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

Vilmaria A. Ribeiro[1], Ryan C. Sekol[2], André D.Taylor[2], Almir Oliveira Neto[1] and Estevam V. Spinacé[1]

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

[2] Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States

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]. PtSn/C electrocatalysts have shown the best performances for ethanol electro-oxidation in acid medium, however, their activities depend greatly on the preparation procedure. In this work, PtSn/C electrocatalysts were prepared by an alcohol-reduction process [2] using $Pt(C_5H_7O_2)_2$ and $SnCl_4 \cdot 5H_2O$ as metal precursors, 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% 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, transmission electron microscopy and cyclic voltammetry. The electro-oxidation of ethanol was studied by chronoamperometry. The commercial PtSn/C BASF (PtSn alloy, 20 wt% of metal and Pt:Sn atomic ratio of 75:25) electrocatalyst was used for comparative purposes.

The cyclic voltammograms of the electrocatalysts in acid solution are shown in Figure 1.

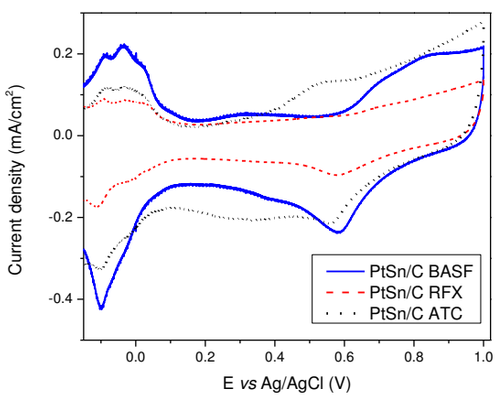

Figure 1: Cyclic voltammograms of the electrocatalysts in 0.5 mol.L^{-1} solution of H_2SO_4 at 10 mV s^{-1}.

The cyclic voltammograms of the electrocatalysts show well-defined adsorption-desorption of hydrogen (0 - 0.4 V) and an increase of the current values in the electrical double layer region (0.4 - 0.8 V), compared to Pt/C, which is associated with the presence of oxide species [3].

The increase of current value in the double layer region was more pronounced for the PtSn/C ACT electrocatalyst and it could be attributed to an increase of Sn oxide species on the surface.

The chronoamperometry experiments were carried out to examine the performance and stability of the electrocatalysts (Figure 2).

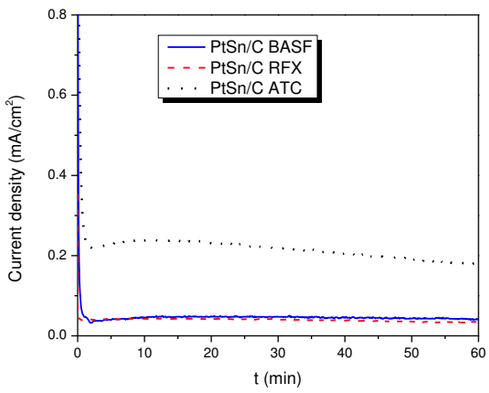

Figure 2: Chronoamperometry curves at 0.3V (vs. Ag/AgCl) in 1 mol L^{-1} ethanol solution in 0.5 mol L^{-1} of H_2SO_4 for the different electrocatalysts.

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 Sn oxide phases on its surface. It has been shown in the literature that PtSn/C electrocatalysts containing Pt(fcc) and SnO_2 phases exhibited superior performance for ethanol electro-oxidation [4-6].

References

[1] Antolini E. Catalysts for direct ethanol fuel cells. J Power Sources 2007; 170(1): 1-12.

[2] Neto AO, Dias RR, Tusi MM, Linardi M, Spinacé EV. Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process. J Power Sources 2007; 166(1): 87-91.

[3] Camara, G, A.; Lima R, B. DE, Iwasita, T. Catalysis of ethanol electrooxidation by PtRu: the influence of catalyst composition. Electrochem. Commun., 2004, **6**, 812.

[4] Jiang L, Colmenares L, Jusys Z, Sun GQ, Behm RJ. Ethanol electrooxidation on novel carbon supported Pt/SnOx/C catalysts with varied Pt:Sn ratio. Electrochim. Acta 2007;53(2):377-89.

[5] Mann J, Yao N, Bocarsly AB. Characterization and analysis of new catalysts for a direct ethanol fuel cell. Langmuir 2006;22(25):10432-6.

[6] Kowal A, Li M, Shao M, Sasaki K, Vukmirovic MB, Zhang J, Marinkovic NS, Liu P, Frenkel AI, Adzic RR. Ternary Pt/Rh/SnO_2 electrocatalysts for oxidizing ethanol to CO_2. Nature Mat. 2009;8(4):325-30.

Acknowledgments

CNPq-Ciência sem Fronteiras is acknowledged for financial support and Chemical & Environmental Engineering Department at Yale University for infrastructure and support.