

Preparation of PtSn/C Electrocatalyst by Successive Reduction for Ethanol Electro-oxidation

Vilmária A. Ribeiro, Almir Oliveira Neto, Marcelo Linardi and Estevam V. Spinacé

Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242 – Cidade Universitária, 05508-900 São Paulo – SP, Tel. 55 11 31339284, Fax: 55 11 31339193.

PtSn/C electrocatalyst was prepared in two steps: i) initially $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was reduced on the carbon support using sodium borohydride as reducing agent. At the second step the obtained Sn/C was used as support and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was reduced by an alcohol-reduction process. The obtained PtSn/C electrocatalyst was characterized by X-ray diffraction and cyclic voltammetry. The electro-oxidation of ethanol was studied by chronoamperometry. The commercial electrocatalyst PtSn/C BASF (PtSn alloy) was used for comparison. The results showed that the PtSn/C electrocatalyst prepared by successive reduction was more active for ethanol electro-oxidation than the commercial PtSn/C BASF electrocatalyst.

Introduction

Fuel cells that use alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are arousing considerable interest, being the Direct Methanol Fuel Cell the most studied and the one showing the best results (1-2). In Brazil, ethanol is a better alternative to methanol because it is produced in large quantities from renewable sources and is less toxic than methanol. On the other hand, the complete oxidation of ethanol to CO_2 is more difficult than that of methanol due to the difficulty of breaking the C-C bond and to the formation of intermediates that poison the platinum anode catalyst (3). For ethanol electro-oxidation PtSn-based electrocatalysts have been shown the best results and the activity of these electrocatalysts is strongly influenced by the method of preparation (2-10). Furthermore, PtSn electrocatalysts where Sn is reduced in the form of an alloy with Pt (5-8), as well, where Pt and SnO_2 phases coexist (4, 9, 10), have shown good activities for ethanol electro-oxidation. In this work, PtSn/C electrocatalyst was prepared by successive reduction, where initially Sn/C was prepared using sodium borohydride as a reducing agent and in a further step Pt^{+4} ions were reduced by an alcohol-reduction and supported on the Sn/C.

Experimental

Preparation and Characterization of the Pt-Sn/C electrocatalyst by successive reduction

PtSn/C electrocatalyst was prepared in two steps: *i*) initially, Sn/C (10 wt% Sn) was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) in ethanol. The carbon support Vulcan XC72 was added to the solution and the resulting mixture was submitted to ultrasound for 5 min. A solution of sodium borohydride (BH_4^- :Sn molar ratio = 5) was then added at once to the mixture, which remained under stirring for 30 min at room temperature. The

mixture was filtered, washed with water and dried at 70°C for 2 h, *ii*) $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in a ethylene glycol/water solution (3/1, v/v) and the obtained Sn/C in the first step was added to the solution. The resulting mixture was treated with ultrasound for 5 min and submitted to reflux for 2 h. The obtained PtSn/C electrocatalyst (12.5 wt% Pt) was separated by filtration, washed with water and dried at 70°C for 2 h.

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 2θ in the range 20° - 90° with step size of 0.05° and scan time of 2 s per step.

Cyclic voltammograms were carried out using the thin porous coating technique [4]. An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min and transferred to the cavity of the working electrode. The working electrodes have a geometric area of 0.3 cm² with a depth of 0.3 mm. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. The electrochemical experiments were performed using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a PC and using the Microquimica software. Cyclic voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂ at 25 °C, in the potential range of 0.05 - 0.8 V and scan rate of 10 mV s⁻¹.

Electro-oxidation of ethanol

The electro-oxidation of ethanol was studied by chronoamperometry using the thin porous coating electrode technique (4). The experiments were performed at room temperature using a 1.0 mol L⁻¹ ethanol solution in 0.5 mol L⁻¹ H₂SO₄ saturated with N₂. In these experiments the values of current (I) are expressed in amperes and were normalized per gram of platinum (A g_{Pt}⁻¹). For comparison purposes the commercial catalyst PtSn/C BASF (20 wt% metals loading, Pt:Sn atomic ratio of 75:25, 16.6 wt% Pt), which is in the form of a PtSn alloy according to the manufacturer, was used.

Results and Discussion

The X-ray diffractograms of PtSn/C BASF, PtSn/C, Sn/C and Carbon Vulcan XC72 are shown in Figure 1.

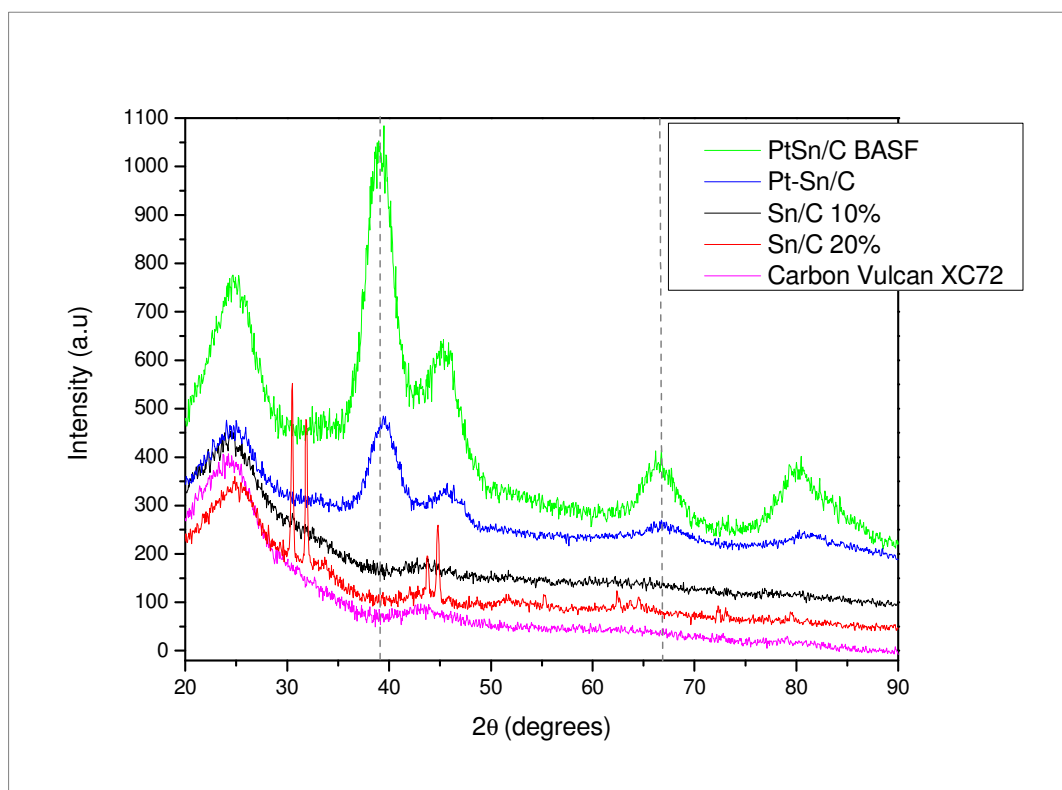


Figure 1: X-ray diffractograms of PtSn/C BASF, Pt-Sn/C, Sn/C and Carbon Vulcan XC72.

In all diffractograms it was observed a large peak at about $2\theta = 25^\circ$, which was associated with the carbon support Vulcan XC72. For Sn/C (10 wt% Sn) the XRD pattern was very similar to the Carbon Vulcan XC72 support showing that no crystalline phases were present, however, the presence of Sn was detected by EDX in this material. Then, it was prepared a Sn/C using the same procedure but with a higher concentration of Sn (20wt%) and, in this case, several peaks corresponding to metallic Sn (11) were observed in the diffractogram. PtSn/C electrocatalyst prepared by successive reduction showed four diffraction peaks at about $2\theta = 40^\circ$, 47° , 67° and 82° which are associated with the planes (111), (200), (220) and (311), respectively, of the face-centered cubic structure (fcc) of platinum and its alloys (4). For the PtSn/C BASF the fcc Pt peaks were also observed, however, they were shifted to smaller angles showing the formation of a PtSn alloy. The (220) plane reflections of the fcc Pt peaks were used to estimate the average crystallite size using Scherrer equation and the values were 2 nm for the PtSn/C electrocatalyst prepared by successive reduction and 2.5 nm for the PtSn/C BASF.

The cyclic voltammograms in acid solution for Sn/C, PtSn/C and PtSn/C BASF electrocatalysts are shown in Figure 2.

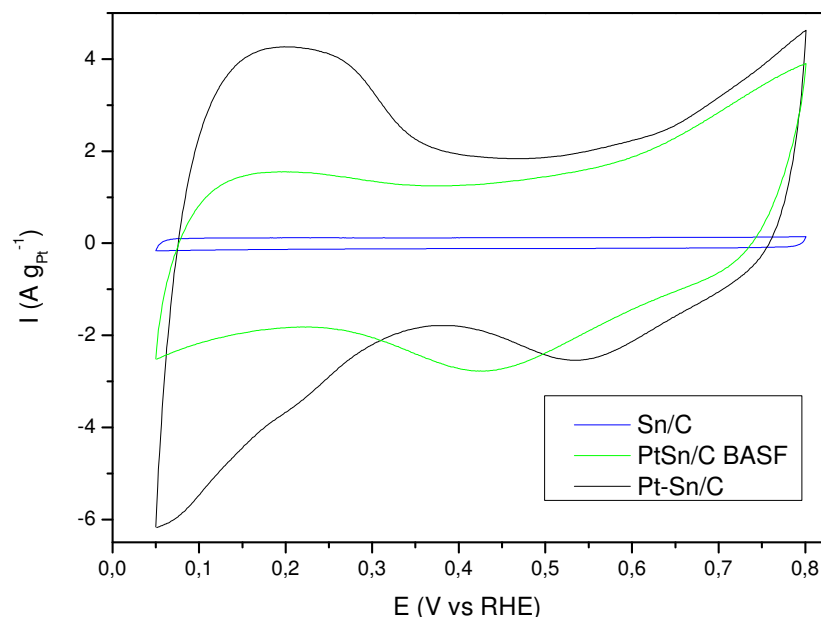


Figure 2: Cyclic voltammograms of Sn/C, PtSn/C and PtSn/C BASF electrocatalysts in 0.5 mol.L^{-1} solution of H_2SO_4 at 10 mV s^{-1} .

The cyclic voltammograms of PtSn/C and PtSn/C BASF electrocatalysts do not have a well-defined adsorption-desorption of hydrogen region (0 - 0.4 V) and an increase of the values current in the electrical double layer region (0.4 - 0.8 V) was observed compared to the Pt/C electrocatalyst (4). However, the cyclic voltammogram of the PtSn/C electrocatalyst showed the region of hydrogen adsorption-desorption more defined than the one observed for the PtSn/C BASF electrocatalyst, which could be attributed to a material having a surface enriched in Pt. This probably is related to the preparation method of the PtSn/C electrocatalyst, where Pt^{+4} ions were reduced and deposited on the Sn/C leading to the formation of a material containing Pt overlayers deposited on carbon-supported Sn nanoparticles (12) forming core/shell-like structures (13).

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

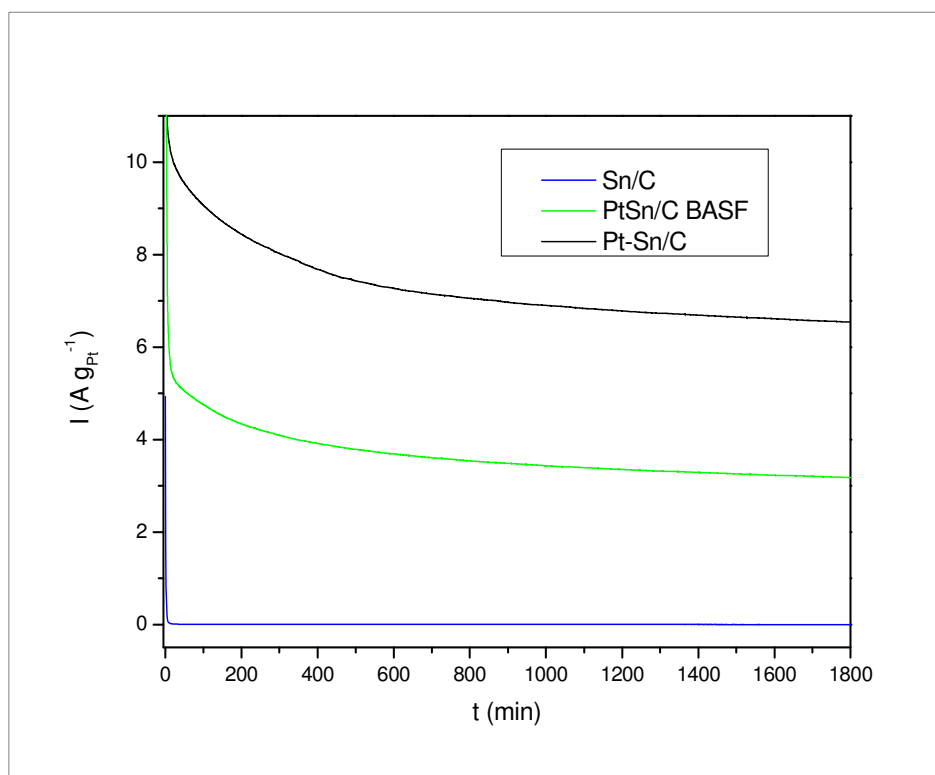


Figure 3: Current-time curves at 0.5 V in 0.5 mol L⁻¹ H₂SO₄ solution containing 1.0 mol.L⁻¹ of ethanol for PtSn/C electrocatalysts.

The results were normalized per gram of Pt, considering that the adsorption and dehydrogenation of ethanol occurs only on Pt sites at room temperature (4). It was observed that the prepared PtSn/C electrocatalyst by successive reduction showed a superior performance for ethanol electro-oxidation compared to the commercial PtSn/C BASF electrocatalyst.

Conclusions

The results showed that the PtSn/C electrocatalyst prepared by successive reduction was about two times more active (amperes per gram of Pt) for ethanol electro-oxidation than the commercial PtSn/C BASF (PtSn alloy) electrocatalyst. Under the conditions in which the PtSn/C electrocatalyst was prepared, the material may have Pt overlayers deposited on carbon-supported Sn nanoparticles forming core/shell-like structures. The material is being evaluated by different surface characterization techniques to determine the structure formed.

Acknowledgments

CNPq, FINEP-ProH₂ e FAPESP.

References

1. H. Wendt, E.V. Spinacé, A.O. Neto, M. Linardi, *Quim. Nova* **28** 1066–1075 (2005).
2. E. Antolini, *J. Power Sources* **170** 1–12 (2007).
3. S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, *J. Power Sources* **158** 18–24 (2006).
4. A.O. Neto, R.R. Dias, M.M. Tusi, M. Linardi, E.V. Spinacé, *J. Power Sources* **166** 87–91 (2007).
5. M. Zhu, G. Suna, Q. Xin, *Electrochim. Acta* **54** 1511–1518 (2009).
6. F. Colmati, E. Antolini, E.R. Gonzalez, *Electrochim. Acta* **50** 5496 (2005).
7. R.F.B. De Souza, L.S. Parreira, D.C. Rascio, J.C.M. Silva, E. Teixeira-Neto, M.L.Calegaro, E.V. Spinacé, A.O. Neto, M.C. Santos, *J. Power Sources* **195** 1589–1593 (2010).
8. D.R.M. Godoi, J. Perez, H.M. Villullas, *J. Power Sources* **195** (2010) 3394–3401.
9. J. Mann, N. Yao, A.B. Bocarsly, *Langmuir* **22** 10432–10436 (2006).
10. A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang, N.S. Marinkovic, P. Liu, A.I. Frenkel, R.R. Adzic, *Nat. Mater.* **8** 325–330 (2009).
11. Y. Yu, Q. Yang, D. Teng, X. Yang, S. Ryu, *Electrochem. Commun.* **12** 1187–1190 (2010).
12. K-S. Lee, S.J. Yoo, D.Ahn, T-Y. Jeon, K.H. Choi, I-S. Park, Y-E. Sung, *Langmuir* **3128-3137** (2011).
13. H.A.Esfahani, L.Wang, Y. Nemoto, Y. Yamauchi, *Chem. Mater.* **22** 6310-6318 (2010).