

## Preparation of PtSn/C Electrocatalysts by an Alcohol-Reduction Process using different conditions for Ethanol Electro-oxidation

V. A. Ribeiro<sup>1</sup>, R. C. Sekol<sup>2</sup>, A. D. Taylor<sup>2</sup>, A. Oliveira Neto<sup>1</sup> and E. V. Spinacé<sup>1</sup>

<sup>1</sup>Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242 – Cidade Universitária, 05508-900 São Paulo – SP, Brazil

<sup>2</sup> Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States

PtSn/C electrocatalysts were prepared by an alcohol-reduction process using  $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  as metal precursors, a mixture of ethylene glycol:water as both a solvent and reducing agent and Carbon Vulcan XC72 as support. The electrocatalysts were prepared with 20 wt% of metal content and Pt:Sn atomic ratio of 50:50 using different conditions: under reflux (RFX) at 160°C for 3 h and in an autoclave (ATC) at 200°C under autogeneous pressure for 30 min. The obtained PtSn/C electrocatalysts were characterized by X-ray diffraction and cyclic voltammetry. The electro-oxidation of ethanol was evaluated by chronoamperometry in acid medium. A similar performance was observed for commercial PtSn/C BASF and PtSn/C RFX while PtSn/C ATC showed a superior performance.

### Introduction

Direct Ethanol Fuel Cells (DEFCs) are attractive power sources for mobile and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage, DEFCs use a liquid fuel, thus simplifying the fuel system. Also, ethanol offers an attractive alternative as a fuel because it is produced in large quantities from biomass [1-3]. In Brazil, ethanol is produced on a large scale; moreover, ethanol has the advantages of being a fuel derived from renewable sources and is less toxic than methanol. However, the complete oxidation of ethanol to  $\text{CO}_2$  in a DEFC is harder than that of methanol due to the difficulty of C-C bond breaking resulting in the formation of acetaldehyde and acetic acid as the principal products. Also, the formation of intermediates like CO and others block the active sites of the Pt-based electrocatalyst leading to its deactivation [4]. Thus, the search for electrocatalysts more effective for the ethanol electro-oxidation is one of the challenges in this area. For this, it has been proposed the addition of several other metals to Pt that can lead to the formation of oxygen species at low potentials (bifunctional mechanism) and/or modify the electronic properties of Pt facilitating the oxidation of CO to  $\text{CO}_2$ . For the case of methanol electro-oxidation the best material found was PtRu electrocatalysts, while for ethanol electro-oxidation PtSn electrocatalysts

have been shown the best performances [3-15]. Also, the performances of the PtSn/C electrocatalysts are very dependent on the method of preparation, which influence the sizes, morphologies and the distribution of the nanoparticles on the carbon support and different Pt and Sn phases could also be formed. Studies have been shown that good performances for ethanol electro-oxidation could be obtained using PtSn electrocatalysts where, Pt and Sn were found as an alloy, as well, where Pt and SnO<sub>2</sub> coexist as a separated phases [3-15]. We have already prepared PtSn/C electrocatalysts by an alcohol-reduction process [3, 4] that showed good results for ethanol electro-oxidation. In this work, some modifications were done in this process and the obtained materials were tested for ethanol electro-oxidation.

## Experimental

### Preparation and Characterization of PtSn/C electrocatalysts

PtSn/C electrocatalysts were prepared by an alcohol-reduction process [3, 4] using Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> and SnCl<sub>4</sub>•5H<sub>2</sub>O as metal sources, a mixture of ethylene glycol:water (75:25 v/v) as both a solvent and reducing agent and Carbon Vulcan XC72 as support. The electrocatalysts were prepared with 20 wt% of metal content and Pt:Sn atomic ratio of 50:50 using different conditions: under reflux (RFX) at 160°C for 3 h and in an autoclave (ATC) at 200°C under autogeneous pressure for 30 min. The obtained PtSn/C electrocatalysts were characterized by X-ray diffraction and cyclic voltammetry. The commercial PtSn/C BASF (PtSn alloy, 20 wt% of metals and Pt:Sn atomic ratio of 75:25) electrocatalyst was used for comparative purposes. The X-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The diffractograms were recorded at  $2\theta$  in the range 20° - 90° with step size of 0.05° and scan time of 2 s per step. Cyclic voltammetry measurements were performed in a 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution saturated with N<sub>2</sub> with a scan rate of 10 mV.s<sup>-1</sup>.

### Electro-oxidation of ethanol

Chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Chronoamperometry experiments were performed with a Microquimica (model MQPG01) potentiostat/galvanostat using 1.0 mol L<sup>-1</sup> of ethanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution saturated with N<sub>2</sub> at 0.3V and at room temperature.

## Results and Discussion

The obtained PtSn/C electrocatalysts were characterized by X-ray diffraction (Figure 1). PtSn/C electrocatalyst prepared under reflux (RFX) and in an autoclave (ATC) showed four diffraction peaks at about  $2\theta = 40^\circ, 47^\circ, 67^\circ$  and  $82^\circ$  which are associated with the planes (111), (200), (220) and (311), respectively, of the face-centered cubic structure (fcc) of Pt and its alloys [3]. For the commercial PtSn/C BASF, which is a PtSn alloy phase, the Pt-fcc peaks were also observed in the diffractogram, however, they were shifted to small angles. Compared to Pt/C electrocatalyst (unit cell parameter  $a = 0.390$  nm), PtSn/C BASF showed the unit cell parameter  $a = 0.401$  nm showing the formation of a PtSn alloy [12]. The Pt-fcc peaks of PtSn/C RFX ( $a = 0.396$  nm) and PtSn/C ATC ( $a = 0.392$  nm) were also shifted to small angles, but for these electrocatalysts, not all of Sn atoms were incorporated into the Pt-(fcc) structure. Moreover, it was observed for these

materials two peaks at about  $2\theta = 34^\circ$  and  $52^\circ$  that were attributed to  $\text{SnO}_2$  phase [4, 12]. The crystallite sizes calculated from the Pt(220) diffraction peaks were around 2 nm for PtSn/C RFX and commercial PtSn/C BASF while for PtSn/C ATC the crystallite size was smaller than 2 nm.

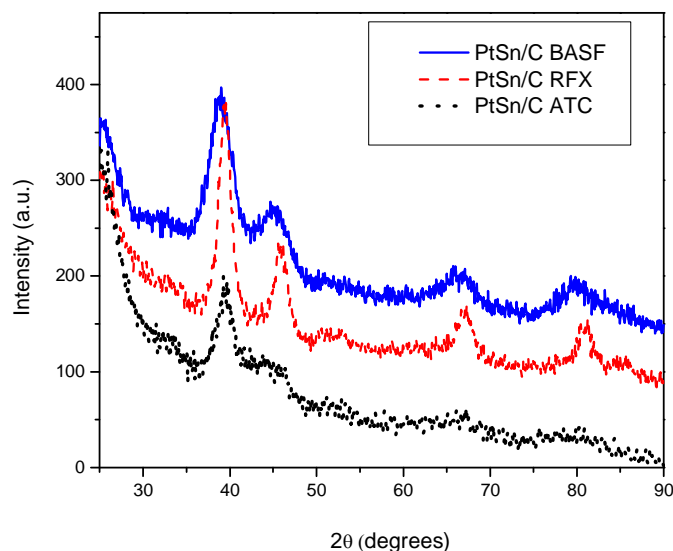


Figure 1: X-ray diffractograms of commercial PtSn/C BASF and PtSn/C (RFX) and (ATC) electrocatalysts.

The cyclic voltammograms in acid solution of PtSn/C BASF, PtSn/C (RFX) and (ATC) electrocatalysts are shown in Figure 2. PtSn/C BASF and PtSn/C ATC showed the hydrogen adsorption-desorption region ( $-0.2 - 0.1\text{V}$  vs Ag/AgCl) more defined than the PtSn/C RFX and an increase of the current values in the electrical double layer region ( $0.2 - 0.5\text{ V}$  vs Ag/AgCl) was also observed for these electrocatalysts. The increase of current values in the double layer region could be attributed to an increase of oxide species on the surface.

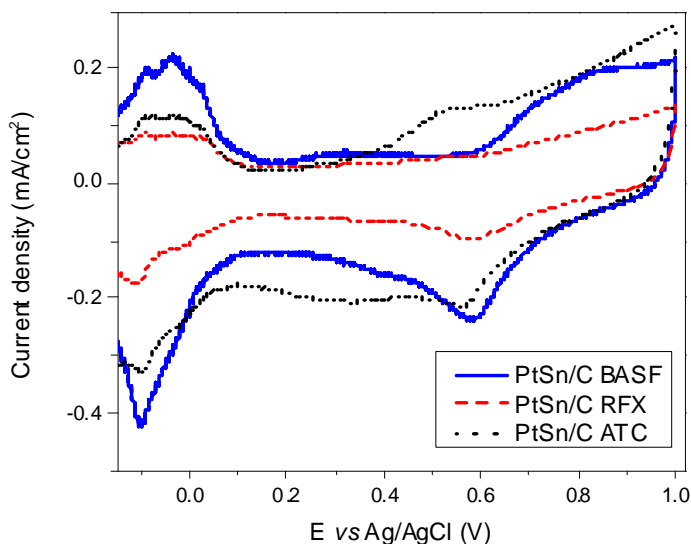


Figure 2: Cyclic voltammograms of the electrocatalysts in  $0.5\text{ mol}\cdot\text{L}^{-1}$  solution of  $\text{H}_2\text{SO}_4$  at  $10\text{ mV s}^{-1}$ .

The chronoamperometry experiments were carried out to examine the performance and stability of the electrocatalysts (Figure 3).

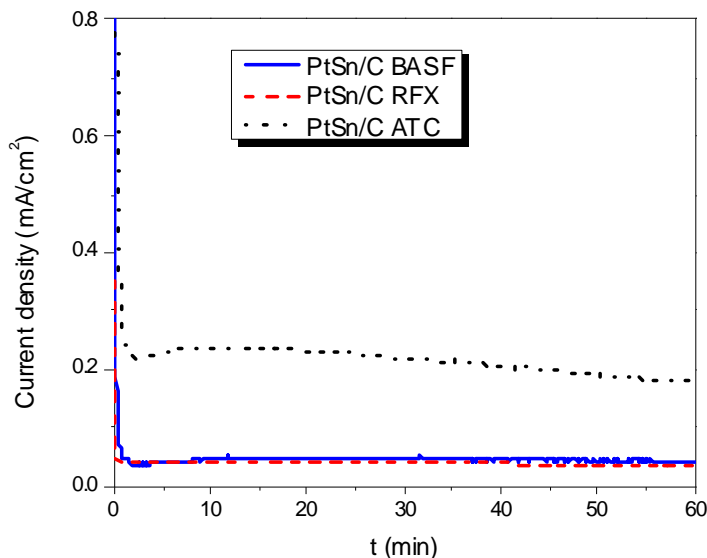


Figure 3: Chronoamperometry curves at 0.3V (vs. Ag/AgCl) in 1 mol L<sup>-1</sup> ethanol solution in 0.5 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> for the different electrocatalysts.

PtSn/C electrocatalyst RFX showed similar performance of the commercial PtSn/C BASF while PtSn/C ATC showed the best performance, which could be attributed to the presence of Pt and SnO<sub>2</sub> phases on its surface. It has been described in the literature that PtSn/C electrocatalysts containing Pt(fcc) and SnO<sub>2</sub> phases exhibited superior performance for ethanol electro-oxidation [4, 7-9]

### Conclusions

PtSn/C electrocatalyst prepared by an alcohol-reduction process under autogeneous pressure showed superior performance (amperes per gram of Pt) compared to the material prepared under reflux and to commercial PtSn/C BASF. The superior performance could be attributed to a small crystallite size and probably to a more homogeneous distribution of Pt-(fcc) and SnO<sub>2</sub> phases on the carbon support. A more detailed analysis of the catalyst surface was necessary to understand its activity and it was under investigation.

### Acknowledgments

CNPq, FINEP-ProH<sub>2</sub> and FAPESP are acknowledged for financial support.

### References

1. E. Antolini, *J Power Sources*, **170**, 1 (2007).
2. C. Lamy C, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Léger, *Electrochim Acta*, **49**, 3901 (2004).
3. A. O. Neto, R. R. Dias, M. M. Tusi, M. Linardi, E. V. Spinacé, *J Power Sources*, **166**, 87 (2007).

4. R. M. Antoniassi, A. O. Neto, M. Linardi, E. V. Spinacé, *Int. J. Hydrogen Energy*, **38**, 12069 (2013).
5. W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, *Appl Catal B: Environmental*, **46**, 273 (2003).
6. S. Rousseau, C. Coutanceau, C. Lamy, J.M. Leger, *J Power Sources*, **158**, 18 (2006).
7. J. Mann, N. Yao, A. B. Bocarsly, *Langmuir* **22**, 10432 (2006).
8. L. Jiang, L. Colmenares, Z. Jusys, G. Q. Sun, R. J. Behm, *Electrochim. Acta*, **53**, 377 (2007).
9. A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel, R. R. Adzic, *Nature Mater.*, **8**, 325 (2009).
10. M. Zhu, G. Sun, Q. Xin, *Electrochim Acta*, **54**, 1511 (2009).
11. D.R.M. Godoi, J. Perez, H.M. Villullas, *J Power Sources*, **195**, 3394 (2010).
12. R. F. B. De Souza, L. S. Parreira, D. C. Rascio, J. C. M. Silva, E. Teixeira-Neto, M. L. Calegari, E. V. Spinacé, A. O. Neto, M. C. Santos, *J Power Sources*, **195**, 1589 (2010).
13. E. Antolini, E.R. Gonzalez, *Catal. Today*, **160**, 28 (2011).
14. F.L.S. Purgato, S. Pronier, P. Olivi, A.R. De Andrade, J. M. Léger, G. Tremiliosi-Filho, K. B. Kokoh, *J Power Sources*, **198**, 95 (2012).
15. B. Liu, Z. W. Chia, Z. Y. Lee, C. H. Cheng, J. Y. Lee, Z. L. Liu, *Fuel Cells*, **12**, 670 (2012).