11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

ICAM2009

A Comparative Study of Ethanol Oxidation Using PtRu/C, PtCe/C, PtSn/C Electrocatalysts

J. C. M. da Silva[(1)], A. E. A. Flausino[(1)], J. P. B. Ladeia[(1)], L. S. Parreira[(1)], E. T. Neto[(1)], M. L. Calegaro[(2)], M. C. dos Santos[(1)*]

(1) LEMN - Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC, Santo André, SP, Brazil,
(2) GMEME – DFQ – Instituto de Química de São Carlos (IQSC), Universidade de São Paulo, São Carlos, SP, Brazil.
**mauro.santos@ufabc.edu.br*

Abstract – Ethanol oxidation process was studied using PtRu/C (1:1 w/w), PtCe/C (3:1 w/w) and PtSn/C (3:1 w/w) electrocatalysts prepared using the polymeric precursor method. The metals load used was 20% (w/w) on carbon. The materials were physically characterized by X-ray diffraction (XRD), X-ray energy dispersive analysis (EDX) and transmission electron microscopy (TEM). Cyclic voltammetry and polarization curves were used for the electrochemical characterization and oxidation process. The electrocatalysts showed similar performances for ethanol electrooxidation at low potentials. Analyzing the results, it is possible to affirm that the $PtCeO_2$/C electrocatalysts are promising candidates toward ethanol oxidation.

The fuel cells are a valuable option for due to finite availability of fossil fuel reserves and also due to environmental concerns, since they have high energy efficiency and low pollutant emission. In the last decades research on the electrooxidation of small organic molecules (SOM) is being of interest for the development of direct liquid fuel cells. Among the SOM ethanol offers an attractive choice. This fuel has emerged as the first choice, mainly in Brazil, because of its non-toxicity and low volatility together with a higher energy density in comparison with methanol (8.01 kWh kg^{-1} vs. 6.09 kWh kg^{-1}). Furthermore, ethanol can be easily produced from biomass thus not contributing to the increase of CO_2 in the atmosphere. Platinum, as well as their alloys, represent some of the most efficient catalytic materials for the oxidation of SOM, such as ethanol [1]. The main problem concerning the use of SOM as fuel is that CO is an intermediate in the oxidation pathway on Pt and alloys, and the existence of parallel reaction channels. For this reason, modification in catalyst composition is necessary to enhance ethanol electrocatalytic oxidation reaction. In order to enhance the electrocatalytical behavior of Pt with the diminishing of CO adsorption, Ru [2], Ce [3] and Sn [4] have received much attention. In this work, ethanol electrooxidation was investigated in an acidic solution ($HClO_4$ 0.5 mol L^{-1} containing alcohol 1 mol L^{-1}) using PtRu/C (1:1 w/w), PtCe/C (3:1 w/w) and PtSn/C (3:1 w/w) as electrocatalysts. The polymeric precursors method used to prepare the nanomaterials was adapted from the works of Freitas *et al.* [5] and Profeti *et al.* [6], where the metals load used was 20% (w/w) on carbon. The materials were characterized by X-ray diffraction and the mean crystallite sizes obtained using Scherrer equation were close to 7 nm for Pt, 8 nm for Ru, 3 nm for CeO_2 and Sn. These results were confirmed using TEM. The onset potential for ethanol oxidation process using PtSn/C is 0.2 V while using PtCe/C and PtRu/C the oxidation process starts at 0.3 V and 0.4 V, respectively. However, ethanol oxidation on PtCe/C showed the highest peak current density at 0.9 V (163,82 mAmg Pt^{-1}). The polarization curves results indicated that all the electrocatalysts had the same performance at low potentials (up to 0.4 V). At higher potentials the best performance for ethanol oxidation was observed for PtCe/C electrocatalysts. The results here obtained suggest that the promoter effect of PtRu on ethanol oxidation is associated to the bifunctional mechanism [2]. The effect of the PtCe/C can be related to the oxidation of reactive intermediates generated during the oxidation process, or breaking C-C bound [3]. For PtSn/C the performance probably is associated to a change in the ethanol oxidation mechanism, promoted by Pt_3Sn_1 alloy formation [7]. Based on the above results and taking into account the lower cost of Ce compared with Ru, it is an attractive material for the development of active electrocatalysts for direct ethanol fuel cells.

Acknowledgments: UFABC, CAPES, CNPq (474732/2008-8) and FAPESP (05/59992-6, 08/58788-4, 08/57288-8).

References

[1] M. Carmo, A. R. dos Santos, J. G. R. Poço, M. Linardi, J. Power Sources, 173 (2007) 860 -866.
[2] S. G. Lemos R. T. S. Oliveira, M. C. Santos, P. A. P. Nascente, L. O. S. Bulhões, E. C. Pereira, J. Power Sources 163 (2007) 695 - 701.
[3] C. Xu, P. K. Shen, J. Power Sources 142 (2005) 27– 29.
[4] J. Ribeiro, D. M. Dos Anjos, J. M. Leger, F. Hahn, P. Olivi, A. R. Andrade, G. Tremiliosi-Filho, K. B. Kokoh, J. Applied Eletrochem. 38 (2008) 653 – 662.
[5] R. G. Freitas, L. F. Q. P. Marchesi, R. T. S. Oliveira, F. I. Mattos-Costa, E. C. Pereira, L. O. S. Bulhões, M. C. Santos, J. Power Sources, 171 (2007) 373 -380.
[6] L. P. R. Profeti, F. C. Simões, P. Olivi, K. B. Kokoh, C. Countanceau, J. M. Leger, C. Lamy, J. Power Sources, 158 (2006) 1195 - 1201.
[7] S. Q. Song; W. J. Zhou; Z. H. Zhou; L. H. Jiang; G. Q. Sun; Q. Xin; V. Leontidis; S. Kontou e P. Tsiakaras, Int. J. Hydrogen Energy, 30 (2005) 995 - 1001.