

EFFECT OF Pt:Sn ATOMIC RATIO ON THE PREPARATION OF PtSn/C ELECTROCATALYSTS USING ELECTRON BEAM IRRADIATION

**Dionísio F. Silva, Almir Oliveira Neto, Eddy S. Pino, Marcelo Linardi, and
Estevam V. Spinacé**

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
dfsilva@ipen.br
espinace@ipen.br

ABSTRACT

PtSn/C electrocatalysts were prepared with Pt:Sn atomic ratios of 3:1, 1:1 and 1:3 in water/2-propanol using electron beam irradiation. The obtained materials were characterized by EDX, XRD and cyclic voltammetry. The ethanol electro-oxidation was studied by chronoamperometry. The XRD diffractograms of the PtSn/C electrocatalysts showed typical face-centered cubic (fcc) structure of platinum and the presence of a SnO₂ phase (cassiterite). The mean crystallite sizes of Pt fcc phase was in the range of 3.0-3.5 nm. The PtSn/C electrocatalysts were active for ethanol electro-oxidation at room temperature and the material prepared with Pt:Sn atomic ratio of 1:1 showed the best activity.

1. INTRODUCTION

Fuel cells convert chemical energy directly into electrical energy with high efficiency, low emission of pollutants and are extremely attractive as power sources for mobile, stationary and portable applications. In the proton exchange membrane fuel cell (PEMFC) the anodic oxidation of hydrogen and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures [1,2]. Carbon-supported platinum or platinum-based nanoparticles are the best electrocatalysts for anodic and cathodic reactions. However, the use of hydrogen as combustible continues to present problems especially for mobile and portable applications [3]. Thus, there has been an increasing interest in the use of alcohols directly as combustible (Direct Alcohol Fuel Cell – DAFC). Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst) the best electrocatalyst [4-6]. In Brazil ethanol is an attractive fuel as it is produced in large quantities from sugar cane and it is much less toxic than methanol, however, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulty in C-C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts [7]. Thus, more active electrocatalysts are essential to enhance the ethanol electro-oxidation. PtSn/C has been considered the best electrocatalyst for ethanol electro-oxidation and the performance depends greatly on its preparation procedure.

Recently, we prepared [8-10] PtRu/C electrocatalysts in a single step using gamma and electron beam irradiation and the obtained materials showed good activity for methanol

oxidation. In this work, PtSn/C electrocatalysts with different Pt:Sn atomic ratios were prepared in water/2-propanol using electron beam irradiation and the obtained materials were tested for ethanol electro-oxidation.

2. EXPERIMENTAL

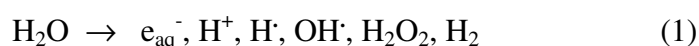
PtSn/C electrocatalysts (20 wt%, Pt:Ru atomic ratio of 3:1, 1:1 and 1:3) were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) as metal sources, which were dissolved in water/2-propanol solution 50/50 (v/v). After this, the Carbon Vulcan[®] XC72R, used as support, was dispersed in the solution using an ultrasonic bath. The resulting mixture was submitted under stirring to electron beam source (Electron Accelerator's Dynamitron Job 188 – IPEN/CNEN – SP) and the total dose was 288 kGy. After irradiation the mixture was filtered and the solid (PtRu/C electrocatalyst) was washed with water and dried at 70°C for 2 h [8-10].

The XRD analyses were performed using a Rigaku diffractometer model Multiflex with a $\text{CuK}\alpha$ radiation source. The measured angle range extended from 20° to 90° with a scanning rate of 2° per minute. The average crystallite size was calculated using Scherrer equation [11].

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [12]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.36 cm² area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry experiments the current values (I) were expressed in amperes and were normalized per gram of platinum ($\text{A g}_{\text{Pt}}^{-1}$). The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica software. Cyclic Voltammetry was performed in a 0.5 mol L⁻¹ H_2SO_4 solution saturated with N_2 . Chronoamperometry experiments were performed using 1.0 mol L⁻¹ of ethanol in 0.5 mol L⁻¹ H_2SO_4 at 0.5V and at room temperature.

3. RESULTS AND DISCUSSION

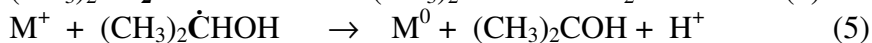
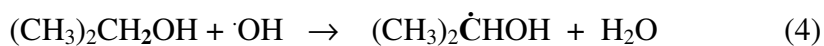
In the preparation of the electrocatalysts the electron beam irradiation causes the ionization and excitation of water molecules present in the reaction medium forming the species showed in Eq. 1 [13].



The solvated electrons, e_{aq}^- , and $\text{H}\cdot$ atoms are strong reducing agents and were able to reduce metal ions down to the zero-valent state (Eq. 2 and 3)



On the other hand, $OH\cdot$ radicals could oxidize the ions or the atoms into a higher oxidation state and thus to counterbalance the reduction reactions (2) and (3). Thus, an $OH\cdot$ radical scavenger is added to the solution, in this case 2-propanol, which reacts with these radicals leading to the formation of radicals exhibiting reducing power that are able to reduce metal ions (Eq. 4 and 5) [13,14].



In this manner, the atoms produced by the reduction of metals ions progressively coalesce leading to the formation of metal nanoparticles.

The X-ray diffractograms of PtSn/C electrocatalysts prepared using electron beam irradiation are shown in Figure 1.

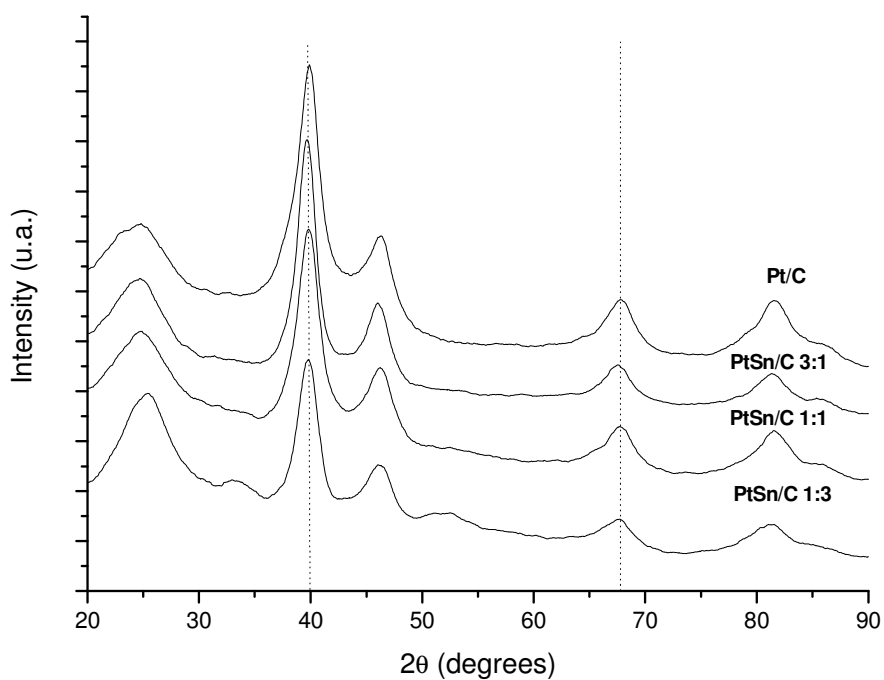


Figure 1: X-ray diffractograms of PtSn/C electrocatalysts prepared using electron beam irradiation.

The XRD diffratograms of Pt/C and PtSn/C electrocatalysts showed a broad peak at about 25° , which was associated to the Vulcan XC72R support material, and five diffraction peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ e 87° that are associated to the (111), (200), (220), (311) e (222) planes, respectively, which are characteristic of the fcc structure of platinum and platinum alloys [15]. The (220) reflections of the fcc structure were used to calculate the average crystallite size according to Scherrer formula [14] and the calculated values were in the range of 3.0 - 3.5 nm. The peaks of Pt (fcc) phase of the PtSn/C electrocatalysts were not shifted compared to those of Pt/C electrocatalyst showing that no PtSn alloy was formed. However, it was also observed in the diffractogram of PtSn/C (Pt:Sn = 1:3) electrocatalysts two peaks at approximately $2\theta = 34^\circ$ and 52° that were identified as a SnO_2 phase (cassiterite) [16, 17].

The cyclic voltammograms in acid medium of the PtSn/C electrocatalysts prepared using electron beam irradiation are shown in Figure 2.

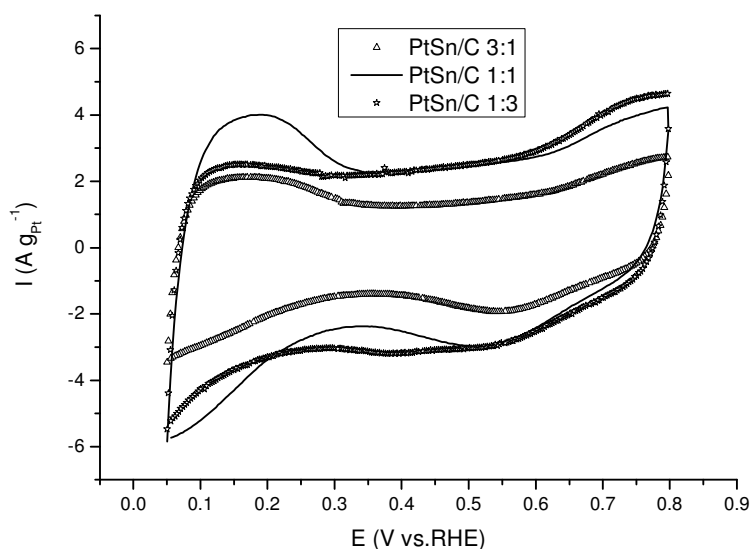


Figure 2. Cyclic Voltammograms of PtSn/C electrocatalysts prepared using electron beam irradiation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1} .

The cyclic voltammograms of PtSn/C electrocatalysts do not have a well-defined hydrogen adsorption-desorption region (0-0.4V) and showed an increase of the current values in the double layer (0.4-0.8V), which are attributed to tin oxide species [17,18].

In Figure 3 are presented chronoamperometric curves of PtSn/C electrocatalysts in 1.0 mol L^{-1} ethanol in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 0.5 V.

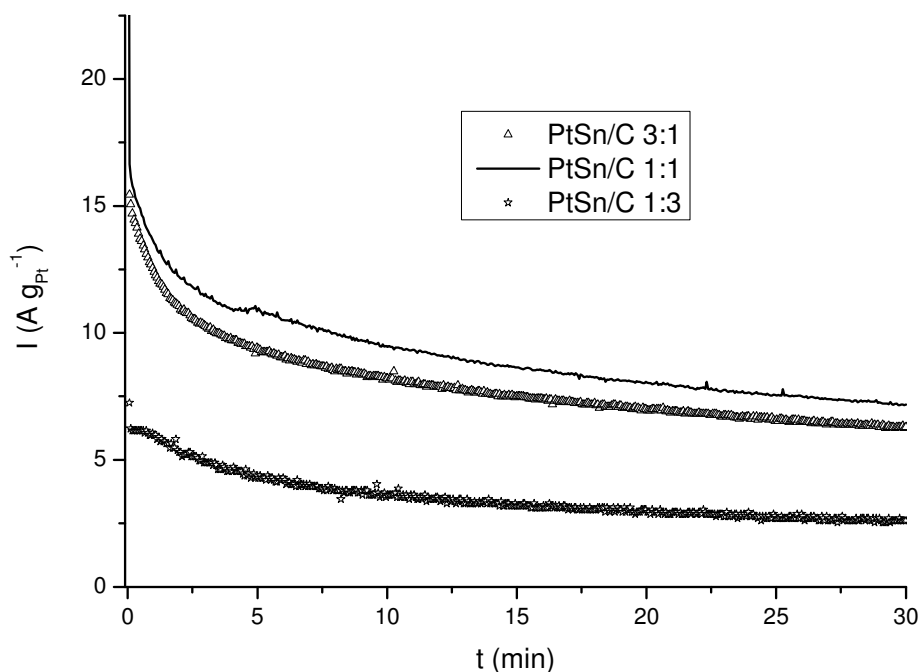


Figure 3: Current-time curves at 0.5 V for PtSn/C electrocatalysts in 1.0 mol L⁻¹ ethanol in 0.5 mol L⁻¹ H₂SO₄.

The currents values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at room temperature [19,20]. In all current-time curves there is an initial current drop in the first minutes followed by a slower decay. The PtSn/C electrocatalyst prepared with Pt:Sn atomic ratio of 1:1 was more active for ethanol oxidation than the electrocatalysts prepared with Pt:Sn atomic ratios of 3:1 and 1:3.

4. CONCLUSIONS

Active PtSn/C electrocatalysts for ethanol oxidation were obtained in a single step at room temperature within few minutes using electron beam irradiation. The PtSn/C electrocatalysts showed the typical fcc structure of platinum and a SnO₂ phase. The average crystallite sizes of the Pt fcc phase was about 3 nm. The PtSn/C electrocatalyst prepared with Pt:Sn atomic ratio of 1:1 showed the best activity. Experiments using these electrocatalysts in gas diffusion electrodes for tests in single direct ethanol fuel cell are currently in progress.

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