Int. J. Electrochem. Sci., 5 **(2010)** 1879 - 1886

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Preparation and Characterization of PtSn/C-Rare Earth Using an Alcohol Reduction Process for Ethanol Electro-Oxidation

Michele Brandalise, Marcelo M. Tusi, Rita M. S. Rodrigues, Estevam V. Spinace´*, *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
*E-mail: aolivei@ipen.br and espinace@ipen.br

Received: 21 October 2010 / *Accepted:* 30 October 2010 / *Published:* 1 December 2010

PtSn/C, PtSn/Er_2O_3-C, PtSn/CeO_2–C, PtSn/La_2O_3–C and PtSn/Nd_2O_3–C electrocatalysts were prepared by an alcohol-reduction process using $H_2PtCl_6.6H_2O$ and $SnCl_2.2H_2O$ as metal sources, ethylene glycol as solvent and reducing agent, 85% Vulcan XC72-15% rare earth (Er_2O_3, CeO_2, La_2O_3 and Nd_2O_3) as support. The platinum and tin metal loadings were always kept at 20 wt%. The electrocatalysts were characterized by EDX, XRD and TEM, while that the performance for ethanol oxidation was investigated by cyclic voltammetry and cronoamperommetry at room temperature. The PtSn/Er_2O_3–C electrocatalyst showed an increase of performance for ethanol oxidation in relation to PtSn/C electrocatalyst. The final current values after holding the cell potential at 0.5 V versus RHE for 30 min were the following: PtSn/Er_2O_3–C > PtSn/CeO_2–C > PtSn/Nd_2O_3–C > PtSn/La_2O_3–C > PtSn/C. In the tests at 100°C on a single cell of a direct ethanol fuel cell (DEFC), the PtSn/Er_2O_3–C electrocatalyst also showed the best performance in relation to the others electrocatalysts.

Keywords: PtSn/Rare Earth–C; PtSn/C, alcohol reduction process, ethanol oxidation, fuel cell

1. INTRODUCTION

Fuel cell employing alcohols directly as combustible (Direct Alcohol Fuel Cell—DAFC) are attractive as power sources for mobile, stationary and portable applications. Ethanol has been considered the most promising fuel, because it is produced in large quantities from biomass and is much less toxic than others combustibles. On the other hand, its complete oxidation to CO_2 and water is not easy due to the difficulties in C–C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts [1-6].

PtSn nanoparticles supported on carbon [7-12] have been used as anode electrocatalysts for Direct Ethanol Fuel Cell (DEFC). The performances of these electrocatalysts depend greatly on the preparation procedure and the principal products formed are acetaldehyde and/or acetic acid, consequently the development of new electrocatalysts and new preparation methods yet are necessary.

In recent years, it is found that certain metal oxides, such as CeO_2 [13-15], can enhance the catalytic activity for ethanol and methanol electro-oxidation through synergetic interaction with Pt. The enhancement of alcohol oxidation by CeO_2 was explained by two mechanisms: by inhibiting CO adsorption or by ceria oxygen storage capacity playing a role to ease the oxidation of adsorbed CO. Neto et al. [16-18] showed that PtSn/CeO_2–C electrocatalysts was more active for ethanol oxidation than the analogous PtSn/C catalyst. The best results for ethanol oxidation were found with a loading of 15 wt% of CeO_2. Others Rare Earth (RE) oxides also exhibit a number of characteristics that make them interesting for catalytic studies. Recently, Neto et al. [19-20] prepared PtLnOx–C catalysts (Ln = Lu, Tb, Er, Ce, Ho, Dy, Tm, Sm, La, Pr, Nd) by alcohol reduction process for ethanol oxidation and the final current values after holding the cell potential at 0.5V versus RHE for 30 min were the following: PtLu/C > PtTb/C > PtEr/C ≈ PtNd/C ≈ PtCe/C > PtHo/C > PtLa/C >PtDy/C > PtTm/C > PtPr/C> PtSm/C > Pt/C.

The aim of this work was to prepare PtSn/C, PtSn/Er_2O_3-C, PtSn/CeO_2–C, PtSn/La_2O_3–C and PtSn/Nd_2O_3–C electrocatalysts by an alcohol-reduction process substituting part of the carbon support by rare earth. The obtained materials were tested for ethanol oxidation using electrochemical techniques and the most active catalyst was also tested in direct ethanol fuel cell.

2. EXPERIMENTAL

PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) were prepared by an alcohol reduction process in a single step using $H_2PtCl_6\cdot6H_2O$, $SnCl_2.2H_2O$ as metal sources and 85% Vulcan XC72-15% Rare Earth as support [16-17]. The platinum and tin metal loadings were always kept at 20 wt%. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and 85% Carbon Vulcan XC72-15% Rare Earth supports were added. The resulting mixtures were treated in an ultrasound bath and were refluxed for 3 h under open atmosphere. The mixtures were filtered and the solids washed with water and dried at 70^oC for 2 h.

The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (l = 0.15406 nm). The diffractograms were recorded from $2\theta = 20°$ to 90° with a step size of 0.05° and a scan time of 2 s per step.

The Pt:Sn atomic ratios were obtained by EDX analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and equipped with EDAX DX-4 microanaliser. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV with a Proscan high-speed slow-scan CCD camera and digitalized (1024×1024 pixels, 8 bits) using the Analysis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software.

Electrochemical studies were carried out using the thin porous coating technique [16]. The working electrodes have a geometric area of 0.4 cm^2 with a depth of 0.3 mm. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. The voltammetry and chronoamperometry experiments were performed at 25°C with 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 using a Microquimica (model MQPG01, Brazil) potenciostat/ galvanostat.

The membrane electrode assemblies (MEA) were made by painting the catalysts inks over the GDL (Carbon cloth Teflon treated e Electrochem ECCC1- 060T). The MEA was prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) prepared in this work as anode (1 mg Pt cm^{-2} catalyst loading) and a 20 wt% Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading) at 125°C for 2 min under a pressure of 220.65 bar. The direct ethanol fuel cell performances were determined in a single cell with an area of 5 cm^2. The temperature was set to 100°C for the fuel cell and 80°C for the oxygen humidifier. The fuel was 2 mol L^{-1} ethanol solution delivered at approximately 2 mL min^{-1}, the oxygen flow was regulated at 500 mL min^{-1} and pressure of 2 bar. Polarization curves were obtained by using a TDI RBL 488 electronic load.

3. RESULTS AND DISCUSSION

PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) were prepared in a single step using (co-reduction of mixed ions) using ethylene glycol as solvent and reducing agent in the presence of carbon 85%Vulcan XC72-15% Rare Earth. The Pt:Sn atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios used in the preparation. The (220) reflections of Pt(fcc) crystalline structure were used to calculate the average crystallite sizes using the Scherrer [16] equation and the calculated values were in the range of 2.0–4.1 nm (Table 1).

Table 1. Pt:Sn atomic ratios and mean particle size of the prepared electrocatalysts

Electrocatalyts	Pt:Sn atomic ratio (nominal	Pt:Sn atomic ratio (EDX)	Average crystallite size (nm)
PtSn/C	50:50	55 :45	2,6
PtSn/C –Er	50:50	63 :37	3,0
PtSn/C –Nd	50:50	57 :43	< 2,0
PtSn/C –Ce	50:50	52 :48	2,1
PtSn/C –La	50:50	56 :44	4,1

The X-ray diffractograms of the electrocatalysts are shown in Figure 1. In all difractograms a broad peak at about 25◦ was associated with the Vulcan XC72 support material.

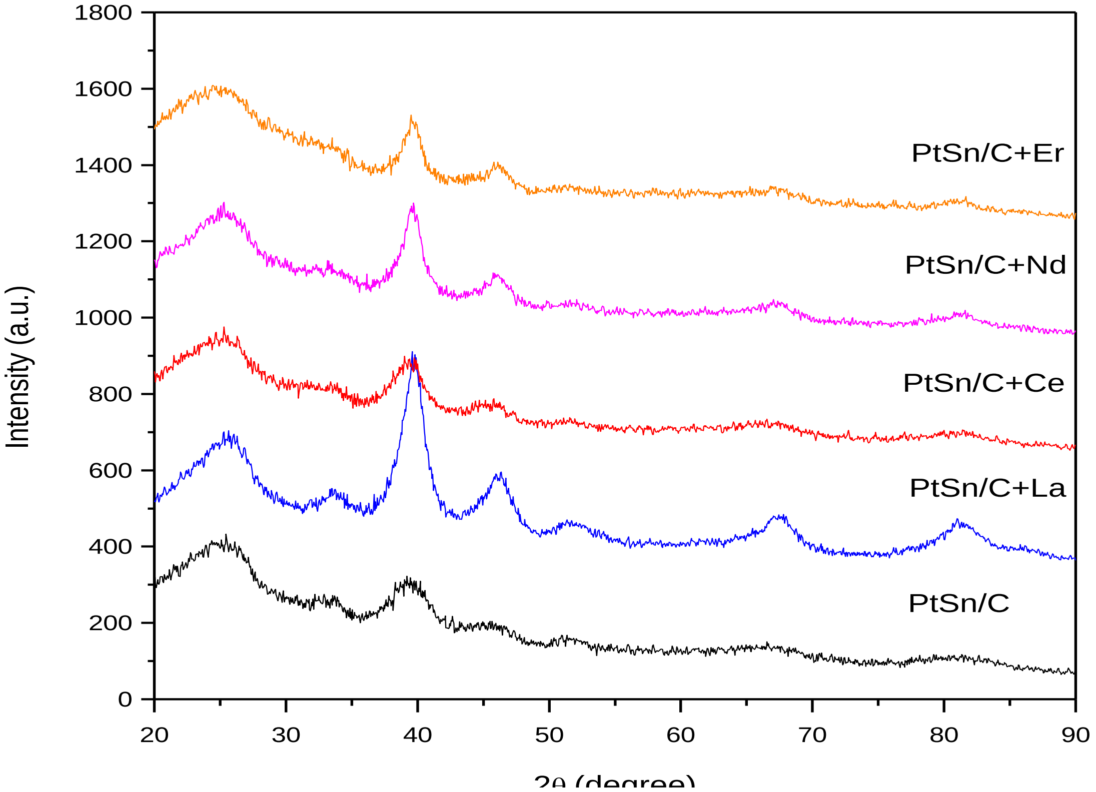


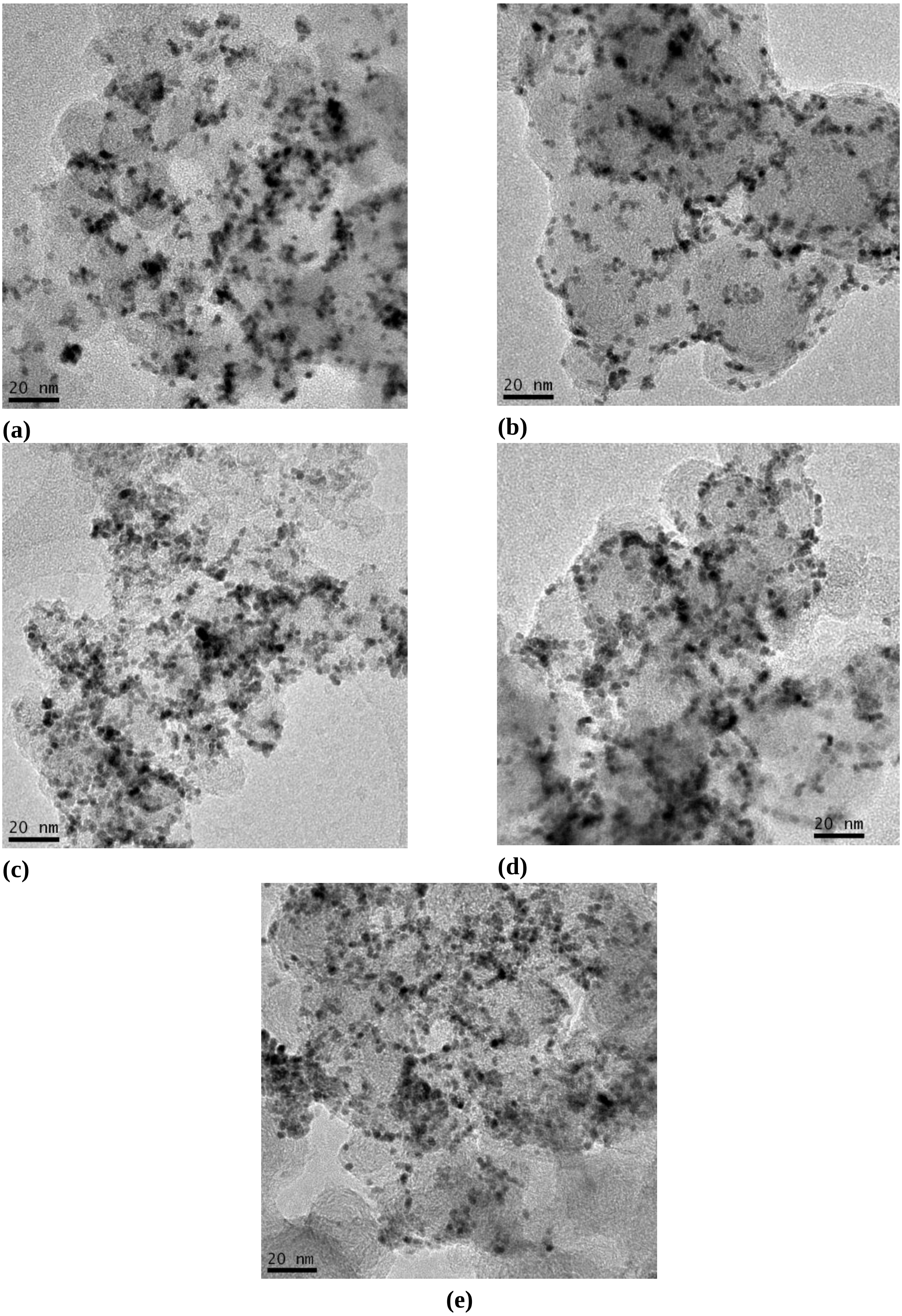
Figure 1. X-ray diffractograms of PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) electrocatalyst.

The diffractograms of PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) electrocatalyst showed peaks at approximately $2\theta = 40^o$, 47°, 67° and 82°, which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of platinum [16]. In the diffractograms of these samples it was also observed two peaks at approximately $2\theta = 34^o$ and 52° that were identified as a SnO_2 phase [16]. No peaks corresponding to CeO_2, Er_2O_3, La_2O_3 and Nd_2O_3 were observed.

The Figure 2 shows TEM micrographs of PtSn/C (Fig. 2a), PtSn/85%C-15%CeO_2 (Fig. 2b), PtSn/85%C-15%Er_2O_3 (Fig. 2c), PtSn/85%C-15%La_2O_3 (Fig. 2d) and PtSn/85%C-15%Nd_2O_3 (Fig. 2e)

All electrocatalysts showed a good distribution of the Pt particles on the carbon support with particle sizes of 2.0±1.0 nm, which is in accordance with XRD results. In agreement Neto et al. [21] also showed that PSn/C and PtSnNi/C electrocatalysts prepared by an alcohol reduction process had a good distribution of the Pt particles on the carbon support with particle sizes of 2.0±1.0 nm.

.



(a) **(b)**

(c) **(d)**

(e)

Figure 2. Transmission electron micrographs of **(a)** PtSn/C, **(b)** PtSn/85%C-15%CeO_2, **(c)** PtSn/85%C-15%Er_2O_3, **(d)** PtSn/85%C-15%La_2O_3 and **(e)** PtSn/85%C-15%Nd_2O_3 electrocatalyst.

Fig. 3a shows the cyclic voltammetry (CV) of PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) obtained in a half cell at a scan rate of $10 mVs^{-1}$ between 0.05 and 0.8V in 1.0mol L^{-1} of ethanol and 0.5 mol L^{-1} H_2SO_4. The Fig. 3b shows the chronoamperometry studies in 1.0 mol L^{-1} of ethanol and 0.5 mol L^{-1} H_2SO_4 at an anodic potential of 0.5V versus RHE.

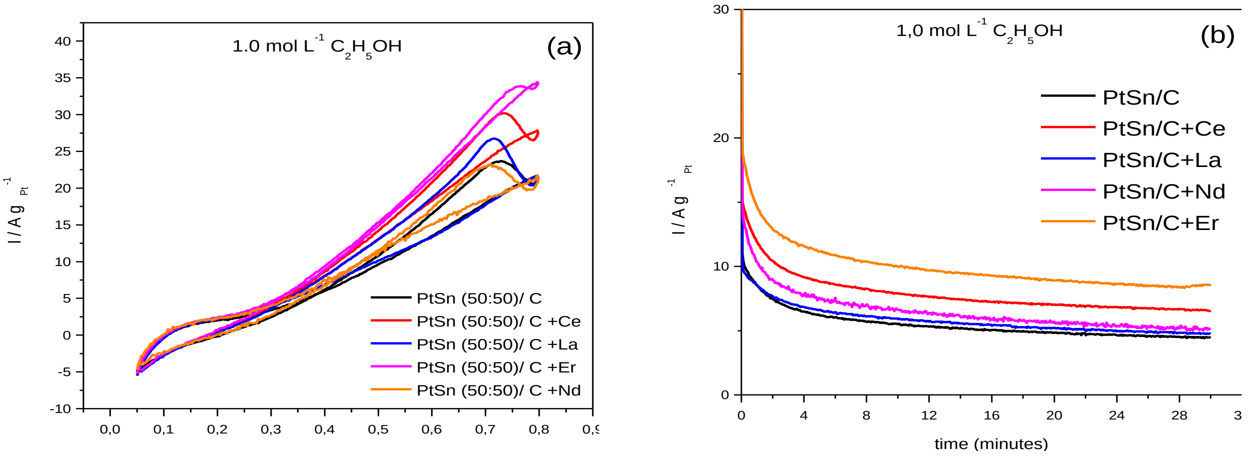


Figure 3. (a) Cyclic Voltammograms of PtSn/C (50:50), PtSn/85%C-15%CeO_2 (50:50), PtSn/85%C-15%Er_2O_3 (50:50), PtSn/85%C-15%La_2O_3 (50:50) and PtSn/85%C-15%Nd_2O_3 (50:50) and **(b)** Chronoamperometry studies in 1.0 mol L^{-1} of ethanol and 0.5 mol L^{-1} H_2SO_4 at an anodic potential of 0.5 V versus RHE.

The electro-oxidation of ethanol started at approximately 0.25 V for all electrocatalysts (Fig. 3a) and the PtSn/85%C-15%Er_2O_3 (50:50) showed the best activity in comparison to the others electrocatalysts. The chronoamperometry experiments were carried out to examine the electrochemical stability of eletrocatalysts. In all chronoamperometric curves, there is a sharp initial current drop in the first 4 min and then the current values practically remain constant until 30 min. The current values obtained for PtSn/ C-Rare Earth were always higher than those obtained for PtSn/C. The PtSn/85%C-15%Er_2O_3 (50:50) also showed the best performance in agreement with cyclic voltammetry. The final current values after holding the cell potential at 0.5V versus RHE for 30 min were the following: PtSn/85%C-15%Er_2O_3 (50:50) > PtSn/85%C-15%CeO_2 (50:50) > PtSn/85%C-15%Nd_2O_3 (50:50) > PtSn/85%C-15%La_2O_3 (50:50) > PtSn/C. Neto et al [17] showed for ethanol oxidation (FTIR studies) that the acetaldehyde and acetic acid were the principal products formed on PtSn/C electrocatalyst, while on PtSn/CeO2–C the principal final products formed were CO_2 and acetic acid. The enhancement of activity for alcohol electro-oxidation resulting from the addition of rare earth to platinum catalysts could be attributed to the bifunctional mechanism, where rare earth favors the formation of chemisorbed oxygen species and promotes the oxidation of adsorbed carbon monoxide or intermediates on the surface of platinum [16-17].

The Fig. 4 shows the performances of single fuel cell with PtSn/C and PtSn/85%C-15%Er_2O_3 (50:50) as anode catalysts.

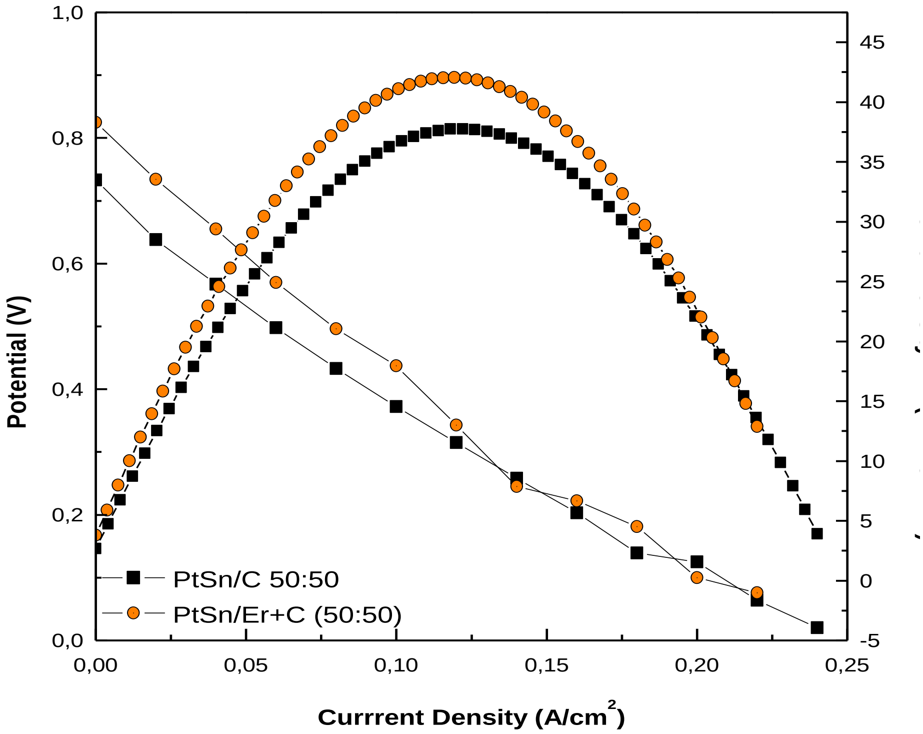


Figure 4. Electrical performances of a 5 cm^2 DEFC at 100°C using PtSn/C and PtSn/85%C-15%Er_2O_3 (50:50) electrocatalysts anodes (1 mg Pt cm^{-2} catalyst loading) and Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading, 20 wt% catalyst on carbon), Nafion 117 membrane, ethanol (2.0 mol L^{-1}) and oxygen pressure (2 bar).

The open circuit voltage of the fuel cell using PtSn/85%C-15%Er_2O_3 (50:50) electrocatalyst was 0.83 V, while the corresponding value for PtSn/C electrocatalyst was 0.73 V .The maximum power density of PtSn/85%C-15%Er_2O_3 (50:50) electrocatalyst (42 mW cm^{-2}) was greater than that of PtSn/C electrocatalyst (38 mWcm^{-2}). The use of PtSn/85%C-15%Er_2O_3 (50:50) electrocatalyst increased the cell performance in agreement to the observed by electrochemical techniques.

4.CONCLUSIONS

All electrocatalysts showed peaks associated with the fcc structure characteristic of platinum and two peaks at approximately 2θ = 34° and 52° that were identified as a SnO_2 phase. No peaks corresponding to CeO_2, Er_2O_3, La_2O_3 and Nd_2O_3 were observed. All PtSn/C-Rare Earth showed higher current values than PtSn/C in the chronoamperometry studies. The PtSn/85%C-15%Er_2O_3 (50:50) electrocatalyst prepared by an alcohol-reduction process exhibited higher performance for ethanol oxidation at room temperature than PtSn/C electrocatalyst. Preliminary tests at 100°C on a single DEFC also confirm these results. Further work is now necessary to investigate the PtSn/85%C-15%Er_2O_3 (50:50) electrocatalyst surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation.

ACKNOWLEDGEMENT
The authors thank FAPESP and CNPq for financial support.

References

1. E.G. Franco, A.O. Neto, M. Linardi and E. Aricó, *J. Braz. Chem. Soc*, 13, (2002) 516.
2. H. Wendt, E.V. Spinacé, A.O. Neto and M. Linardi: *Química Nova*, 28 (2005) 1066.
3. E.V. Spinacé, A.O. Neto, E.G. Franco, M. Linardi and E.R. Gonzalez, *Química Nova*, 27 (2004) 648.
4. E. V. Spinacé, R. R. Dias, M. Brandalise, M. Linardi, A. O. Neto, *Ionics*, 16, (2010) 91.
5. F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir and C. Lamy, *J. Appl. Electrochem*. 34 (2004) 439.
6. A.O. Neto, R. W. R. Verjulio-Silva, M. Linardi and E.V. Spinacé, *Int. J. Electrochem. Sci*. 4 (2009) 954.
7. E. Antolini, *J. Power Sources* 170 (2007) 1.
8. E.V. Spinace, L.A.I. do Vale LAI, R.R.Dias, A.O. Neto and M. Linardi, *Stud Surf Sci Catal* 162 (2006) 617.
9. S.Q. Song, W.J. Zhou, Z.H. Zhou, L.H. Jiang, G.Q. Sun and Q. Xin, *Int J Hydrogen Energy* 30 (2005) 995.
10. E.V. Spinace´, M. Linardi and A.O. Neto, *Electrochem Commun* 7 (2005) 365.
11. A.O. Neto, R.R. Dias, M.M. Tusi, M. Linardi and E.V. Spinace´, *J Power Sources* 166 (2007) 87.
12. L. Jiang, G. Sun, S. Sun, J. Liu, S. Tang and H. Li, *Electrochim Acta* 50 (2005) 5384.
13. J. Xi, J. Wang, L. Yu, X. Qin, L. Chen, *Chem. Commun.* (2007) 1656.
14. J. Wang, J. Xi, Y. Bai, Y. Shen, J. Sum, L. Chen, W. Zhu, X. Qin, *J. Power Sources* 164 (2007) 555.
15. Y. Bai, J. Wu, X. Qin, J. Yi, J. Wang, J. Li, W. Zhu, L. Chen, *Appl. Catal. B* 73 (2007) 144.
16. A.O. Neto, L. A. Farias, R. R. Dias, M. Brandalise,M. Linardi, E. V. Spinacé, *Electrochem. Comm.*10 (2008) 1315.
17. A.O. Neto, M. Linardi, D. M. dos Anjos, G. Tremiliosi-Filho, E. V. Spinace, *J Appl Electrochem.* 39 (2009) 1153.
18. R. F. B. De Souza, M. M. Tusi, M. Brandalise, R.R. Dias, M. Linardi, E. V. Spinacé, M. C. dos Santos, A.O. Neto, *Int. J. Electrochem. Sci.* 5 (2010) 895.
19. A. O. Neto, A. Y. Watanabe, R. M. de S. Rodrigues, M. Linardi, C. A. L. G. O. Forbicini, E. V. Spinacé, *Ionics* 14 (2008) 577.
20. O. Neto, A. Y. Watanabe, M. Brandalise, M. M. Tusi, R. M. de S. Rodrigues, M. Linardi, E. V. Spinacé, C.A.L.G.O. Forbicini, *J. of Alloys and Compounds* 476 (2009) 288.
21. E. V. Spinacé, L. A. Farias, M. Linardi, A. O. Neto, *Materials Letters* 62 (2008) 2103.