PtSnCe/C and PtSnIr/C Electrocatalysts for Ethanol Oxidation: DEFC and In Situ FTIR studies

Rodrigo F. De Souza, Júlio César M. Da Silva, Luanna S. Parreira, Melina D'Villa-Silva, Fernando Carmona Simões, Marcelo Luiz Calegaro, Martha Janete De Giz, Giuseppe Abíola Câmara, Almir Oliveira Neto and Mauro C. Santos

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PtSnCe/C and PtSnIr/C Electrocatalysts for Ethanol Oxidation: DEFC and *in situ* FTIR studies

R.F.B. de Souza [a], J.C.M. Silva [a], L. S. Parreira, M. D-Villa Silva, F. C. Simões [a], M.L. Calegaro [b], M. J De Giz [c], G. A. Câmara [c], A. O. Neto [d], M.C. Santos [a]

[a] LEMN – CCNH - UFABC – CEP 09.210-170, Santo André, SP, Brazil.
[b] GMEME - IQSC - USP – Caixa Postal 780, 13566-590 São Carlos, SP, Brazil.
[c] DQ – UFMS – P. O. Box 549, 79070-900, Campo Grande, MS, Brazil.
[d] IPEN, CNEN/SP, CEP 05508-900, São Paulo, SP, Brazil

In the present work, we investigated PtSnCe/C (68:22:10), PtSnIr/C (33:33:33) and commercial PtSn/C (E-Tek) electrocatalysts as anodes in a DEFC. The effects of decreasing the Pt content in the electrocatalysts were also investigated. The product distributions resulting from the ethanol oxidation reaction (EOR) in acid solutions using PtSnCe/C, PtSnIr/C and the commercial PtSn/C materials as electrocatalysts were determined by *in situ* FTIR spectroscopy. All of the anodes contained 20% (w/w) metal on carbon. From *in situ* FTIR experiments using 2.0 mol L^{-1} ethanol, it was observed that the PtSnCe/C and PtSnIr/C materials led to the formation of acetic acid as the predominant oxidation product. The best results for the EOR were obtained with the PtSnCe/C material. However, it was observed that the PtSnIr/C electrocatalyst material tolerated a decrease in Pt content while still showing good performance.

Introduction

Ethanol is one of the most promising fuels for use in polymer exchange membrane fuel cells (PEMFCs) [1-2], due to its low toxicity, high energy density and abundant availability, as well as the fact that it can be obtained from naturally occurring biomass [1-3]. The development of materials for the ethanol oxidation reaction (EOR) is of great importance for improving the efficiency of direct ethanol fuel cells (DEFCs) [4-5]. However, the complete electro-oxidation of ethanol to CO_2 is a challenge because it requires the cleavage of the strong C-C bonds of ethanol molecules. Pt is the most active metal for the oxidation of this alcohol; however, it has limited efficiency for the C-C bond cleavage. The electrocatalytic activity of Pt can be improved by the addiction of other metals, such as Ir [6-7], Sn [8-9], Ce [10-11] or Rh [12-13]. Ceria has a fluorite oxide structure in which the metallic center is surrounded by oxygen atoms and is a cationic species that can exist in the +3 and +4 oxidation states. The improved performance that was achieved by using ceria with platinum in the electrocatalysis was attributed to a synergy of the efficiency of Pt with the ability of ceria to act as a source of OH_{ads} at low potentials, which is necessary to oxidize poisons generated during the methanol or ethanol oxidation reactions [10]. Iridium is a promising metal for electrocatalysis, as anodes in DEFCs. Cao *et al.* [14] demonstrated high activity for Ir/C and Ir_3Sn/C in ethanol electro-oxidation. In DEFC experiments, the Ir/C catalyst performed comparably to Pt/C, and Ir_3Sn/C showed activities similar to Pt_3Sn/C. These results indicate that Ir is an excellent candidate to replace Pt in electrocatalysis. The effect of Sn on the activity of Pt catalysts in the EOR has been reported by others [15-18]. PtSn/C electrocatalysts, fabricated by alloying Pt with Sn [15-16] or by combining Pt with SnO_2 [17-18], have shown improved performance for the EOR. Therefore, PtSn/C is a promising material for DEFCs. The aim of this work is to study the use of PtSnCe/C, PtSnIr/C and commercial PtSn/C electrocatalysts in the ethanol oxidation reaction. The materials were tested in a DEFC, and the oxidation mechanism for the EOR was studied using *in situ* FTIR spectroscopy.

Materials preparation and characterization

The materials were prepared using a modified version of the polymeric precursor method (PPM) [8, 10]. The PtSnCe/C electrocatalyst with a mass ratio of 68:22:10 and PtSnIr/C with a mass ratio of 33:33:33 were compared to the commercial PtSn/C material from E-Tek with a mass ratio of 75:25. All the catalysts were 20% on carbon. Single direct ethanol cell tests were carried out using PtSnCe/C, PtSnIr/C and the commercial PtSn/C electrocatalysts as anodes and commercial 20 % Pt/C (E-Tek) as the cathode. The electrocatalyst was painted over the gas diffusion layer (GDL – carbon-cloth Teflon-treated, Electrochem ECCC1-060T) by casting a homogeneous dispersion made with a solution of Nafion® (5%, Aldrich) in isopropanol (J.T. Baker). All electrodes contained 1 mg Pt per cm^2 in the anode and cathode except for the PtSnIr/C sample, which contained 1 mg of Pt + Ir (1:1) per cm^2. After preparation, the electrodes were hot-pressed on both sides of a Nafion® 117 membrane at 100 ºC for 2 minutes at a pressure of 225 kgf cm^{-2}. The performance of the ethanol fuel cell containing each catalyst was determined in a single cell with a geometric area of 5 cm^2. The temperature was set to 100 ºC for the fuel cell and 80 ºC for the oxygen humidifier. The fuel (an aqueous solution of 2 mol L^{-1} ethanol) was delivered at a rate of approximately 2 mL min^{-1}, and the oxygen flow was set to 500 mL min^{-1} at 2 bar of pressure. The polarization curves were obtained using a TDI RBL 488 electronic load. The cell mechanism was studied through electrochemical experiments using a Solartron SI 1287 in acid media using an aqueous solution of 0.1 mol L^{-1} $HClO_4$ plus ethanol at a concentration of 2 mol L^{-1}. The catalyst dispersion fluid was drop cast onto the surface (0.78 cm^2) of the gold support. The experiments were monitored using a Nexus 670 spectrometer (Nicolet) with an MCT detector. The experiments were carried out at a controlled temperature of 25 ± 1.0 °C. Reflectance spectra were collected as a ratio of R/R_0 where R represents a spectrum at a selected potential and R_0 is the spectrum collected at 0.05 V. The spectra were recorded from an average of 128 interferograms.

The catalyst morphology and particle size were determined using JEOL 3010 HR-TEM and JEOL JSM-5900LV microscopes. XRD patterns for the catalyst samples were recorded using a Rigaku Miniflex diffractometer with Cu-Kα radiation (1.5406 Å, 30 kV and 15 mA).

Results and Discussion

X-ray diffraction analysis (Figure 1) indicated changes to the unit cell parameters for Pt, suggesting the incorporation of Sn and Ce into the Pt crystalline network with the formation of an alloy between Pt and Sn and/or Ce in PtSnCe/C. In PtSnIr/C, X-ray diffraction analysis indicated that metallic Pt and Ir. SnO_2 was present in the baseline, suggesting the formation of an amorphous SnO_2 phase.

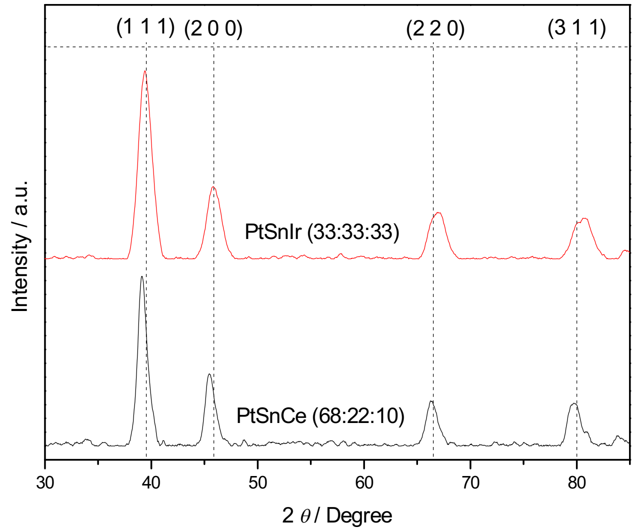

Figure 1. X-ray diffraction patterns of PtSnIr/C and PtSnCe/C with the indicated peak patterns for metallic Pt.

Transmission electron microscopy (TEM) showed that the particles are also homogeneous in size with average sizes of 2 to 5 nm in PtSnCe/C (Figure 2a), 2 to 4 nm in PtSnIr/C (Figure 2b) and 2 to 5 nm in PtSn/C E-TEK (Figure 2c). It is important to point out that 100% of the particles are between 2 and 10 nm in size for all electrocatalysts.

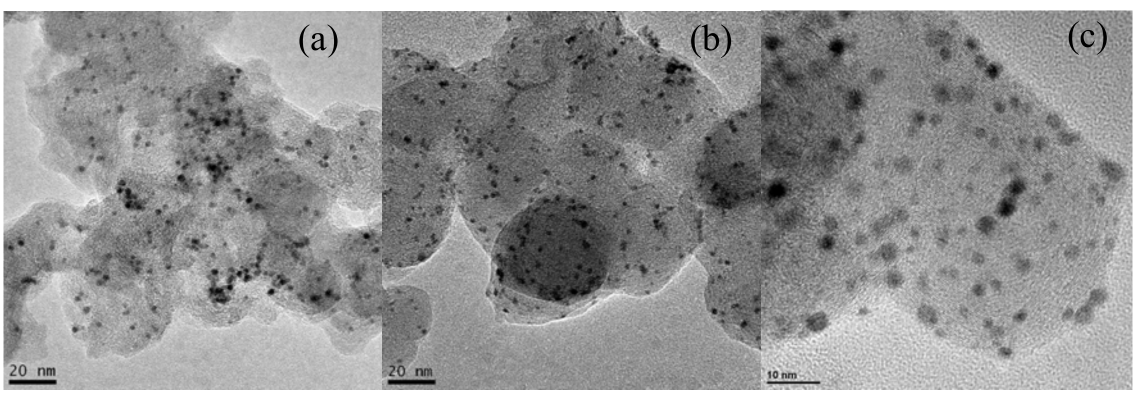

Figure 2. TEM micrograph of the PtSnCe/C (a), PtSnIr/C (b) and PtSn/C E-TEK (c) elecrocatalysts.

The performances of DEFCs using PtSnCe/C (68:22:10), PtSnIr(33:33:33) and the commercial PtSn/C (75:25) electrocatalysts are shown in Figure 3a and Figure 3b. In the polarization curves (Figure 3a) it is possible to observe that the open-circuit voltage (OCV) of the DEFC is about 0.77 V, 0.69 V and 0.73 V using the commercial PtSn/C, PtSnCe/C and PtSnIr/C electrocatalysts, respectively, as anodes. The maximum power (Figure 3b) obtained using PtSnCe/C was approximately 30 % higher than was produced using the commercial material and 10 % higher than was generated using the PtSnIr/C material (42 mW cm^{-2} vs. 33 mW cm^{-2} and 38 mW cm^{-2}, respectively). The enhancement of activity for alcohol electro-oxidation resulting from the addition of CeO_2 to platinum catalysts was attributed to the bifunctional mechanism proposed by Wang and co-workers

[19] where CeO_2 favors the formation of chemisorbed oxygen species. Ribeiro *et al.* [7] reported that Iridium induced to a decrease in platinum poisoning. Also, the authors observed that ethanol adsorption led to the formation of linearly bonded CO on Ir, which can be oxidized more easily than bridged bonded CO (ethanol concentration of 0.1 mol L^{-1}). The authors reported that the synergistic effect obtained using Pt, Sn and Ir could be explained by the activation of interfacial water molecules at lower potentials (bifunctional mechanism).

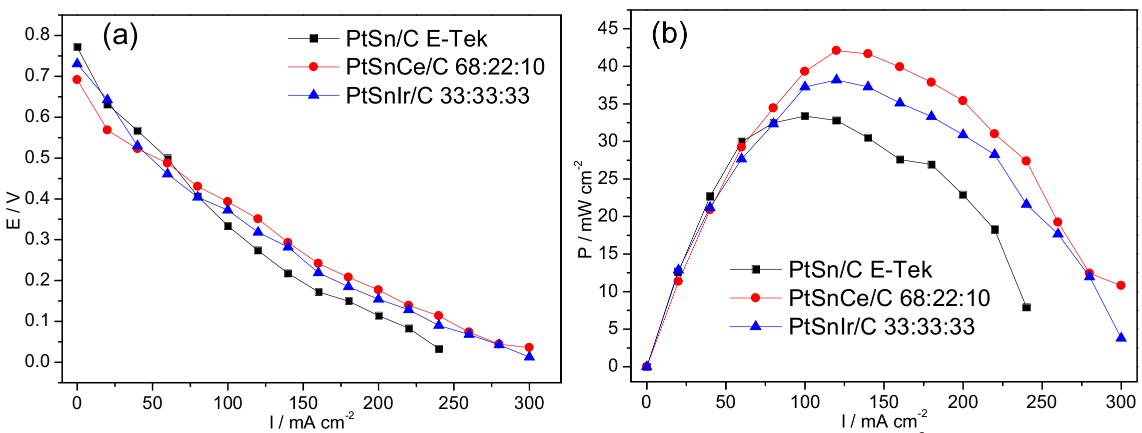

Figure 3. (a) Polarization curves and (b) power density curves in 5 cm^2 DEFC at 100 °C. Nafion® 117 was used as the membrane with 2 mol L^{-1} ethanol and a 2 mL s^{-1} flux.

In the next stage of our investigation, we investigated the effects of reducing the Pt content in the electrocatalyst. For this purpose, the amount of Pt was decreased from 1.0 mg of Pt per cm^2 to 1 mg of Pt + Ir (1:1) per cm^2. In Figure 4, the maximum power density was 38 mW cm^{-2} using PtSnIr (33:33:33) with 1.0 mg of Pt per cm^2 and 33 mW cm^{-2} using PtSnIr (33:33:33) with 1.0 mg of Pt + Ir per cm^2. These results are satisfactory because, with a 50 % decrease of the Pt content, the maximum power density was only decreased by 15 %. The result obtained with 1.0 mg of Pt + Ir per cm^2 is the same as was observed for the commercial PtSn/C material containing 1.0 mg of Pt per cm^2 (Figure 3b). Therefore, it has been demonstrated that in a DEFC, the PtSnIr/C (33:33:33) electrocatalyst containing 1.0 mg of Pt + Ir per cm^2 displays a cell performance similar to that observed for the commercial PtSn/C anode with half the platinum content.

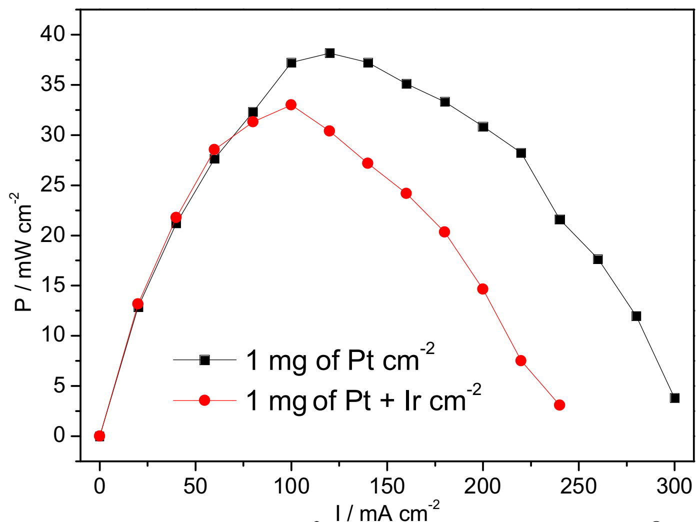

Figure 4. Power density curves in a 5 cm^2 DEFC at 100 °C. Nafion® 117 was used as the membrane with 2 mol L^{-1} ethanol and 2 mL s^{-1} flux. The circle curve is PtSnIr/C with 0.5 mg Pt cm^{-2} and the square curve is PtSnIr/C with 1 mg Pt cm^{-2}.

Integrated intensity plots for acetic acid, acetaldehyde and CO_2 obtained by *in situ* IR spectroscopy on PtSnCe/C, PtSnIr/C and PtSn/C E-TEK electrocatalysts in 2 mol L^{-1} CH_3CH_2OH and 0.1 mol L^{-1} $HClO_4$ solutions are shown in Figure 5a, 5b and 5c, respectively.

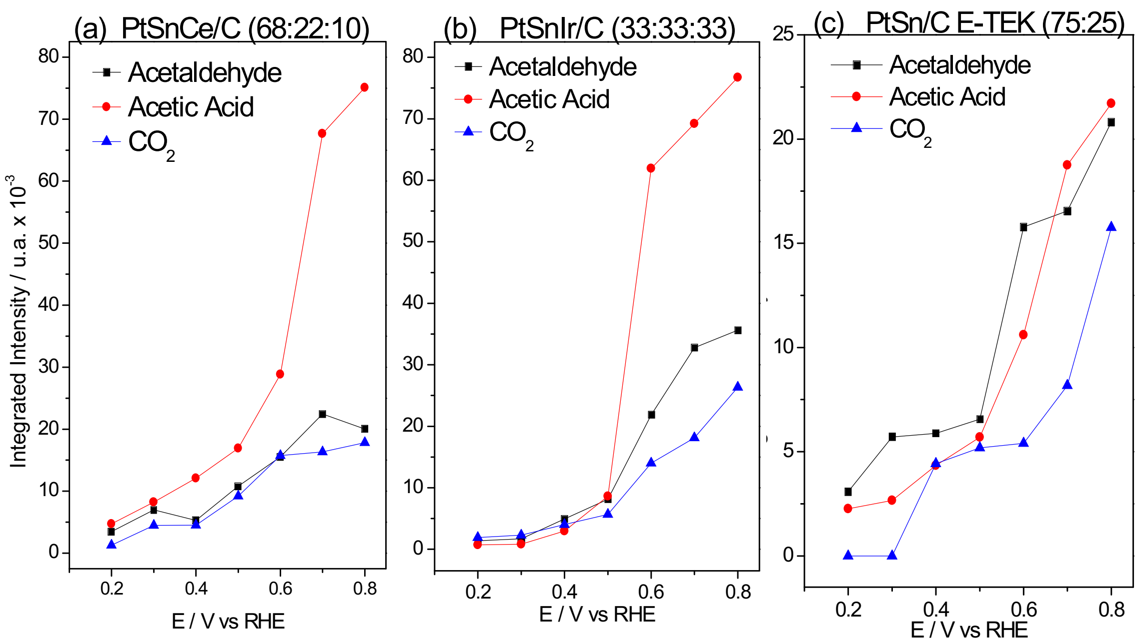

Figure 5. Integrated IR bands for the main products of ethanol oxidation: acetaldehyde, acetic acid and CO_2.

A comparison of the band intensities shows that the production of acetic acid is favored for PtSnCe/C catalysts, while low concentrations of acetaldehyde and CO_2 are produced. Using the PtSnIr/C catalyst, it was observed that acetic acid and acetaldehyde production increased with increasing electrode potential. The onset potential for acetic acid formation occurred at 0.4 V, while the CO_2 production increased before 0.5 V. The acetaldehyde formation was greater than CO_2 production, but it was lower than acetic acid formation. For the commercial PtSn/C catalyst, acetic acid and acetaldehyde were produced at the same concentration, and CO_2 was produced at a slightly lower concentration.

PtSnCe/C, PtSnIr/C electrocatalysts showed superior activity when compared with the commercial PtSn/C catalyst for ethanol oxidation in a DEFC. For both materials, acetic acid was the predominant product formed. The platinum content in the electrocatalyst can be decreased when iridium is used in the electrocatalyst.

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