PtBi/C Electrocatalysts for Formic Acid Electro-Oxidation in Acid and Alkaline Electrolyte

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Pt/C and PtBi/C with different PtBi atomic ratio (90:10, 80:20, 70:30, 60:40 and 50:50) were prepared by borohydride reduction method using $H_2PtCl_6 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ as metal sources and Vulcan XC72 as carbon support. The electrocatalysts prepared were characterized by X-ray diffraction, transmission electron microscopy and cyclic voltammetry. The activity for the formic acid electro-oxidation in acid and alkaline electrolyte was investigated at room temperature by cyclic voltammetry and chronoamperometry. X ray diffraction showed for all PtBi/C the presence of Pt face-centered cubic (fcc) system, while for PtBi/C (70:30, 60:40 and 50:50) electrocatalyst it was also observed the presence of some peaks that could be attributed to the presence of Bi metallic, Bi oxide species or PtBi phases. TEM micrographs and histograms for PtBi/C electrocatalysts showed that the nanoparticles are well dispersed on the support with particle sizes of 2.5±1.5 nm for all electrocatalysts prepared, however some agglomerates were also observed. The electrochemical studies showed that PtBi/C (90:10) had superior performance for formic acid electro-oxidation at 25°C in presence of acidic electrolyte compared to Pt/C, this result indicated that the addition of Bi to Pt could favor the electro-oxidation of formic acid and this effect could be attributed to the bifunctional mechanism associated to electronic effect. However in the alkaline electrolyte it was observed that Pt/C electrocatalysts had superior performance in comparison with PtBi/C, this result indicated that an optimization of the formic acid concentration for alkaline studies is still necessary.

1. INTRODUCTION

The use of hydrogen as a fuel still presents problems of production, storage, and delivery, therefore the use of a liquid as fuel has been considering very attractive as power sources for

stationary, mobile, and portable applications [1-6]. Methanol has been the fuel most studied for direct liquid fuel cell (DLFC) due to their low cost, low pollutant emissions and high theoretical energy density, though the use of methanol is not safe because it is a toxic, evaporable and burnable compound [7-8]. Recently, the formic acid has been proposed as an alternative to methanol because it is not inflammable and the storage and transportation are safe [8-9].

Pt electrocatalyst has been considered for the electro-oxidation of formic acid, even though it is very susceptible to poisoning species, which significantly reduces its catalytic performance at low potentials [10]. In order to improve its activity by minimizing the poisoning effects, Pt has been modified by adding of Ru, Pd, Au, Pb, Sn and Bi, where they showed better performances in formic acid oxidation in comparison with pure Pt [11]. Among the electrocatalysts prepared, the PtBi was recognized as one of the most active bimetallic systems for formic acid oxidation [11-12], where Roychowdhury et al. [13] described that the use of PtBi nanoparticles for formic acid oxidation in acid medium enhanced electrocatalytic activity compared to Pt and PtRu nanoparticles, however in alkaline media, more information is still necessary.

Demarconnay et al. [14] showed that PtBi/C electrocatalysts promoted the catalytic activity towards ethylene glycol electro-oxidation in alkaline medium when compared to Pt/C, Neto et al. [15] showed that PtBi/C electrocatalysts promoted a significant increase of performance for ethanol oxidation in comparison with pure Pt, however there is no information on formic acid oxidation using PtBi in alkaline media.

Thus, the aim of this work was prepare PtBi/C electrocatalysts with different Pt/Bi atomic ratios by borohydride reduction and test these electrocatalysts for the formic acid oxidation reaction in acid and alkaline electrolyte by cyclic voltammetry and chronoamperometry.

2. EXPERIMENTAL

PtBi/C were prepared using $H_2PtCl_6\cdot6H_2O$ and $Bi(NO_3)_3\cdot5H_2O$ as metal sources, sodium borohydride as reducing agent and carbon Vulcan XC72 as support. All PtBi/C were prepared with 20 wt% of metals loading, with Pt/Bi atomic ratios of 90:10, 80:20, 70:30, 60:40 and 50:50. In borohydride process the metal sources were dissolved in a mixture of water/2-propanol (50:50, v/v), while the support was dispersed in this solution. The resulting mixture was submitted to an ultrasonic bath for 10 min, after a solution of sodium borohydride was added under stirring in one portion at room temperature and finally, the mixture was filtered and the solid was washed with water and dried at 70 °C for 2 h.

X-ray diffraction analyses were carried out in a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (l = 0.15406 nm). All diffractograms were recorded from 2θ = 20° to 90° with a step size of 0.05° and a scan time of 2s per step. Transmission electron microscopies (TEM) were carried using a JEOL JEM-2100 electron microscope operated at 200 kV. The mean nanoparticle sizes were determined by counting more than 200 particles from different regions of each sample.

The cyclic voltammetry and chronoamperometry measurements were carried out at room temperature using a Microquimica potentiostat in presence of 0.5 mol L^{-1} H$_2$SO$_4$ as acid and 1 mol L^{-1} KOH as alkaline electrolyte.

These study were performed using a working electrode (geometric area of 0.3 cm^2 with a depth of 0.3 mm) prepared using the thin porous coating technique [1]. For the acid media experiments it was used a reversible hydrogen electrode (RHE) as reference and as counter electrode a Pt plate. The electrochemical measurements in acid electrolyte were realized in presence of 0.5 mol L^{-1} H$_2$SO$_4$ or 1.0 mol L^{-1} of formic acid+0.5 mol L^{-1} H$_2$SO$_4$ solutions saturated with N$_2$. For alkaline electrolyte it was used Ag/AgCl (KCl 3mol L^{-1}) as reference electrode and Pt plate as counter electrode while the electrochemical measurements in alkaline electrolyte were realized in presence of 1.0 mol L^{-1} KOH or 1.0 mol L^{-1} of formic acid+1.0 mol L^{-1} KOH. Amperometric curves were recorded in presence of alkaline or acid electrolyte containing formic acid considering the potentials of -0.30 V (alkaline electrolyte) or 0.5 V (acid electrolyte) by 30 minutes.

3. RESULTS AND DISCUSSION

The X-ray diffractograms of Pt/C and PtBi/C electrocatalysts are shown in Fig. 1. For all PtBi/C it was observed a broad peak at about 25° associated with the Vulcan XC72 support material; five peaks at approximately $2\theta = 40°$, 47°, 67°, 82° and 87°, which are associated with the (111), (200), (220), (311) and (222) planes, respectively, of the face-centered cubic (fcc) structure characteristic of Pt alloys. For PtBi (70:30), PtBi (60;40) and PtBi (50:50) it was also observed the presence of some peaks that could be attributed to the presence of Bi metalic, Bi oxide species and the presence of a mixture of BiPt or Bi$_2$Pt phases [15-16].
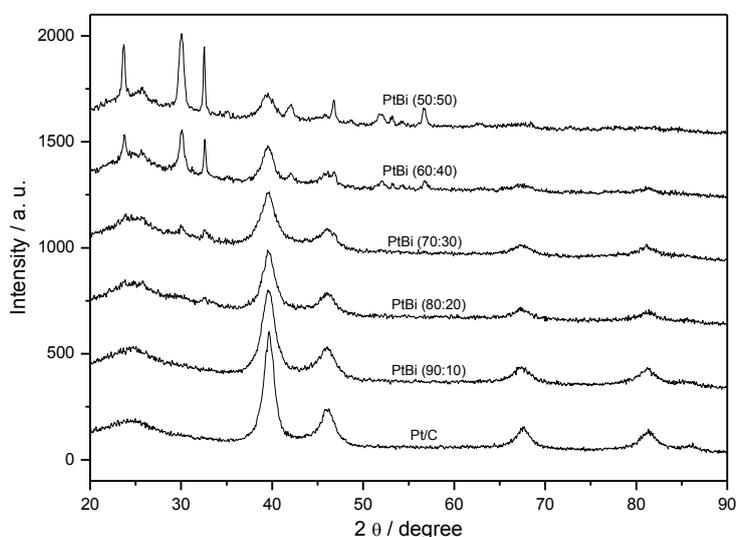

Figure 1. X-ray diffractograms of Pt/C and PtBi/C electrocatalysts.

Fig. 2 presents TEM micrographs of Pt/C and PtBi/C (Pt:Bi atomic ratios of 90:10, 80:20, 70:30, 60;40 and 50:50) electrocatalysts. Pt/C and PtBi/C images showed the nanoparticles well dispersed on the support, however some agglomerates were also observed. The mean particle size of Pt/C, PtBi (90:10), PtBi (80:20), PtBi (70:30), PtBi (60:40) and PtBi (50:50) were 3.3, 4.0, 4.2, 3.3, 2.8 and 2.5 nm, respectively. The Bi content increasing in PtBi/C electrocatalysts did not result in the mean particle size increasing, since for all PtBi/C electrocatalysts prepared the particle sizes were 2.5 ± 1.5 nm.

The cyclic voltammograms of Pt/C and PtBi/C electrocatalysts in presence of 0.5 mol L^{-1} H_2SO_4 or in 1.0 mol L^{-1} KOH solutions are shown in Fig. 3a and Fig 3b, respectively.
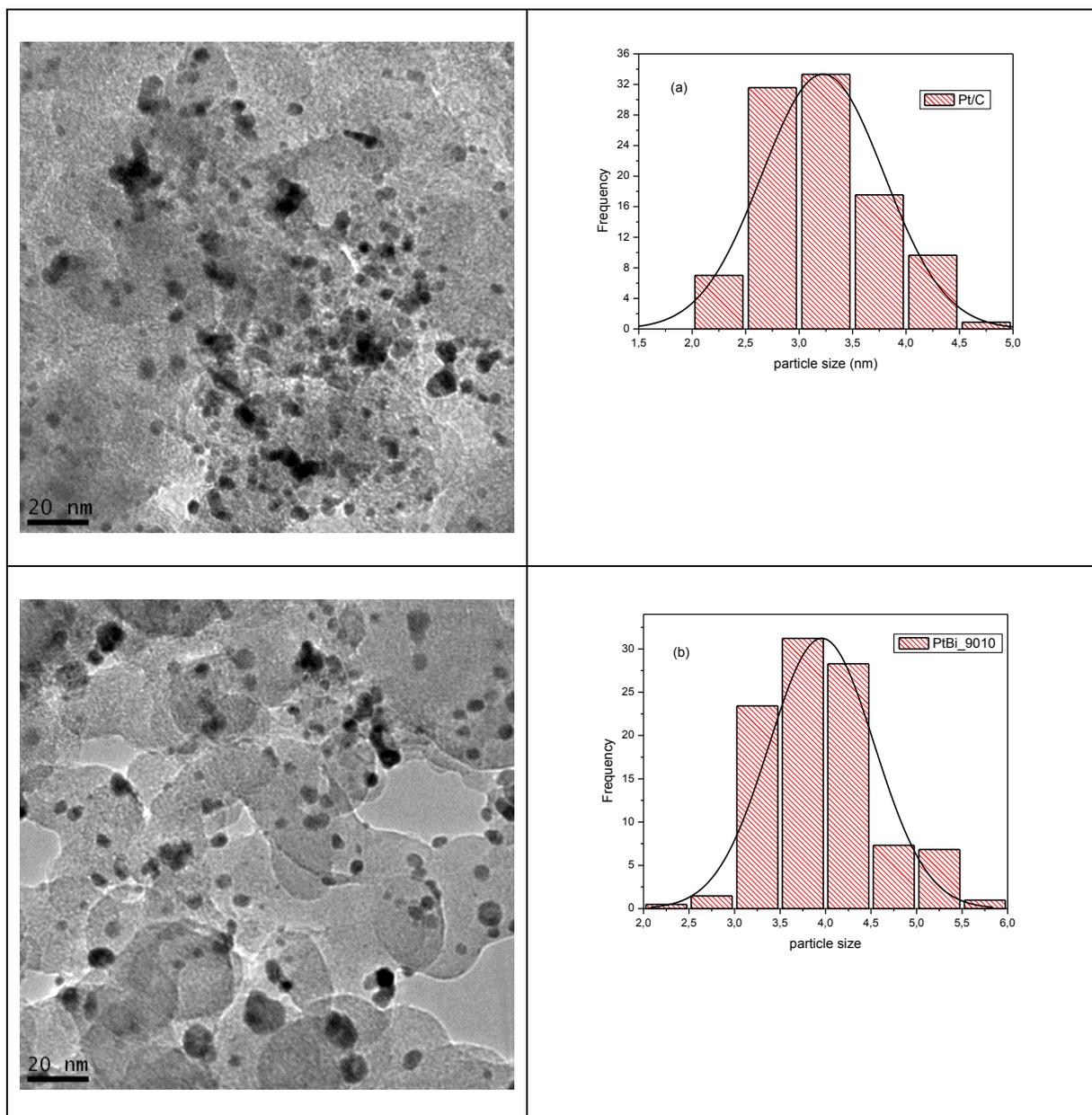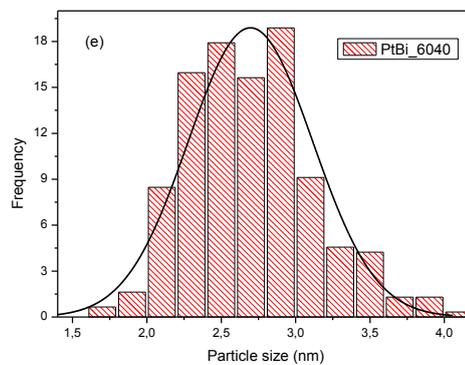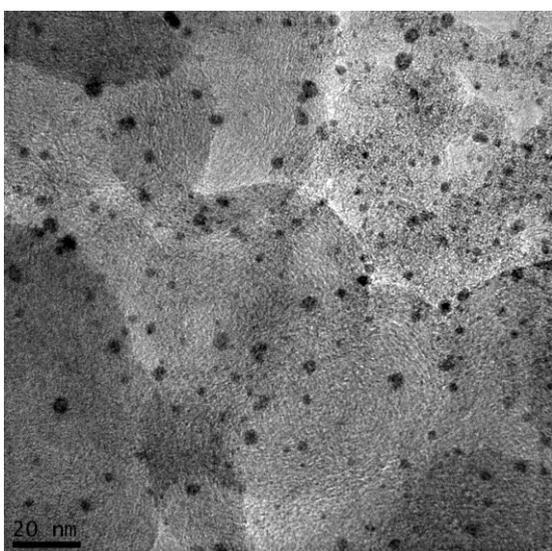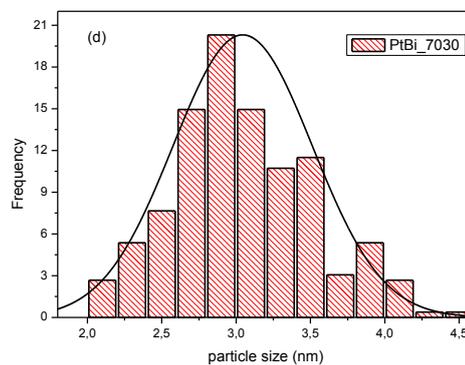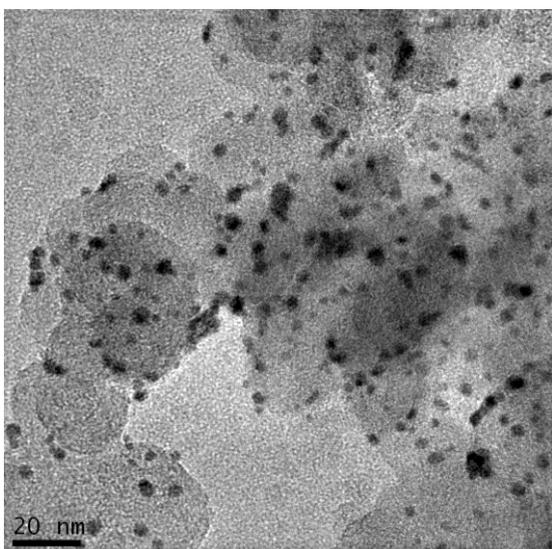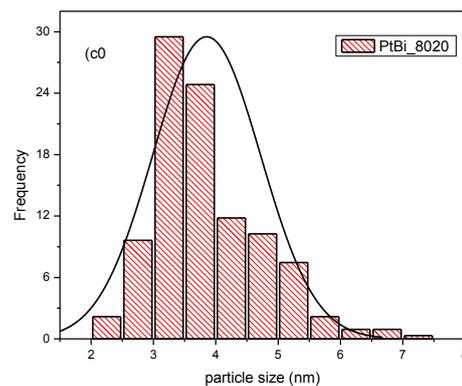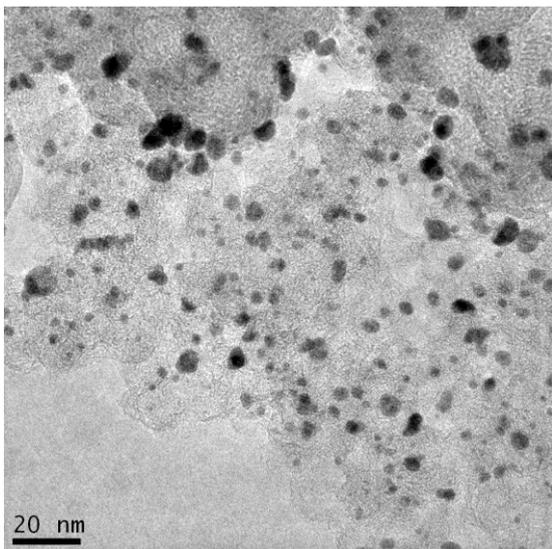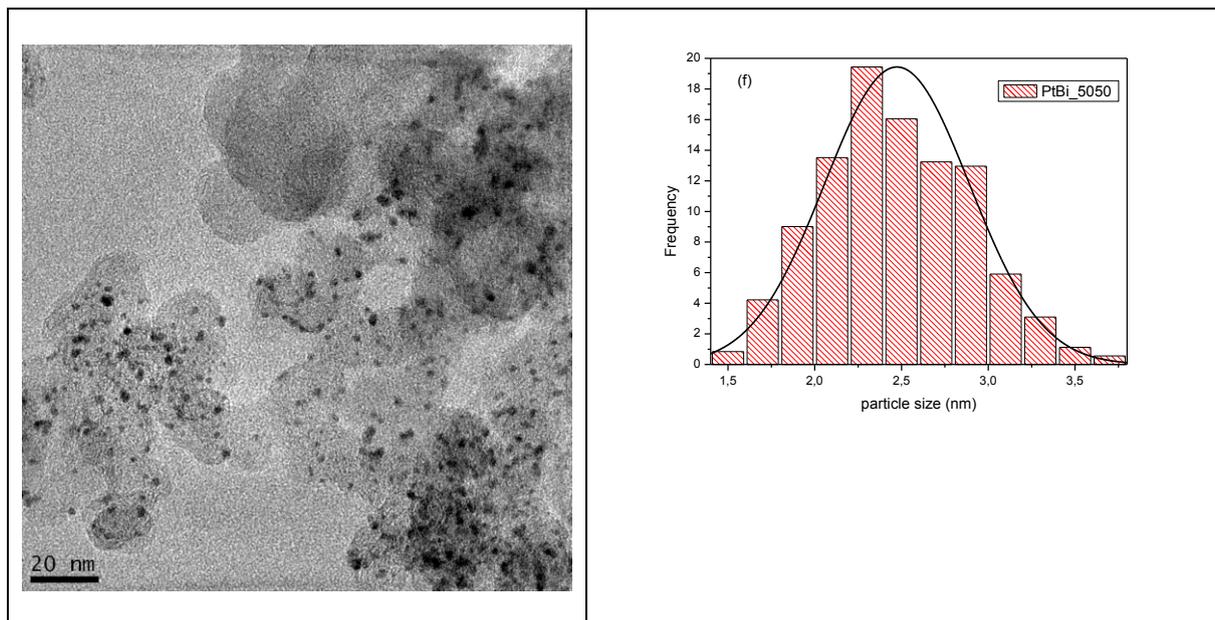
Figure 2. TEM micrograph and a histogram of (a) Pt/C, (b) PtBi/C (90:10), (c) PtBi/C (80:20), (d) PtBi/C (70:30), (e) PtBi/C (60:40) and (f) PtBi/C (50:50) with the mean diameter and particle distribution .

The CV of PtBi/C electrocatalysts (Fig 3a and 3b) showed that the hydrogen adsorption region was greatly reduced compared to the Pt/C electrocatalyst, this behavior is associated with the presence of bismuth species, since these species inhibits hydrogen adsorption on platinum.
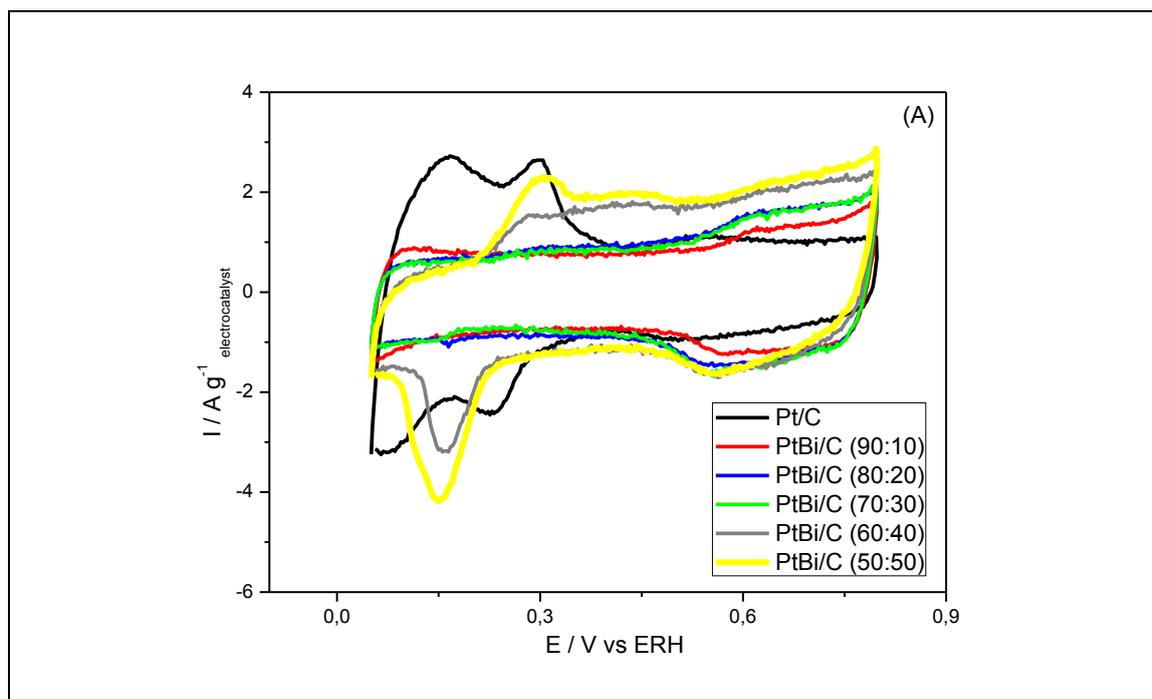
Figure 3. Cyclic voltammograms of Pt/C and PtBi/C electrocatalysts in 0.5 mol L^{-1} H$_2$SO$_4$ (a) or1.0 mol L^{-1} KOH with a sweep rate of 10 mV s^{-1}.
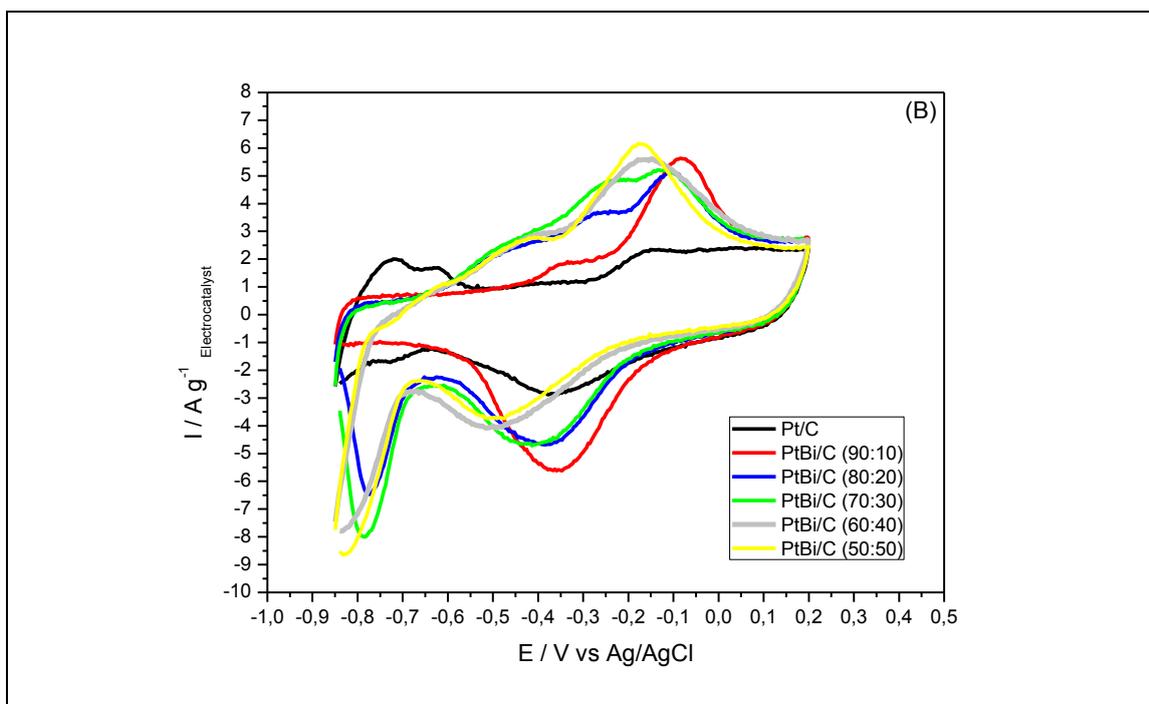
The CV features in H$_2$SO$_4$ (Fig 3a) are similar to those reported by Yang [17], Daniele and Bergamin [18] and Lee [19], where the authors assign a formation of adsorbed Bi(OH)$_2$, soluble Bi(OH)$^+_2$/Bi(OH)$^{+2}$, and Bi^{+3}, respectively.

These authors also observed the gradual leaching of bismuth from PtBi alloy, this behavior was also related in others works [20]. PtBi/C (Fig 3b) showed two processes on anodic scan that could be ascribed to the formation of Bi$_2$O$_3$ and Bi$_2$O$_5$, while for cathodic scan it was also observed a reduction of Bi$_2$O$_5$ as the reduction of Bi$_2$O$_3$ to Bi [17]. This behavior could be responsible for the catalytic different performances of PtBi nanoparticles in acid and alkaline electrolyte [17].

Figure 4a shows the cyclic voltammograms of Pt/C and PtBi/C electrocatalysts prepared at 25 °C in the presence of 1.0 mol L^{-1} formic acidic in 0.5mol L^{-1} H$_2$SO$_4$, while that Fig 4b shows the cyclic voltammograms of Pt/C and PtBi/C electrocatalysts in presence of 1.0 mol L^{-1} formic acidic in 1.0 mol L^{-1} KOH solutions.

All PtBi/C (Fig 4a) showed the highest current values in all potential range in comparison with Pt/C, however, PtBi/C (90:10) showed better performance in all potential range in comparison with others PtBi/C prepared. The enhancement of formic acid electro-oxidation on PtBi/C electrocatalysts in comparison with Pt/C could be caused by the electronic effect [21] or Bi atoms could improve the OH$_{ad}$ adsorption on the Pt sites, and could reduce the inclination for CO adsorption on PtBi surfaces [11, 17]. PtBi/C in presence of formic acid/alkaline electrolytes also showed the highest current values in the potential of 0.0V in comparison with Pt/C, however in the potential of -0.3 V Pt/C showed similar performance in comparison with all PtBi/C eletrocatalysts prepared by borohydride reduction

method, therefore current–time curves are necessary, because studies in the potential of -0.3 V are more interesting by fuel cell application.

PtBiC/ also showed for formic acid oxidation a less positive onset potential and slightly higher current until in acid electrolyte in comparison with alkaline media, the possible reason for the catalytic ability is the electronic effect or Bi atoms could improve the OH_{ad} adsorption on the Pt sites and could reduce the inclination for CO adsorption on PtBi surfaces [17]. For alkaline electrolyte the carbonate formation can occurs, leading to a high potential oxidation onset.
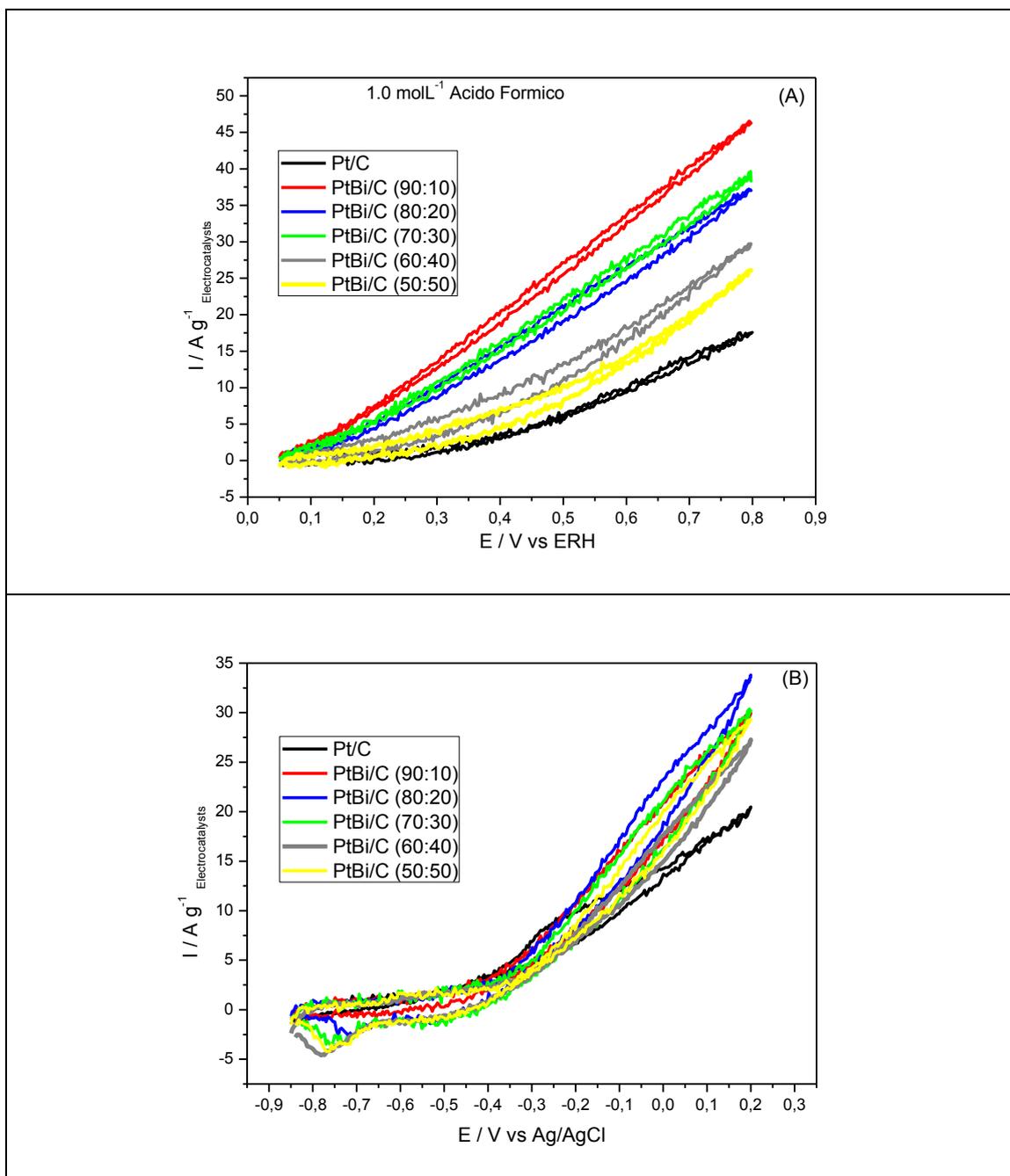

Figure 4. Cyclic voltammograms Pt/C and PtBi/C electrocatalysts prepared at 25 °C in the presence of 1.0 mol L^{-1} formic acidic in 0.5mol L^{-1} H$_2$SO$_4$ (a) and 1.0 mol L^{-1} formic acidic in 1.0 mol L^{-1} KOH (b) with a sweep rate of 10 mV s^{-1}.

Abruna [22] and Tripković [23] concluded that the electronic modification of Pt by Bi enhances the affinity towards formic acid adsorption (acid electrolyte), thus increasing interaction of formic acid molecules with the catalyst surface, which results in lowering the onset potential of the reaction compared with Pt. Wang [24] concluded by FTIRS experiments that during the oxidation of formic acid their oxidation to CO_2 proceeds via non-COa_{ds}, therefore a PtBi electrode can accelerate the bulk oxidation of HCOOH due to electronic modification on Pt.

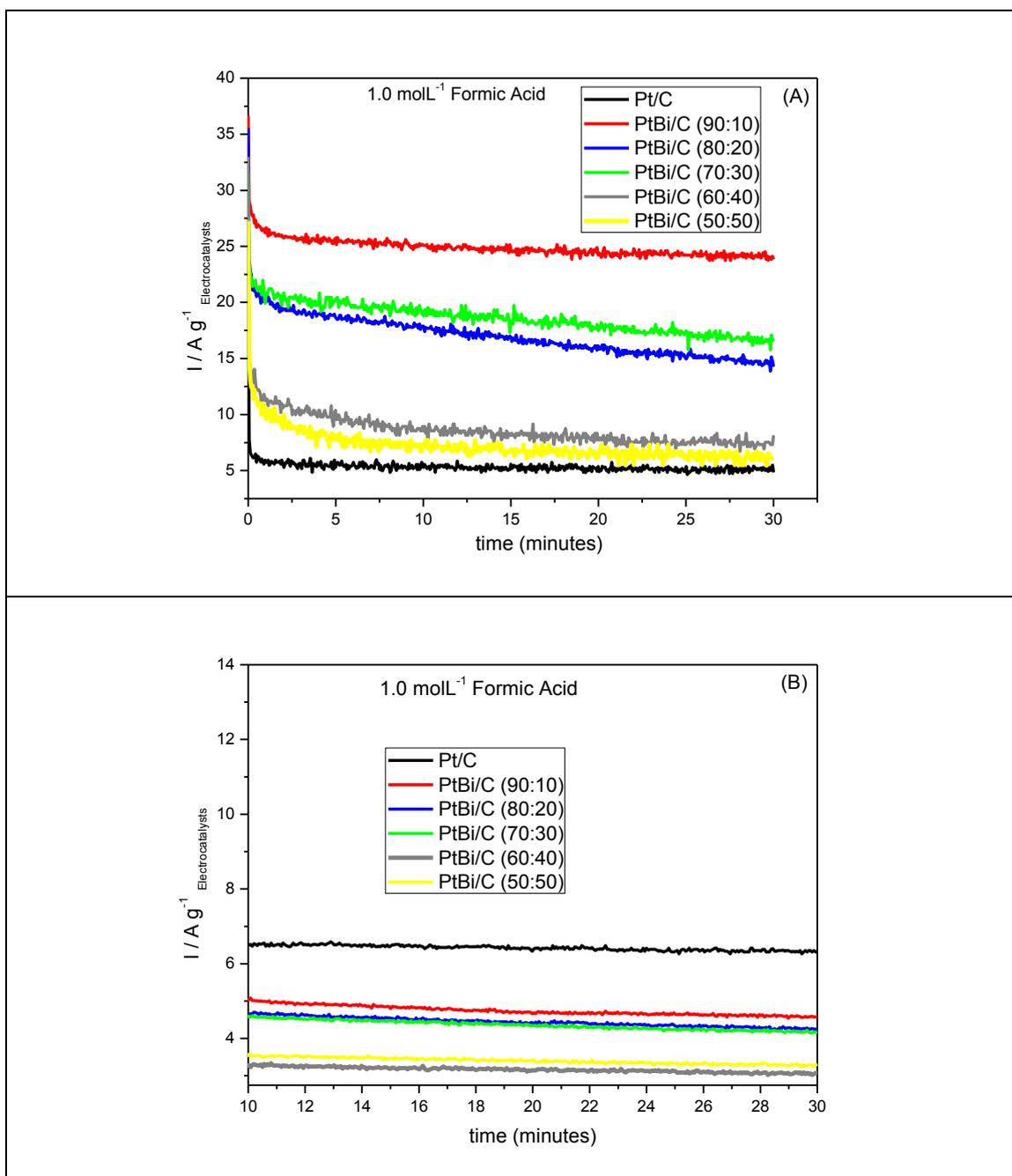**Figure 5.** Current–time curves at 0.5 V in 1 mol L^{-1} for formic acid solution in 0.5 mol L^{-1} H_2SO_4 (a) and current–time curves at -0.3 V for 30 min for formic acidic in 1.0 mol L-1 KOH for Pt/C and PtBi/Celectrocatalysts at 25 °C.

Figure 5a shows the current–time curves for formic acidic electro-oxidation for Pt/C and PtBi/C electrocatalysts at 25 °C in the potential of 0.5 V for 30 min, while the Figure 5b shows the current–time curves for formic acidic electro-oxidation for Pt/C and PtBi/C electrocatalysts in the potential of -0.3 V for 30 min.

The current values at 0.5 V in 1 mol L^{-1} for formic acid solution in 0.5 mol L^{-1} H_2SO_4 showed that PtBi/C (90:10) have higher activity in comparison with others PtBi/C prepared. All PtBi/C prepared showed highest current values in comparison with Pt/C in agreement with cyclic voltammetry experiments. The final current values at 0.5 V (T=25 °C) increase in the following order: PtBi/C (90:10)> PtBi/C (70:30) > PtBi/C (80:20)> PtBi/C (60:40)> PtBi/C (50:50)> Pt/C. All of the catalysts featured a pronounced current decay in the first 2 min due to the accumulation of poisonous intermediates, however the activity of PtBi/C (90:10) was 4.6 times higher than the observed for Pt/C, indicating that the activity and stability of Pt could be significantly improved due to the co-presence of Bi, therefore the electronic modification of Pt by Bi might be the possible reasons for the enhanced activity, as the proximity of Bi oxide species on the Pt surface (bifunctional mechanism).

However in current values at -0.3 V for 30 min for formic acidic in 1.0 mol L^{-1} KOH (electrolyte alkaline) it was observed that Pt/C electrocatalysts had superior performance in comparison with PtBi/C, these results indicated that a presence of Bi did not favor formic acid oxidation in presence of alkaline electrolyte or that optimizations are still necessary for the formic acid oxidation in alkaline media, such as concentration of KOH and formic acid. The final current values at -0.3 V (T=25 °C) increase in the following order: Pt/C>PtBi/C (90:10)>PtBi/C (80:20)= PtBi/C (70:30)> PtBi/C (60:40)= PtBi/C (50:50).

4. CONCLUSIONS

The borohydride reduction method was an efficient process to produce of PtBi/C for formic acid electro-oxidation. PtBi/C electrocatalysts showed a broad peak at about 25º associated with the Vulcan XC72 support and five peaks at approximately 2θ=40°, 47°, 67°, 82° and 87°, which are associated with the (111), (200), (220), (311) and (222) planes, respectively, of the face-centered cubic (fcc) structure characteristic of Pt alloys. For PtBi (70:30), PtBi (60;40) and PtBi (50:50) it was also observed the presence of some peaks that could be attributed to the presence of Bi metalic, Bi oxides species and the presence of a mixture of BiPt or Bi_2Pt phases.

PtBi/C exhibited superior performance for formic acid electro-oxidation in acid media in comparison with Pt/C, where the highest catalytic activity of PtBi/C seems to be related to the combination of the bifunctional mechanism and the electronic effect, while for alkaline electrolyte Pt/C electrocatalysts had superior performance in comparison with PtBi/C, indicating that optimizations are still necessary for formic acid oxidation in alkaline such as concentrations of KOH and also formic acid. Further work is now necessary to investigate the mechanism of formic acid electro-oxidation using these electrocatalysts and a study with different concentration of formic acid for alkaline electrolyte.

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