

Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt–Sn electrocatalysts

Estevam V. Spinacé *, Marcelo Linardi, Almir Oliveira Neto *

*Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP, Av. Prof. Lineu Prestes, 2242,
Cidade Universitária, 05508-900 São Paulo, SP, Brazil*

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Abstract

PtSn/C electrocatalysts with Pt:Sn molar ratios of 75:25, 50:50 and 25:75 and PtSnNi/C electrocatalyst with a Pt:Sn:Ni molar ratio of 50:40:10 were prepared by the alcohol-reduction process using ethylene glycol as solvent and reducing agent. The electrocatalysts were characterized by EDX, XRD and cyclic voltammetry. The electro-oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry using the thin porous coating technique. PtSnNi/C electrocatalyst showed a superior performance compared to PtSn/C electrocatalysts in the potential range of interest for direct ethanol fuel cell.

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1. Introduction

Fuel cells employing alcohols directly as fuel – direct alcohol fuel cell (DAFC) – are attractive as power sources for mobile, stationary and portable applications. The alcohol is fed directly into the fuel cell without any previous chemical modification and is oxidized at the anode while oxygen is reduced at the cathode. This feature avoids problems related to production, purification and storage of hydrogen [1–6].

Ethanol is a renewable and attractive fuel as it can be produced in great quantities from biomass and it is less toxic than methanol. However, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulty in C–C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts. In this context, more active electrocatalysts are essential to enhance the ethanol electro-oxidation [7].

Recently, Lamy and co-workers [8,9] observed that PtSn/C electrocatalysts were more active than PtRu/C electrocatalysts for ethanol oxidation. PtSn/C electrocatalysts with Pt:Sn atomic ratios varying from 100:10 to 100:50 were prepared by co-impregnation-reduction method and the optimum tin composition was found to be in the range of 10–20 at.%. In these conditions, the electrode activity was enhanced and the poisoning due to CO intermediates coming from the ethanol dissociative chemisorption was reduced. On the other hand, the electro-oxidation of ethanol was not complete leading to the formation of products like acetaldehyde and acetic acid.

Xin and co-workers [10–14] studied the electro-oxidation of ethanol using binary and ternary platinum-based electrocatalysts prepared by a polyol method and observed that the addition of W improved the PtRu/C activity, however, the activity of PtRuW/C electrocatalyst was inferior to that of PtSn/C electrocatalysts. Moreover, PtSn/C electrocatalysts with Pt:Sn molar ratios of 66:33, 60:40 and 50:50 were more active than electrocatalysts with 75:25 and 80:20 molar ratios. The

* Corresponding authors. Tel./fax: +55 11 3816 9440.

E-mail addresses: espinace@ipen.br (E.V. Spinacé), aolivei@ipen.br (A.O. Neto).

superior performance of PtSn/C electrocatalysts in ethanol oxidation was attributed to the so-called bifunctional mechanism and to the electronic interaction between Pt and Sn [14].

In this work, PtSn/C electrocatalysts with Pt:Sn atomic ratios of 25:75, 50:50 and 75:25 and a new formulation of PtSnNi/C electrocatalyst with a Pt:Sn:Ni atomic ratio of 50:40:10 were prepared by alcohol-reduction process [15,16] and tested for ethanol oxidation using cyclic voltammetry and chronoamperometry.

2. Experimental

PtSn/C and PtSnNi/C electrocatalysts were prepared by alcohol reduction process [15,16] using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) as metal sources, ethylene glycol (Merck) as solvent and reducing agent and Carbon Vulcan XC72R as support. The metal sources and the carbon support were added to a mixture of ethylene glycol/water (75/25, v/v) and the mixture was refluxed for 2 h. Then, the solid was filtered, washed with water and dried. The nominal loading of metals in the electrocatalysts was 20 wt%.

The atomic ratios were obtained by EDX analysis using a scanning electron microscope Phillips XL30 with a 20 keV electron beam and equipped with EDAX DX-4 microanalyser.

The XRD analyses were performed using a Rigaku diffractometer model Multiflex with a Cu $\text{K}\alpha$ radiation source.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [17,18]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.36 cm^2 area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of 0.0003 g cm^{-2} . In cyclic voltammetry and chronoamperometry experiments the current values (I) were ex-

pressed in amperes and were normalized per gram of platinum ($\text{A g}_{\text{Pt}}^{-1}$). The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquímica software. Cyclic Voltammetry was performed in a 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 . For chronoamperometry, the electrolyte solution was 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H_2SO_4 .

3. Results and discussion

The measured Pt:Sn and Pt:Sn:Ni atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios and the mean particle sizes were in the range of 2.0–2.5 nm (Table 1). The X-ray diffractograms of the electrocatalysts are shown in Fig. 1. The PtSn/C electrocatalysts with a Pt:Sn atomic ratio of 50:50 and 75:25 showed four diffraction peaks at about $2\theta = 40^\circ$, 47° , 67° and 82° characteristic of the fcc structure of platinum and platinum alloys [18].

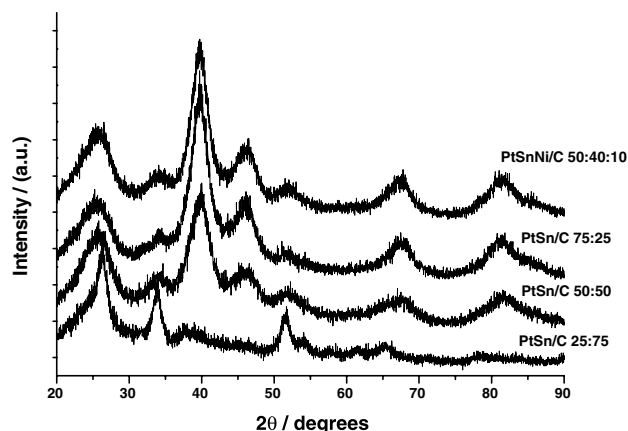


Fig. 1. X-ray diffractograms of PtSn/C and PtSnNi/C electrocatalysts.

Table 1

Pt:Sn and Pt:Sn:Ni atomic ratios and mean particle size of the prepared electrocatalysts

Electrocatalyst	Nominal atomic ratio			Atomic ratio – EDX ($\pm 5\%$)			Particle size ^a (nm)
	Pt	Sn	Ni	Pt	Sn	Ni	
PtSn/C	75	25	–	72	28	–	2.4
PtSn/C	50	50	–	52	48	–	2.0
PtSn/C	25	75	–	29	71	–	–
PtSnNi/C	50	40	10	52	42	6	2.4

The electron beam spot size used was 200 μm .

^a Mean particle size calculated from X-ray diffraction data using the Debye–Scherrer equation.

The broad peak at about 25° was associated with the Vulcan XC 72 R support material. Interestingly, the typical peaks relative to the fcc structure of platinum were not evident for PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 25:75. The diffractogram of this sample showed peaks at about $2\theta = 27^\circ, 34^\circ, 52^\circ, 54^\circ, 62^\circ$ and 66° that are characteristic of cassiterite SnO_2 phase [19]. The peaks of the cassiterite phase ($2\theta = 34^\circ$ and 52°) were also observed in the diffractograms of PtSn/C electrocatalysts with a Pt:Sn atomic ratio of 50:50 and 75:25. However the extend of cassiterite formation in the nanocatalysts produced by the alcohol reduction method could not be determined by the employed techniques. Xin and co-workers [10–14] prepared PtSn/C electrocatalysts by a similar procedure using ethylene glycol as reducing agent. The analysis of the diffractograms also revealed the typical peaks relative to the fcc structure of platinum alloy, however, no peaks of cassiterite phase were observed. This is probably because the electrocatalysts were prepared under argon flow while in this work the electrocatalysts were prepared in open atmosphere. The diffractogram of PtSnNi/C electrocatalyst (50:40:10) also shows the characteristic peaks of the platinum fcc structure and the presence of cassiterite phase like observed for PtSn/C (50:50) electrocatalyst. Choi et al. [20] prepared non-supported PtRu (50:50) and PtRuNi (50:40:10) nanoparticles using a conventional reduction with NaBH_4 . The XRD analysis showed the characteristic peaks of platinum fcc structure; no peaks of fcc Ni and hcp Ru metals or oxides/hydroxides were observed. However, the XPS analysis revealed that about 40% of the ruthenium species were found as ruthenium oxides and 85% of nickel species were found as NiO , Ni(OH)_2 and NiOOH .

The cyclic voltammograms (CV) of PtSn/C and PtSnNi/C electrocatalysts in the absence of ethanol are shown in Fig. 2. In this case, all CV do not have a well-defined hydrogen adsorption–desorption region

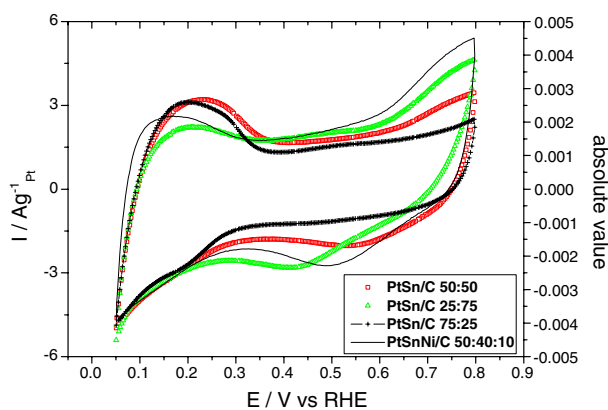


Fig. 2. Cyclic voltammetry of PtSn/C and PtSnNi/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1} .

(0–0.4 V). The CV of PtSn/C electrocatalysts showed an increase in the currents in the double layer (0.4–0.8 V) with increasing the tin content, which may be attributed to the increasing tin oxide species [21–23], as observed on the X-ray diffractograms. Analysis of the cathodic scan shows only an increase of oxide reduction with increasing Sn content in the catalyst. This analysis do not shows, however the extend of cassiterite formation. The CV of PtSnNi/C electrocatalyst showed higher currents values in the double layer region than the PtSn/C electrocatalyst (50:50) and this is probably due to the presence of tin and nickel oxide species.

The PtSn/C and PtSnNi/C electrocatalysts performances in ethanol oxidation are shown in Fig. 3. The anodic cyclic voltammetry responses were plotted after subtracting the background currents [17,18] and the current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [24–27]. The electro-oxidation of ethanol started at low potentials ($\sim 0.25 \text{ V}$) for PtSn/C electrocatalysts with Pt:Sn molar ratios of 50:50 and 25:75, which showed similar current values in range of 0.25–0.40 V. Above 0.4 V the electrocatalysts with Pt:Sn molar ratio of 50:50 showed a superior performance. For the electrocatalyst with Pt:Sn molar ratio of 75:25 the oxidation started only at approximately 0.35 V and the currents values were lower than those observed for the electrocatalysts with more tin content. These results were similar to the obtained by Xin and co-workers [10–14] using PtSn/C electrocatalysts prepared by a similar procedure but different from those obtained by Lamy and co-workers [8,9] using electrocatalysts prepared by co-impregnation-reduction method. These observations suggest that the performance of PtSn/C electrocatalysts depends greatly on its preparation procedure.

For PtSnNi/C electrocatalyst with a Pt:Sn:Ni atomic ratio of 50:40:10 the substitution of a small amount of tin by nickel practically did not change the onset potential

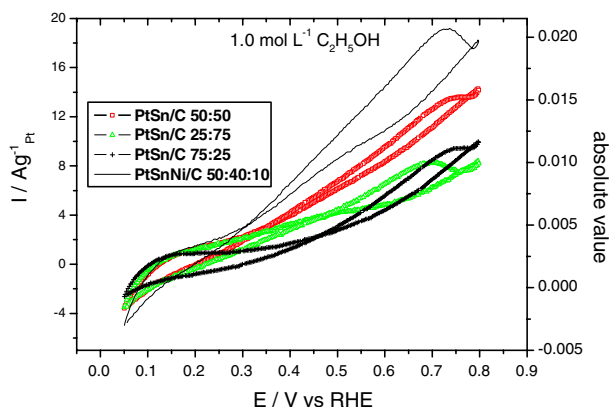


Fig. 3. Cyclic voltammetry of PtSn/C and PtSnNi/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol L^{-1} of ethanol with a sweep rate of 10 mV s^{-1} .

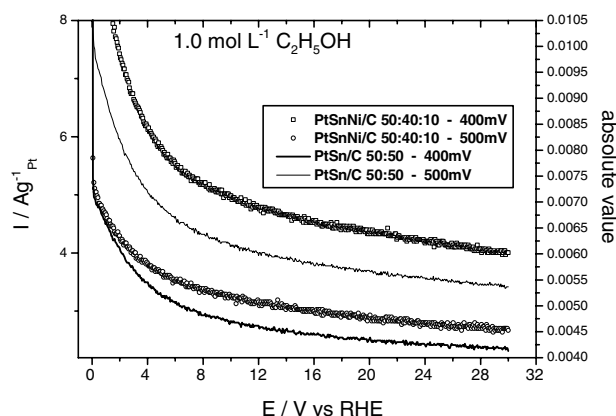


Fig. 4. Current–time curves at 0.4 and 0.5 V in 1 mol L^{−1} ethanol solution in 0.5 mol L^{−1} H₂SO₄ for PtSn/C 50:50 and PtSnNi/C 50:40:10 electrocatalysts.

(~0.25 V) but the current values were greater than those obtained for PtSn/C (50:50) electrocatalyst in all range of the potential (Fig. 3). The superior performance of the PtSnNi/C electrocatalyst was also observed by chronoamperometry measurements (Fig. 4). In all current–time curves there is an initial current drop in the first 5 min followed by a slower decay, but the current values obtained for PtSnNi/C electrocatalyst were always higher than those obtained for PtSn/C (50:50) electrocatalyst. Similar results were also observed in methanol oxidation using non-supported PtRu (50:50) and PtRuNi (50:40:10) electrocatalysts [20,28,29]. The superior activity of the PtRuNi electrocatalyst was attributed to the modification of electronic properties of platinum and to the presence of nickel oxide species resulting in a combination of electronic effect and bifunctional mechanism [20,28,29]. Recently, Dumesic and co-workers [30] reported the aqueous-phase reforming of oxygenated hydrocarbons, like glycerol and ethylene glycol, at temperatures near 500 K using non-precious metal catalysts. They observed that the addition of Sn to Raney-Ni catalysts facilitated C–C bond cleavage and promoted removal of adsorbed CO species by water-gas shift reaction, which increased the selectivity for hydrogen production.

4. Conclusions

The alcohol-reduction process was found to be an effective method for making active PtSn/C and PtSnNi/C (50:40:10) electrocatalysts for ethanol oxidation. The X-ray diffractograms of electrocatalysts showed the typical fcc structure of platinum and platinum alloys with the presence of a cassiterite SnO₂ phase, which increases with tin content. PtSnNi/C electrocatalyst (50:40:10) showed higher current values and stability than PtSn/C electrocatalysts in the potential range

of interest for direct ethanol fuel cell (0.2–0.6 V). Further work is however necessary to know if this is the optimum Pt:Sn:Ni composition and to investigate the nanoparticles morphology. Experiments using these electrocatalysts in gas diffusion electrodes for tests in single direct ethanol fuel cell, as well as long term investigations are currently in progress.

Acknowledgments

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