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Preparation of PtSn/C electrocatalysts using electron beam irradiation

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Abstract

PtSn/C electrocatalyts are claimed to be active electrocatalysts for ethanol electro-oxidation and their performances depends greatly on the preparation procedure and Pt:Sn atomic ratio. In this work, PtSn/C electrocatalysts with Pt:Sn atomic ratios of 9:1, 3:1, 1:1 and 1:3 were prepared in water/ethylene glycol using electron beam irradiation. The obtained materials were characterized by EDX and XRD and tested for ethanol electro-oxidation in acid medium using chronoamperometry. X-ray diffractograms of PtSn/C electrocatalysts showed typical face-centered cubic (fcc) structure of Pt with average crystallite size of 2 nm and the presence of a SnO_2 phase (cassiterite). PtSn/C electrocatalysts prepared with Pt:Sn atomic ratios of 9:1 and 3:1 were more active for ethanol electro-oxidation than commercial PtSn/C BASF electrocatalyst.

Keywords: PtSn/C electrocatalyst, electron beam irradiation, ethanol, fuel cell

1. Introduction

Direct alcohol fuel cells (DAFC) are very attractive as power sources for mobile and portable applications. Methanol has been considered the most promising fuel because it is more efficiently oxidized than other alcohols. 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 CO_2 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. 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 and Pt:Sn atomic ratio [1,2]. Belloni *et al*. [3] prepared carbon-supported PtRu nanoparticles using electron beam irradiation and the obtained catalysts were found to be efficient for methanol electro-oxidation. In this work, PtSn/C electrocatalysts with different Pt:Sn atomic ratios were prepared in water/ethylene glycol using electron beam irradiation.

2. Experimental

2.1. Preparation and characterization of PtSn/C electrocatalysts

PtSn/C electrocatalysts (20 wt% of metal loading) were prepared with different Pt:Sn atomic ratios using $H_2PtCl_6.6H_2O$ (Aldrich) and $SnCl_2.2H_2O$ (Aldrich) as metal sources, which were dissolved in a water/ethylene glycol 25/75 (v/v) solution. After this, the Carbon Vulcan® XC72R, used as support, was dispersed in the solution using an ultrasonic bath. The resulting mixtures were submitted at room temperature under

stirring to electron beam irradiation (Electron Accelerator's Dynamitron Job 188 – IPEN/CNEN – SP) and the total dose applied was 288 kGy (dose rate 1.6 kGy s^{-1}, time 3 min). After electron beam irradiation, the mixtures were filtered and the solids (PtSn/C electrocatalysts) were washed with water and dried at 70°C for 2 h.

The Pt:Sn atomic ratios were obtained by EDX analysis using a Philips XL30 scanning electron microscope with a 20 keV electron beam and provided with EDAX DX-4 microanaliser.

The X-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using Cu Kα radiation (λ = 0.15406 nm). The diffractograms were recorded at 2Θ in the range 20° - 90° with step size of 0.05° and scan time of 2 s per step. The average crystallite size was calculated using Scherrer equation [2].

2.2. Electro-oxidation of ethanol

Chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts. An amount of 20 mg of the electrocatalyst was added to 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 cm^2 area) of the working electrode. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Chronoamperometry experiments were performed with a Microquimica (model MQPG01) potentiostat/galvanostat using 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H_2SO_4 solution saturated with N_2 at 0.5V and at room temperature. For comparative purposes a commercial PtSn/C BASF electrocatalyst (20 wt%, Pt:Sn atomic ratio of 3:1, alloy, Lot #F0930203) was used.

3. Results and Discussion

The electron beam irradiation causes the ionization and excitation of water molecules present in the reaction medium forming the species showed in Eq. 1 [3].

$$H_2O \rightarrow e_{aq}^-, H^+, H^\cdot, {}^\cdot OH, H_2O_2, H_2 \quad (1)$$

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

$$M^+ + e_{aq}^- \rightarrow M^0 \quad (2)$$

$$M^+ + H^\cdot \rightarrow M^0 + H^+ \quad (3)$$

On the other hand, ${}^\cdot OH$ 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 ${}^\cdot OH$ radical scavenger (ethylene glycol) is added to the reaction medium, which reacts with these radicals leading to the formation of radicals exhibiting reducing power that are also able to reduce metal ions (Eq. 4 and 5) [3].

$$(CH_2OH)_2 + {}^\cdot OH \rightarrow HOH_2C\dot{C}HOH + H_2O \quad (4)$$

$$M^+ + HOH_2C\dot{C}HOH \rightarrow M^0 + HOH_2CCHO + H^+ \quad (5)$$

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

PtSn/C electrocatalysts were prepared with Pt:Sn atomic ratios of 9:1, 3:1, 1:1 and 1:3 (Table 1). The EDX analysis showed that the obtained materials have Pt:Sn atomic ratios very similar to the nominal ones.

Table 1. Pt:Sn atomic ratios and average crystallite sizes of PtSn/C electrocatalysts

Pt:Sn atomic ratio (nomimal)	Pt:Sn atomic ratio (EDX)	Crystallite size (nm)
9 : 1	9 : 1	< 2
3 : 1	2.8 : 1.2	< 2
1 : 1	1 : 1	2
1 : 3	1.2 : 2.8	2

The X-ray diffractograms of PtSn/C electrocatalysts are shown in Figure 1.

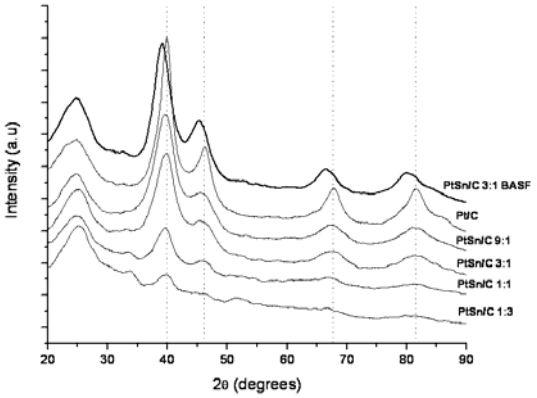

Fig. 1 X-ray diffractograms of PtSn/C electrocatalysts

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 2θ = 40°, 47°, 67°, 82° e 87°, which are characteristic of the fcc structure of platinum and platinum alloys [2]. For comparative purposes it is shown in Figure 1 the diffractogram of the commercial PtSn/C BASF electrocatalyst (PtSn alloy), that showed a shift of the peaks relative to Pt(fcc) phase to lower angles compared to those of Pt/C electrocatalyst. On the other hand, this shift was not observed for all prepared PtSn/C electrocatalysts showing that no PtSn alloys were formed. However, two peaks at approximately 2θ = 34° and 52° were observed in the diffractograms of the PtSn/C electrocatalysts, which increase with the increase of tin content in the samples and were identified as a SnO_2 phase (cassiterite) [2]. Henglein and Giersig [4] described the preparation of colloidal tin by radiolytic reduction of $SnCl_2$ in water/2-propanol. In this case, all process steps were performed under controlled argon atmosphere. In our case, the experiments were performed in open atmosphere and the SnO_2 phase was probably formed through hydrolysis-oxidation of $SnCl_2$ [5]. Thus, only Pt(IV) ions were reduced to the metallic state under the used conditions.

The chronoamperometric curves of PtSn/C electrocatalysts in 1 mol L^{-1} ethanol in 0.5 mol L^{-1} H_2SO_4 at 0.5 V for 30 min are shown in Figure 2 . The current

values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at room temperature [2].

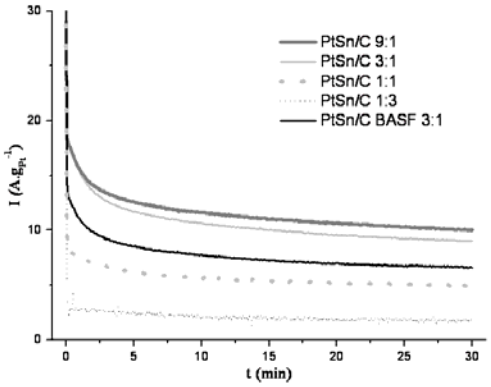

Fig. 2 Current-time curves at 0.5 V for PtSn/C electrocatalysts in 1.0 mol L^{-1} ethanol in 0.5 mol L^{-1} H_2SO_4

In all current-time curves there is an initial current drop in the first minutes followed by a slower decay. PtSn/C electrocatalysts prepared with Pt:Sn atomic ratio of 9:1 and 3:1 showed a superior performance for ethanol oxidation compared to the commercial PtSn/C BASF electrocatalyt.

4. Conclusions

In the preparation of PtSn/C electrocatalyts the electron beam irradiations were performed in open atmosphere which results only in the reduction of Pt(IV) ions to the metallic state. Sn(II) ions suffers hydrolysis-oxidation forming a SnO_2 phase. Current studies have been shown that PtSn electrocatalysts containing Pt and SnO_2 have good performances for ethanol electro-oxidation [2, 6].

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