

Preparation of PtAu/C and PtAuBi/C electrocatalysts using electron beam irradiation for ethanol electro-oxidation in alkaline medium

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ABSTRACT

PtAu/C (50:50) and PtAuBi/C electrocatalysts with Pt:Au:Bi atomic ratios of 50:40:10, 50:30:20 and 50:10:40 were prepared in water/2-propanol using electron beam irradiation. The materials were characterized by X-ray diffraction (XRD) and the electro-oxidation of ethanol was studied by chronoamperometry at room temperature. The X-ray diffraction measurements for all electrocatalysts prepared showed four peaks, which are associated with the planes of the face-centered cubic (fcc) structure characteristic of Pt and Pt alloys. For PtAuBi/C it was also observed the presence of a mixture of BiPt alloys and bismuth phases. The average crystallite sizes for Pt/C, PtAu/C, PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) were in the range of 2.0 - 4.0 nm. The activity of the electrocatalysts for ethanol oxidation in alkaline medium showed that PtAuBi/C (50:40:10) had a higher performance for ethanol oxidation compared to others electrocatalysts prepared.

1. INTRODUCTION

Fuel cells employing alcohols directly (direct alcohol fuel cell, DAFC) are attractive as power sources for mobile, stationary and portable applications, because the use of liquid fuels simplifies the fuel delivery system compared to hydrogen-fed fuel cells [1]. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols, however, a slow anode kinetics is observed and methanol is also toxic [1]. An alternative to methanol is the use of ethanol for Direct Alcohol Fuel Cells, because it could be produced in large scale from renewable sources and it also is less toxic than methanol [1].

PtSn/C electrocatalysts has been described to be more active for ethanol electro-oxidation in acid medium [1]. On the other hand, gold is generally considered as a poor electrocatalyst in acid medium, but its activity in alkaline medium is much greater [1].

Sung et al. [2] synthesized a PtAu/C electrocatalyst by the conventional borohydride reduction method and found that this alloy had enhanced activity for methanol oxidation with relation to Pt/C electrocatalysts. Demarconnay et al. [3] showed that PtBi/C electrocatalysts promoted the catalytic activity towards ethylene glycol electro-oxidation in alkaline medium when compared to Pt/C, while Tusi et al [4] showed that PtBi/C electrocatalysts had a significant increase of performance for ethanol oxidation in alkaline medium compared to Pt/C, while Bi/C electrocatalyst showed no activity. Da Silva et al prepared PtRu/C electrocatalysts for methanol oxidation using gamma irradiation and electron beam irradiation [5], however an active PtRu/C electrocatalyst was prepared with few minutes using electron beam irradiation. Da Silva et al [6] also prepared PtSnO₂/C electrocatalysts for ethanol electro-oxidation using electron beam irradiation and the material prepared with Pt:Sn atomic ratio of 50:50 showed the best performance [6].

In this context, the aim of this work was to prepare PtAu/C and PtAuBi/C with different Pt:Au:Bi atomic ratios using electron beam irradiation and to test these electrocatalysts for ethanol electro-oxidation in alkaline medium.

2. EXPERIMENTAL

PtAu/C (50:50) and PtAuBi/C (20 wt.% of metals loading; Pt:Au:Bi atomic ratios of 50:40:10, 50:30:20 and 50:10:40) electrocatalysts were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Chloroplatinic acid-Aldrich), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Chloride trihydrate-Aldrich) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Bismuth (III) nitrate pentahydrate –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 for 10 min. The resulting mixtures were submitted (at room temperature and open atmosphere) 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} and time of 3 min). After electron beam irradiation, the mixtures were filtered and the solids were washed with water and dried at $70 \text{ }^\circ\text{C}$ for 2 h [6].

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

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [1]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate. The chronoamperometry curves of the PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) electrocatalysts were performed holding the cell potential at -0.4 V vs Ag/AgCl electrode (0.5 V vs RHE) in 1.0 mol L^{-1} KOH solution containing 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ at room temperature.

3. RESULTS AND DISCUSSION

The X-ray diffractograms of the Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) are shown in Fig.1, while the chronoamperometry curves at -0.4 V in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} of ethanol for Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) electrocatalysts are shown in Fig .2.

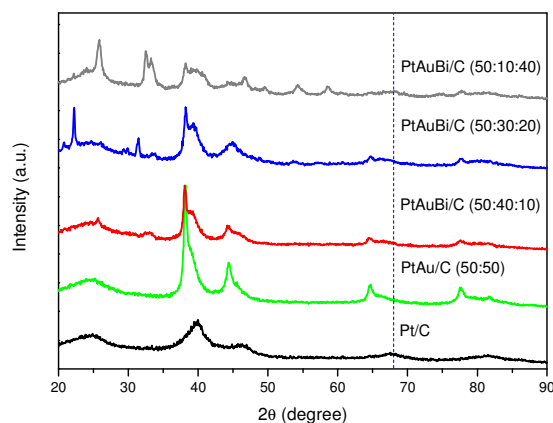


Figure 1. X-ray diffractograms of the Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40).

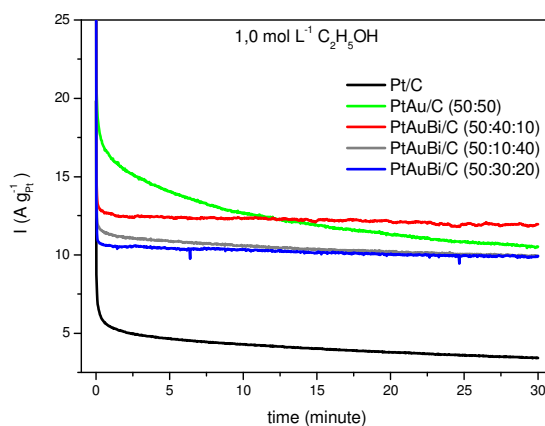


Figure 2. Current–time curves at -0.4V in 1.0 mol L⁻¹ KOH containing 1.0 mol L⁻¹ C₂H₅OH for Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) electrocatalysts.

In all diffractograms can be clearly seen a broad peak at about 25° associated with the Vulcan XC72R support. For Pt/C electrocatalyst it was observed four peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ$ and 82° , which are associated with the (111), (200), (220) and (311) planes, respectively, of the face-centered cubic (fcc) structure characteristic of platinum and platinum alloys [6]. For PtAu/C (50:50) electrocatalysts the diffraction peaks of the fcc phase are shifted to lower angles compared to Pt/C electrocatalyst, which indicates some lattice expansion and that part of Au atoms could be incorporated into the Pt lattice. For PtAuBi/C electrocatalysts was observed the presence of some peaks that could be attributed to the presence of Bi and/or PtBi alloyed phases [4]. The mean crystallite sizes determined using Scherrer equation [4] for the electrocatalysts prepared by electron beam irradiation were in the range of 2–4 nm. In chronoamperometry experiment, the current values decays rapidly on Pt/C, however the current values decays slowly on PtAu/C and PtAuBi/C. All electrocatalysts prepared were more active for ethanol oxidation than Pt/C indicating the beneficial effect of the addition of gold and bismuth to platinum. The final current values

after holding the cell potential at -0.4 V vs Ag/AgCl for 30 min were the following: PtAuBi/C (50:40:10) > PtAu/C > PtAuBi/C (50:30:20) \approx PtAuBi/C (50:10:40) > Pt/C. The addition of Bi to PtAu/C electrocatalysts enhanced the performances of these electrocatalysts, however the addition of small quantity of Bi (10 at.%) was necessary to obtain good performances. These results for ethanol oxidation suggest that the electronic effect brought by the addition of Au contributes to the higher catalytic activity of the PtAuBi/C (50:40:10) electrocatalyst and the presence of Bi species facilitate the oxidative desorption of the intermediates.

4. CONCLUSION

The electron beam irradiation showed to be an effective method for producing active electrocatalysts for methanol and ethanol oxidation in alkaline medium. The X-ray diffractograms of Pt/C, PtAu/C and PtAuBi/C electrocatalysts showed the presence of the peaks of Pt and Bi phases and PtAu and PtBi alloys. PtAuBi/C (50:40:10) was more effective for ethanol oxidation. These results suggest that the electronic effect brought by the addition of Au contributes to the higher catalytic activity of the PtAuBi/C (50:40:10) electrocatalyst and the presence of Bi species facilitate the oxidative desorption of the intermediates.

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