV. Data obtained from cyclic voltammetry curves.

Electrocatalyst	**Positive sweep**			**Negative sweep**	
	i ($mA.cm^{-2}$)	**E_{max} (mV)**	**E_{onset} (mV)**	**i ($mA.cm^{-2}$)**	**E_{max} (mV)**
Pt/C	4.67 ± 1.09	678 ± 14	524 ± 29	4.00 ± 1.19	451 ± 3
PtSnNi/C	56.95 ± 19.48	779 ± 24	308 ± 33	50.53 ± 13.38	572 ± 28
PtNi/C	81.60 ± 7.69	719 ± 43	326 ± 19	68.62 ± 9.89	530 ± 60
PtSn/C	24.89 ± 4.83	697 ± 43	393 ± 30	24.78 ± 6.48	507 ± 45

It was possible to verify that Sn and Ni added to Pt (in binary or ternary alloy) decrease significantly the onset potential to ethanol electrooxidation (Table IV), observed in the positive sweep. However the maximum potential peak (in the positive and negative sweeps) was not significantly affected. Current density values had a huge increase with Sn and Ni addition, compared to Pt/C, for both positive and negative sweeps (Table IV). These data are consistent with the result obtained by other authors in the literature [14], which state that the presence of both co-catalysts, Ni and Sn, significantly reduces the onset potential to ca. 0.2 V vs. RHE related to Pt_{100}/C and raises the current densities at the PtSnNi/C electrocatalyst. Nevertheless, PtNi/C showed the highest current density value.

4. Conclusion

The results obtained by Rutherford Backscattering Spectroscopy analysis showed that impregnation reduction is a reasonable method to obtain PtSn, PtNi and Pt-Sn-Ni alloy particles with a composition control. Moreover, X-ray diffractions showed that synthesized electrocatalysts have face centered cubic platinum crystalline structure, and Sn promote a dilatation in reticular lattice, whereas Ni promoted a contraction of it. When Sn and Ni are added simultaneously reticular lattice *a* value were not affected. Crystallite size is decreased with Ni or simultaneous Sn and Ni addition to Pt, while Sn addition promoted an increase in crystallite size. PtSnNi/C particles showed the lowest crystallite size. HRTEM images showed that metal particles are in nanometric scale, in agreement with XRD analysis, and that the particles distribution on the carbon support is heterogeneous, with some agglomerates over carbon particles. Except for Pt nanoparticles, catalysts present an uniform size particle distribution.

Cyclic voltammetries showed that all synthesized binary and ternary alloys had higher catalytic activity than platinum, demonstrated through an increase in current density values and a decrease in onset potential. Moreover, PtNi/C nanoparticles have highest catalytic activity toward ethanol electrooxidation.

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References

[1] MA Scibioh, SK Kim, EA Cho, TH Lim, S Hong, HY Ha, “Pt-CeO_2/C anode catalyst for direct methanol fuel cells”, in Appl Catal B Environ 2008; Vol 84, pp. 773 – 782.

[2] W Zhou, Z Zhou, S Song, W Li, G Sun, P Tsiakaras, Q Xin. “Pt based anode catalysts for direct ethanol fuel cells”, in Appl Catal B Environ 2003; Vol 46, pp. 273-285.

[3] SG Rodríguez, F Somodi, I Borbáth, JL Margitfalvi, MA Peña, JLG Fierro, S Rojas, “Controlled synthesis of Pt-Sn/C fuel cell catalysts with exclusive Sn–Pt interaction Application in CO and ethanol electrooxidation reactions”, in Appl Catal B Environ 2009; Vol 91, pp.83 – 91.

[4] C Lamy, S Rousseau, EM Belgsir, C Coutanceau, J.-M Léger, “Recent progress in the direct ethanol fuel cell: development of new platinum-tin catalysts”, in Electrochim Acta 2004; Vol 49, pp. 3901 - 3908.

[5] E Antolini, “Catalysts for direct ethanol fuel cells”, in J Power Sources 2007;Vol. 170, pp. 1- 12.

[6] EV Spinacé, M Linardi, AO Neto, “Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt–Sn electrocatalysts”, in Electrochem Commun 2005; Vol. 7, pp. 365 - 369.

[7] L Jiang, G Sun, S Sun, J Liu, S Tang, H Li, B Zhou, Q Xin, “Structure and chemical composition of supported Pt–Sn electrocatalysts for ethanol oxidation”, in Eletrochim Acta 2005; Vol. 50, pp. 5384 - 5389.

[8] Z Jiujun, PEM Fuel Cell, Electrocatalysts and Catalyst Layers – Fundamentals and Application, Springer, 2008, pp. 907.

[9] JH Kim, SM Choi, SH Nam, MH Seo, SH Choi, WB Kim, “Influence of Sn content on PtSn/C catalysts for electrooxidation of C1–C3 alcohols: Synthesis, characterization, and electrocatalytic activity”, in Appl Catal B Environ 2008; Vol. 82, pp. 89 - 102.

[10] F Colmati, E Antolini, ER Gonzalez, “Ethanol oxidation on a carbon-supported $Pt_{75}Sn_{25}$ electrocatalyst prepared by reduction with formic acid: Effect of thermal treatment”, in Appl Catal B Environ 2007; Vol. 73, pp.106 - 115.

[11] Callister, W. D.; Ciência e Engenharia de Materiais: Uma Introdução. LTC; 2002, 37.

[12] T. Swanson, Natl. Bur. Stand. (U.S.), Circ. 539, Vol I, pp. 31 (1953).

[13] E Antolini, JRC Salgado, ER Gonzalez, “Carbon supported $Pt_{75}M_{25}$ (M = Co, Ni) alloys as anode and cathode electrocatalysts for direct methanol fuel cells”, in J Electroanal Chem 2005; Vol. 580, pp. 145 - 154.

[14] TS Almeida, KB Kokoh, AR de Andrade, “Effect of Ni on Pt/C and PtSn/C prepared by the Pechini method”, in Int J Hydrogen energy 2011; Vol. 36, pp. 3803 - 3810.