

Preparation of PtAu/C and PtAuBi/C Electrocatalysts Using Electron Beam Irradiation for Methanol and Ethanol Electro-Oxidation in Alkaline Medium

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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), transmission electron microscopy (TEM) and cyclic voltammetry (CV). The electro-oxidation of methanol and ethanol were studied by cyclic voltammetry and 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. TEM micrographs of all electrocatalysts showed a good distribution of the particles on the carbon support. The activity of the electrocatalysts for alcohol oxidation in alkaline medium showed that PtAu/C electrocatalysts had a higher performance for methanol oxidation compared to others electrocatalysts prepared, while PtAuBi/C (50:40:10) showed higher performance for ethanol oxidation in alkaline medium. Pt/C, PtAu/C and PtAuBi/C electrocatalysts were also tested for methanol or ethanol electro-oxidation in acid medium and the final current values were compared to the ones obtained in alkaline medium. The results confirmed that PtAu/C and PtAuBi/C are emerging as an alternative to Pt/C electrocatalysts for methanol and ethanol oxidation in alkaline DEFCs, while that for ethanol oxidation in acidic DEFCs are not effective.

Keywords: Electron beam irradiation, PtAuBi/C, PtAu/C, ethanol electro-oxidation, alkaline medium

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, which need a reforming system or have problems of hydrogen storage [1-2]. 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 [3]. For methanol oxidation, PtRu/C has been considered the best electrocatalysts [4]. 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 [5-9]. PtSn/C electrocatalysts has been described to be more active than Pt/C and PtRu/C electrocatalysts for ethanol electro-oxidation in acid medium [10-11].

On the other hand, gold is generally considered as a poor electrocatalyst in acid medium, but its activity in alkaline medium is much greater [12]. The reactivity of ethanol on gold in alkaline medium is related to the fact that practically no poisoning species (CO-like species) can be formed and adsorbed on the surface.

Sung et al. [13] 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. Jin et al. [14] also showed that PtAu/C electrocatalysts have high activity and stability in alkaline solution for ethylene glycol oxidation.

Demarconnay et al. [15] 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 [16] 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.

Jiang et al. [17] showed that the ethanol oxidation currents of Pt/C and PtSn/C electrocatalysts in alkaline medium were higher than those obtained in acid medium, while the onset potentials in alkaline medium were less positive than those obtained in acid medium, however, the activity of Pt electrocatalysts for ethanol oxidation in alkaline medium needs to be improved. Thus, a new preparation method or new electrocatalysts developments are necessary for the electro-oxidation of methanol or ethanol in alkaline medium. Depending on the preparation procedure, Pt binary and ternary electrocatalysts have been obtained with different particle sizes and surface composition. The chemical and physical characteristics of these electrocatalysts also are dependent on the preparation procedure and the way of preparation becomes a key factor regarding their electrochemical activity [6].

The carbon-supported metal nanoparticles have been prepared for fuel cell applications by radiation-induced reduction of metal ions precursors [4]. Da Silva et al prepared PtRu/C electrocatalysts for methanol oxidation using gamma irradiation and electron beam irradiation [18-19], however an active PtRu/C electrocatalyst was prepared with few minutes using electron beam irradiation. Da Silva et al [4] 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 [4].

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 methanol and ethanol electro-oxidation in alkaline medium. The results obtained in alkaline medium also will be compared to the ones obtained in acid medium.

2. EXPERIMENTAL

The atomic composition of the PtAu/C electrocatalysts prepared using electron beam irradiation was chosen to be 50:50, the most active composition for the ethanol electro-oxidation [4].

PtAu/C (50:50) and PtAuBi/C (20 wt.% of metals loading; Pt: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 [18-19].

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.

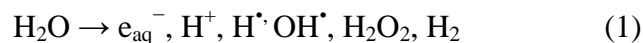
Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [2]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% solution 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 0.47 cm^2 area) of the working electrode. In cyclic voltammetry and chronoamperometry 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 an Ag/AgCl electrode and the counter electrode was a Pt plate.

Cyclic voltammetry experiments were performed in 1.0 mol L^{-1} KOH solution saturated with N_2 using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat in presence and absence of 1.0 mol L^{-1} of methanol or ethanol, while that 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} CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ at room temperature.

3. RESULTS AND DISCUSSION

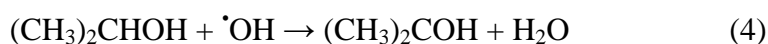
Belloni et al [20] showed that the electron beam irradiation of a water solution can cause the ionization and excitation of water molecules producing the following species shown in Eq. (1) [4,20]:



The solvated electrons (e_{aq}^-) and H^\bullet species are strong reducing agents and also are able to reduce metal ions down to the zero-valent state (Eqs. (2) and (3)):



The OH^\bullet radicals presents 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^\bullet 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 (Eqs. (4) and (5)) [4,20]:



In this manner, the atoms produced by the reduction of metals ions progressively coalesce leading to the formation of the metal nanoparticles [4].

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.

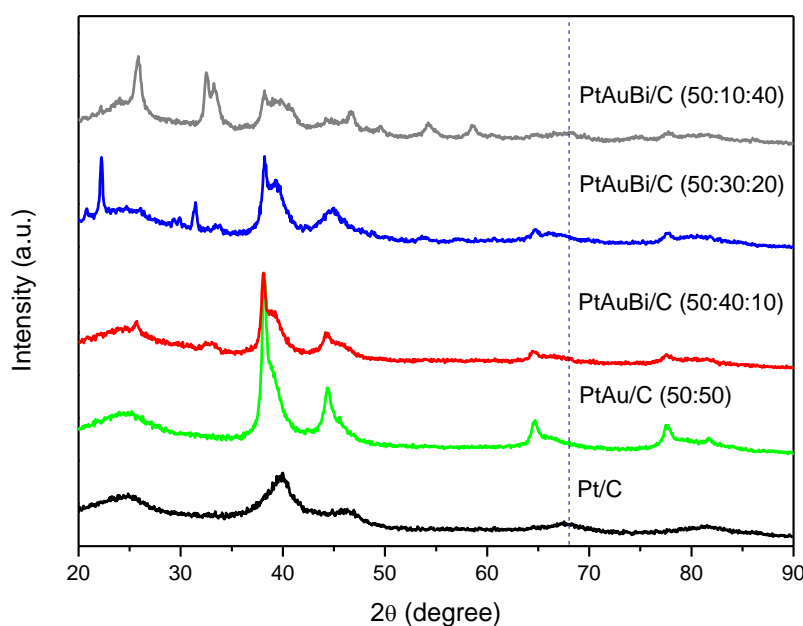


Figure 1. X-ray diffractograms of the Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40).

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. Besides this shift to lower angles a smooth peak was clear seen at the (111) peak. Similar results were observed by other authors [3,21,22], which were attributed to a PtAu alloy-like phase formation in PtAu/C catalysts. For PtAuBi/C electrocatalysts besides these peaks it was also observed the presence of some peaks that could be attributed to the presence of Bi and/or PtBi alloyed phases [16]. The (220) reflections of the fcc structure were used to calculate the average crystallite sizes. The mean crystallite sizes determined using Scherrer equation [5] for the electrocatalysts prepared by electron beam irradiation were in the range of 2–4 nm.

TEM micrographs of the obtained electrocatalysts are shown in Fig. 2.

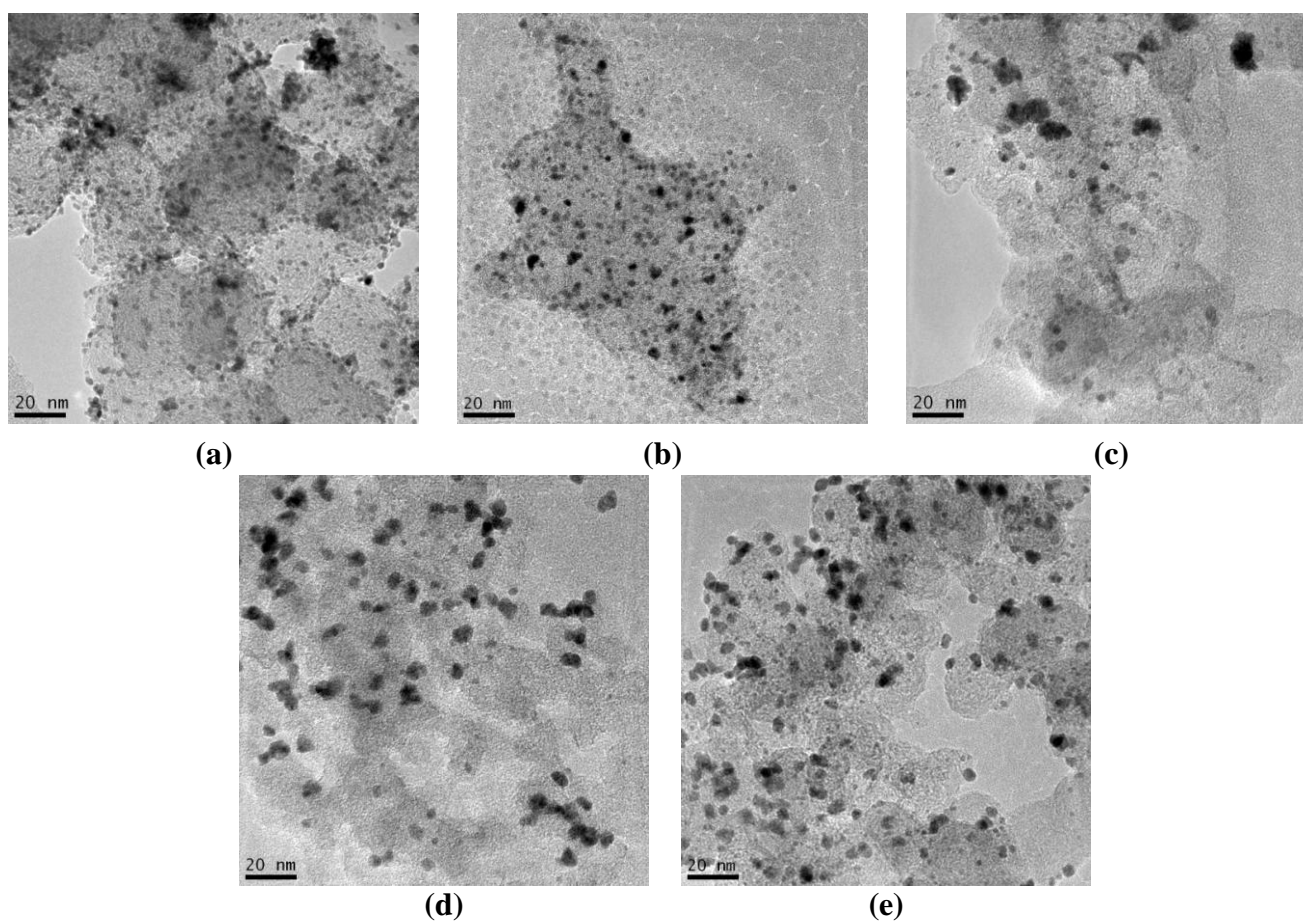


Figure 2. TEM micrographs of (a) Pt/C, (b) PtAu/C (50:50), (c) PtAuBi/C (50:40:10), (d) PtAuBi/C (50:30:20) and (e) PtAuBi/C (50:10:40) electrocatalysts.

All electrocatalysts prepared using electron beam irradiation showed a good distribution of the nanoparticles on the carbon support, however it can be observed some agglomerates. The nanoparticles are roughly in a spherical shape.

The CV of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) in 1.0 mol L⁻¹ KOH are shown in Fig. 3. The cyclic voltammetry responses were normalized per gram of platinum, considering that alcohol adsorption and dehydrogenation occur only on platinum sites at ambient temperature.

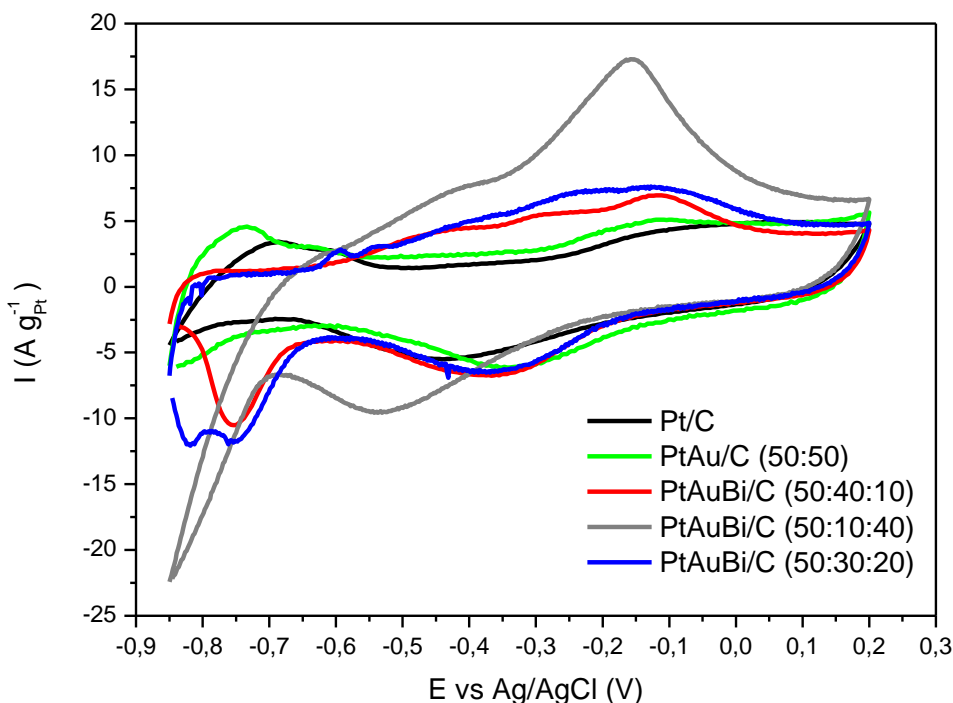


Figure 2. Cyclic voltammograms of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) in 1.0 mol L⁻¹ KOH with a sweep rate of 10 mV s⁻¹.

The humps in the potential region -850 to -500 mV on Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) are associated with hydrogen adsorption process in the anodic scan. The hydrogen adsorption/desorption peaks and pre-oxidation peaks for PtAu/C (50:50) and Pt/C are clearly similar. The CV of PtAuBi/C electrocatalyst showed that the hydrogen adsorption region was greatly reduced compared to the Pt/C and PtAu/C electrocatalysts, this effect could be attributed to the presence of bismuth in PtAuBi/C electrocatalysts [15]. PtAuBi/C electrocatalysts also showed an increase in the current values in the double layer (-0.4 to 0.0 V) in comparison with Pt/C and PtAu/C electrocatalysts, which may be attributed to the formation of bismuth oxide species. The cathodic peaks, at around -0.35 V, is attributed to the reduction of the platinum and bismuth oxide during the cathodic scan.

The CV of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10) and PtAuBi/C (50:10:40) in 1.0 mol L⁻¹ KOH containing 1.0 mol L⁻¹ CH₃OH are shown in Fig. 3.

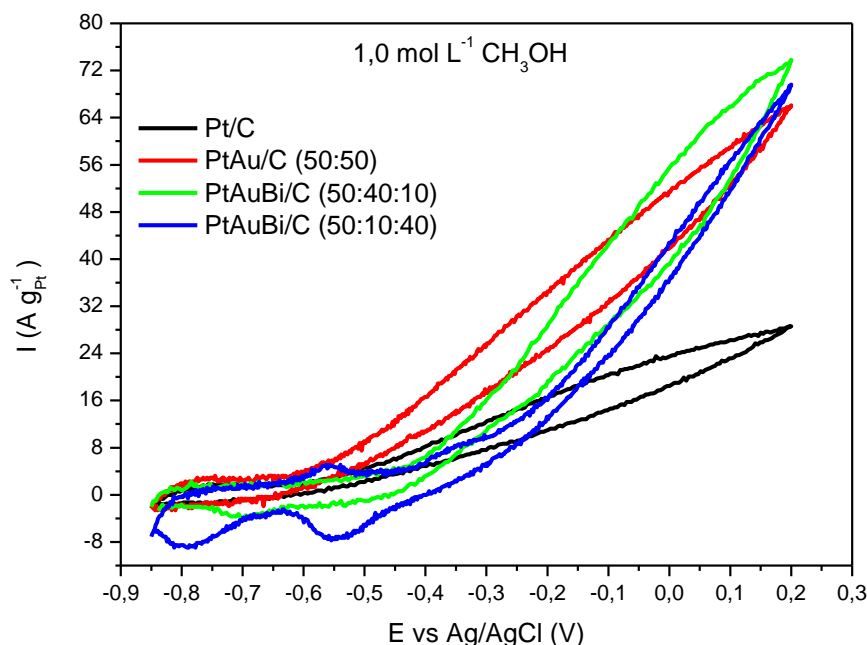


Figure 3. Cyclic voltammograms of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} CH_3OH with a sweep rate of 10 mV s^{-1} .

The cyclic voltammogram of the Pt/C, PtAu/C and PtAuBi/C electrocatalysts showed the hydrogen desorption/sorption region was significantly suppressed in the presence of methanol in the solution. The methanol electro-oxidation started at approximately -0.6 V for PtAu/C, -0.5 V for Pt/C, -0.4 V for PtAuBi/C (50:40:10), while that for PtAuBi/C (50:10:40) the methanol electro-oxidation started at approximately -0.3 V . In the potential range of interest for a direct ethanol fuel cell (-0.6 to -0.3 V), the current values of the PtAu/C were higher than that of others electrocatalysts prepared. For PtAu/C electrocatalyst, however, the interactions among platinum, gold and co-existing species of these metals such as $\text{Au}(\text{OH})_{\text{ad}}$ and $\text{Pt}(\text{CO})_{\text{ad}}$ probably lead to further oxidation of CO_{ad} to CO_2 more easily, such that active platinum is regenerated and no severe poisoning is observed. The cyclic voltammetry also showed that the current densities are higher in 0.0 V on PtAuBi/C (50:40:10) electrocatalyst than on PtAu/C. For PtAuBi/C (50:40:10) and PtAuBi/C (50:10:40) were observed higher current densities in -0.1 V with relation to Pt/C electrocatalyst.

The CV of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ are shown in Fig. 4. The cyclic voltammograms of the Pt/C, PtAu/C and PtAuBi/C electrocatalysts also showed the hydrogen desorption/sorption region was significantly suppressed in the presence of ethanol in the solution. The ethanol electro-oxidation started at approximately -0.6 V for PtAu/C, while that for PtAuBi/C and Pt/C the ethanol electro-oxidation started at approximately -0.45 V and -0.4 V , respectively. In the potential range of interest for a direct ethanol fuel cell (-0.6 to -0.3 V), the current values of PtAu/C and PtAuBi/C electrocatalysts were higher than Pt/C, however PtAu/C and PtAuBi/C (50:40:10)

electrocatalysts showing the best performance for ethanol oxidation. These results showed the beneficial effect of adding co-catalyst in the platinum.

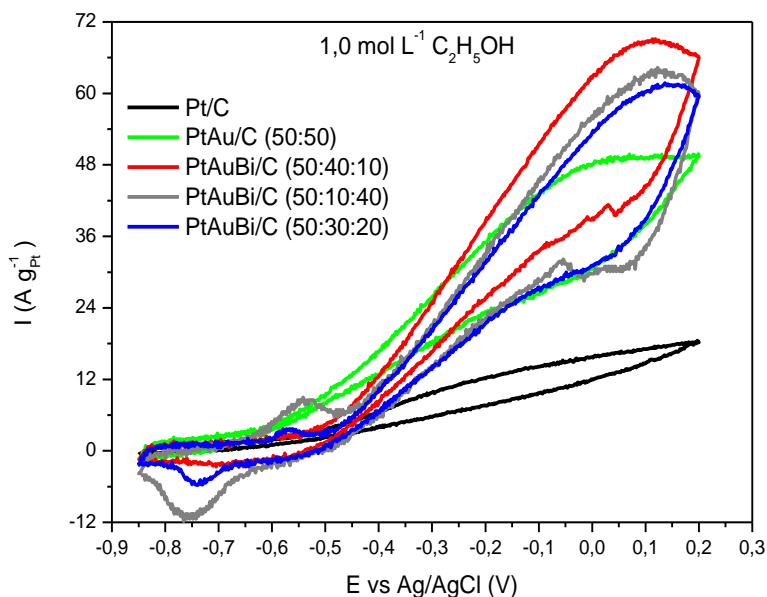


Figure 4. Cyclic voltammograms of Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) in 1.0 mol L⁻¹ KOH containing 1.0 mol L⁻¹ C₂H₅OH with a sweep rate of 10 mV s⁻¹.

The chronoamperometry experiments were carried out to examine the electrochemical stability of the electrocatalysts and the curves at -0.4 V in 1.0 mol L⁻¹ KOH containing 1.0 mol L⁻¹ of methanol for Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10) and PtAuBi/C (50:10:40) electrocatalysts are shown in Fig .5.

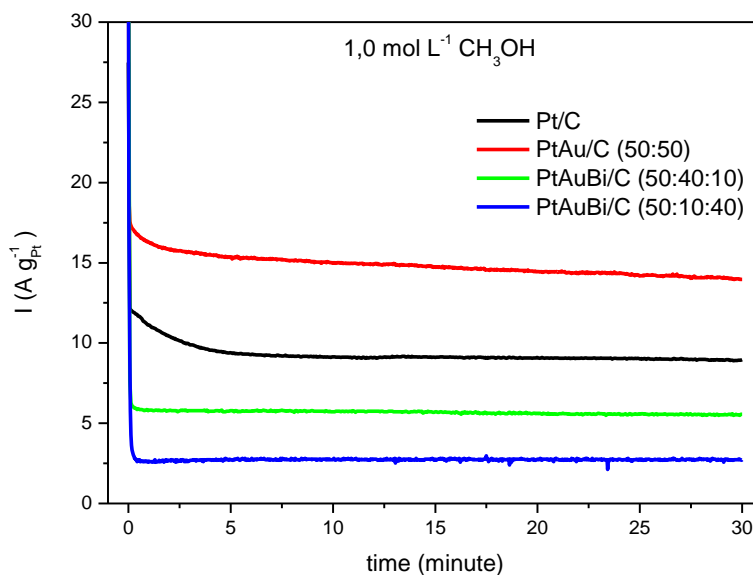


Figure 5. Current–time curves at -0.4V in 1.0 mol L⁻¹ KOH containig 1.0 mol L⁻¹ CH₃OH for Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10) and PtAuBi/C (50:10:40) electrocatalysts.

The final current values after holding the cell potential at -0.4 V vs Ag/AgCl for 30 min were the following: PtAu/C > Pt/C > PtAuBi/C (50:40:10) > PtAuBi/C (50:10:40). The results show that PtAu/C had higher catalytic activity for methanol electro-oxidation than Pt i.e. they are in agreement with cyclic voltammetry experiments. PtAuBi/C (50:40:10) and PtAuBi/C (50:10:40) showed a great initial current drop and a very low performance for methanol oxidation at room temperature in relation to PtAu/C and Pt/C electrocatalysts. For PtAuBi/C the current values decrease with the increase of Bi content in the sample. This effect is related with the presence of bismuth, where this element inhibits the hydrogen adsorption in Pt active sites [23,24], consequently the methanol adsorption and dehydrogenation could not be favored, because the adsorption of methanol occurs only on platinum sites at ambient temperature.

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 .6.

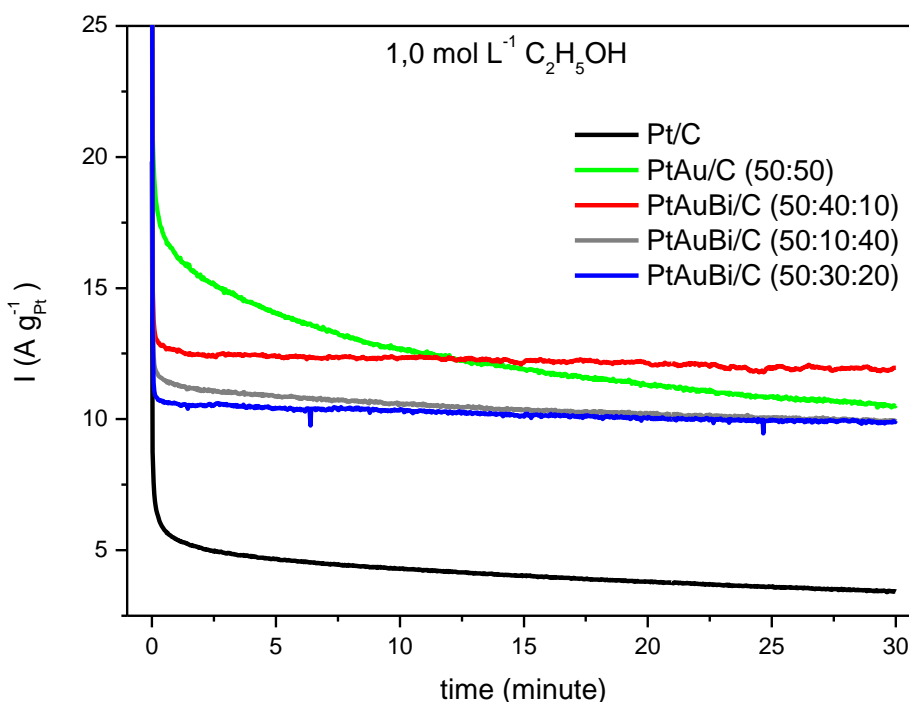


Figure 6. Current–time curves at -0.4 V in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ for Pt/C, PtAu/C (50:50), PtAuBi/C (50:40:10), PtAuBi/C (50:30:20) and PtAuBi/C (50:10:40) electrocatalysts.

In this experiment, the current values decays rapidly on Pt/C, however the current values decays slowly on PtAu/C and PtAuBi/C. These results show that PtAu/C and PtAuBi/C had better steady-state electrolysis than Pt/C for ethanol oxidation in alkaline medium. The results confirmed that PtAu/C and PtAuBi/C are good electrocatalysts for ethanol oxidation in alkaline medium in comparison with Pt/C and that these results also are important to develop direct ethanol fuel cells. 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. For PtAuBi/C, the current values for ethanol oxidation also decrease with the increase of Bi content in the sample. 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.

Pt/C, PtAu/C and PtAuBi/C electrocatalysts were also tested for methanol electro-oxidation in acid medium and the final current values obtained after holding the cell at -0.4 V for 30 min were compared to the ones obtained in alkaline medium (Figure 7).

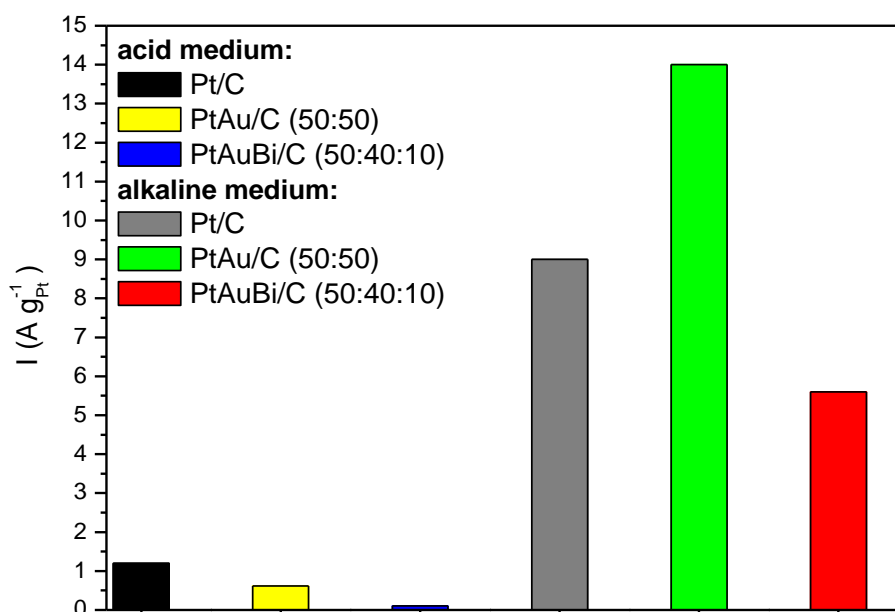


Figure 7. Current value at -0.4 V after 30 min for methanol electro-oxidation on Pt/C, PtAu/C and PtAuBi/C electrocatalysts in alkaline and acid medium.

The results confirmed that PtAu/C and PtAuBi/C are not good electrocatalysts for methanol oxidation in acidic medium, however these electrocatalysts are good for methanol oxidation in alkaline medium, because the final current values in alkaline medium were respectively about twenty and fifty times higher than the currents values obtained in acidic medium.

Pt/C, PtAu/C and PtAuBi/C electrocatalysts were also tested for ethanol electro-oxidation in acid medium and the final current values obtained after holding the cell at -0.4 V for 30 min were compared to the ones obtained in alkaline medium (Figure 8).

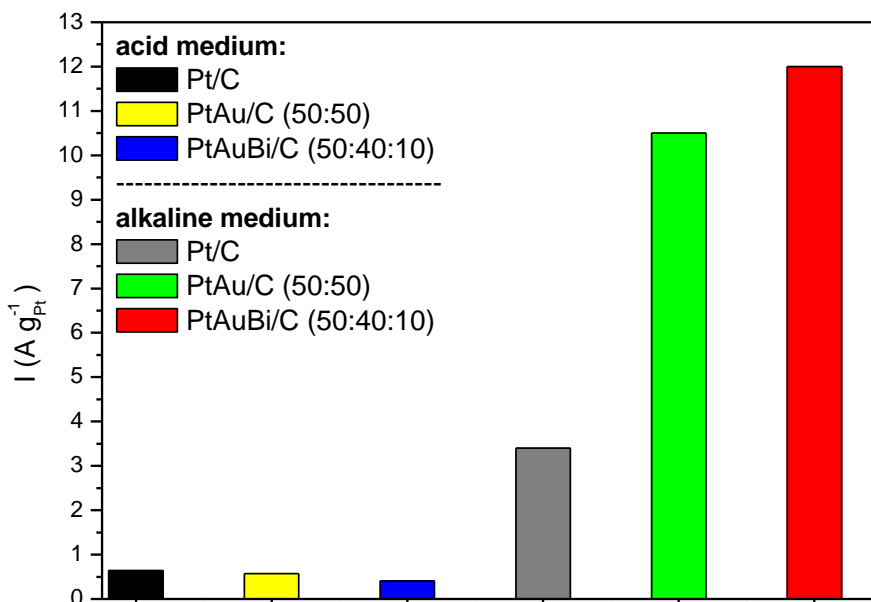


Figure 8. Current value at -0.4 V after 30 min for ethanol electro-oxidation on Pt/C, PtAu/C and PtAuBi/C electrocatalysts in alkaline and acid medium.

PtAu/C and PtAuBi/C also are not a good electrocatalyst for ethanol oxidation in acidic medium, however the final current values in alkaline medium were respectively about eighteen and thirty times higher than the currents values obtained in acidic medium. The ethanol oxidation current of Pt/C electrocatalyst in alkaline medium also was higher than those obtained in acid medium.

The results for methanol and ethanol oxidation showed that PtAuBi/C electrocatalysts was the best electrocatalysts for ethanol oxidation, while that PtAu/C was the best electrocatalyst for methanol oxidation. The addition of Bi to PtAu/C electrocatalysts enhanced the performances of these electrocatalysts for ethanol oxidation, while that the performances of these electrocatalysts for methanol oxidation were lower. The presence of bismuth in PtAuBi/C electrocatalysts not favors the adsorption of methanol in Pt actives sites [23,24], consequently the kinetics of methanol oxidation is slower.

4.CONCLUSIONS

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. The chronoamperometry experiments showed that PtAu/C electrocatalyst was more active than others electrocatalysts prepared for methanol oxidation in alkaline medium at room temperature, while that 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. The methanol and ethanol oxidation currents of Pt/C, PtAu/C and PtAuBi/C electrocatalysts in alkaline medium were higher than those obtained in acid medium indicating that in alkaline medium the kinetics could be significantly improved. Further work is now necessary to investigate the PtAu/C and PtAuBi/C electrocatalysts surface by different techniques and to elucidate the mechanism of methanol and ethanol electro-oxidation in alkaline medium.

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