

Pd-Based Electrocatalysts Prepared by Borohydride Reduction Method for Methanol and Ethanol Electro-Oxidation in Alkaline Medium

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Abstract. Pd/C, Au/C, AuBi/C, PdAu/C, PdAuBi/C electrocatalysts (with different atomic ratios and 20 wt% of metal loading) were prepared by borohydride reduction method using a water/2-propanol mixture as solvent, Pd(NO₃)₂.2H₂O, HAuCl₄.3H₂O and Bi(NO₃)₃.5H₂O as metal sources, carbon black Vulcan XC72 as support and NaBH₄ as reducing agent. The activities of the prepared electrocatalysts for methanol and ethanol electro-oxidation in alkaline medium were investigated by chronoamperometry using the thin porous coating technique. Chronoamperometry experiments showed that PdAu/C (Pd: Au atomic ratio of 50:50) has superior activity and stability for methanol and ethanol electro-oxidation compared with other catalysts.

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]. An alternative to methanol is the use of ethanol for DAFC, because it could be produced in large scale from renewable sources and is less toxic than methanol [4-8].

Most part of the studies on carbon-supported anode catalysts for DAFC showed that Pt-based catalysts have superior performance in acid medium [9,10]. The recent advances in the development of anion exchange membranes for application in fuel cells directly fed with liquid fuels have led to an increase in the interest about electrocatalysis in alkaline medium [10-13]. Compared to acidic Direct Alcohol Fuel Cells (DAFC), the alkaline direct alcohol fuel cells (ADAFC) present the follow advantages: (i) The flow of the charge transport from cathode to anode avoids the crossover of alcohol provide from anode to cathode; (ii) the kinetics of alcohol oxidation and oxygen reduction reactions in alkaline medium are faster than in acidic medium; (iii) the fuel cell components practically do not corrode, consequently, low costs materials can be used and a potential greater longevity can be observed; (iv) it allows the use of Pt-free electrocatalysts [11,14].

Studies on the development of Pt-free electrocatalysts for alcohol oxidation have indicated that Pd is a good electrocatalyst for alcohol electro-oxidation in alkaline medium. It was reported that Pd/C presents an electrocatalytic activity higher than that of Pt/C, the onset potential for ethanol oxidation on Pd/C also was shifted to lower potentials compared to that of Pt in alkaline medium and the Pd/C electrocatalysts also shown high stability for alcohol electro-oxidation in alkaline medium [1,15]. Pd-based electrocatalysts are attractive because Pd is at least fifty times more abundant than Pt [16,17]. However, the price of Pd is relatively expensive and therefore Pd loading must be decreased. One effective approach to cost reduction is to reduce the usage of the Pt and Pd catalysts by addition of other metals such as Au [18,19] and Bi [10,12].

In this work, Pd/C, Au/C, AuBi/C (80:20), AuBi/C (95:05), PdAu/C (50:50), PdAu/C (80:20), PdAu/C (95:05), PdAuBi/C (50:45:05), PdAuBi/C (80:10:10) and PdAuBi/C (90:05:05) electrocatalysts were prepared by borohydride reduction method and were tested for methanol and ethanol electro-oxidation in alkaline medium by chronoamperometry using the thin porous coating technique.

Experimental

Pd/C, Au/C, AuBi/C (80:20), AuBi/C (95:05), PdAu/C (50:50), PdAu/C (80:20), PdAu/C (95:05), PdAuBi/C (50:45:05), PdAuBi/C (80:10:10) and PdAuBi/C (90:05:05) electrocatalysts with (20 wt% of metal loading) were prepared by borohydride reduction method as reported in a previous study [20].

The working electrodes were prepared using the thin porous coating technique [20-22]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate. The chronoamperometry experiments were performed in 1.0 mol L⁻¹ KOH solution containing 1.0 mol L⁻¹ of methanol or ethanol saturated with N₂ at room temperature using an AutoLab PGSTAT 30 potentiostat/galvanostat. The cell potential was kept at -0.4 V vs Ag/AgCl electrode (0.5 V vs RHE) and the obtained current values (I) in Amperes were normalized per gram of palladium (A g_{Pd}⁻¹) considering that the adsorption and dehydrogenation of alcohols occurs only in Pd sites.

Results and Discussion

The physicochemical characterizations of the electrocatalysts were described in a previous work where they were tested for ethylene glycol electro-oxidation [20]. Here it is shown the performance of these electrocatalysts for methanol and ethanol electro-oxidation in alkaline medium using chronoamperometry measurements.

The Fig. 1a presents the current-time curves of methanol electro-oxidation on Pd/C, PdAu/C, Au/C, AuBi/C and PdAuBi/C electrocatalysts in alkaline medium. It is possible observe that the Au/C electrocatalyst did not show any electroactivity for methanol electro-oxidation.

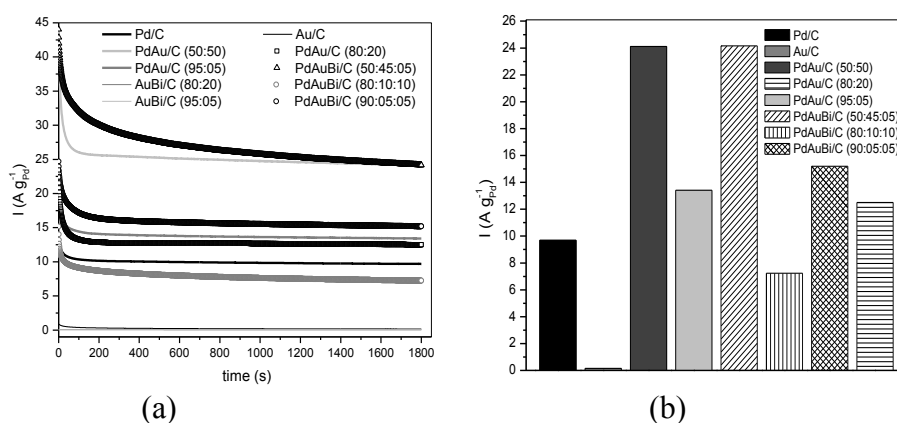


Fig. 1. (a) Chronoamperometry of methanol electro-oxidation on Pd/C, PdAu/C, Au/C, AuBi/C and PdAuBi/C electrocatalysts at -0,4 V versus Ag/AgCl during 30 min at room temperature. (b) Final currents at -0,4 V versus Ag/AgCl after 30 min for methanol electro-oxidation on Pd/C, Au/C, PdAu/C and PdAuBi/C electrocatalysts

According to Tremiliosi et al. [23], the low activity of Au catalyst for ethanol electro-oxidation could not be attributed due its poison. In fact, it was observed that Au catalysts have an inert nature and none deactivating species, like CO, could be formed and adsorbed on the catalytic sites. The ethanol electro-oxidation was only observed for potentials higher than 1.0 V vs RHE [23]. Tateish et al. [24] also described that the ethanol electro-oxidation occurs in high potential region where the surface layer of oxides is not completely formed. Thus, possibly, the potential used in this work (-0,4 V versus Ag/AgCl) can be not sufficiently high to occurs any methanol electro-oxidation on Au, justifying the despicable electroactivity of Au/C electrocatalyst. The addition of Bi to Au/C

electrocatalysts (AuBi/C) practically does not affect the activity. Thus, Pd is essential to obtain a good activity for methanol electro-oxidation in alkaline medium. The addition of Au to Pd/C electrocatalyst (PdAu/C) could increase its activity and a superior performance was observed only with a Pd:Au atomic ratio of 50:50. In this case, a synergistic effect could occur facilitating the dehydrogenation of the methanol molecule and the oxidation of the adsorbed intermediates formed during the reaction. The addition of small quantities of Bi to PdAu/C (Pd:Au:Bi atomic ratios of 50:45:5 and 90:5:5) electrocatalysts could also increase its activity compared to PdAu/C 50:50 and 95:05, respectively. This is more evident for PdAuBi/C with Pd:Au:Bi atomic ratio of 50:45:5 that showed higher current values than PdAu/C (50:50) electrocatalyst in the first minutes (Fig. 1a). On the other hand, after that period a steady decline of current values occurs, which could be associated to a structural change due the redox process of bismuth [20,25,26]. Increasing the quantity of Bi leads to a decrease of activity of PdAuBi/C (80:10:10) electrocatalyst compared to Pd/C and PdAu/C (80:20) electrocatalysts possibly due to the greater coverage of Pd sites by Bi inhibiting the adsorption and, consequently, the dehydrogenation of the methanol [10,20,27,28]. The final current values for methanol electro-oxidation after 1800 s at -0,4 V versus Ag/AgCl electrode (Fig. 1a and b) presented the following order: PdAuBi/C (50:45:05) \approx PdAu/C (50:50) > PdAuBi/C (90:05:05) > PdAu/C (95:05) > PdAu/C (80:20) > Pd/C > PdAuBi/C (80:10:10) > Au/C > AuBi/C (95:05) > AuBi (80:20). The bargraph (Fig. 2b) show clearly that all PdAu/C (50:50) electrocatalysts presented final current values higher than Pd/C and Au/C electrocatalysts.

The current-time curves for ethanol electro-oxidation on Pd/C, PdAu/C, Au/C, AuBi/C and PdAuBi/C electrocatalysts are shown in Fig. 2a.

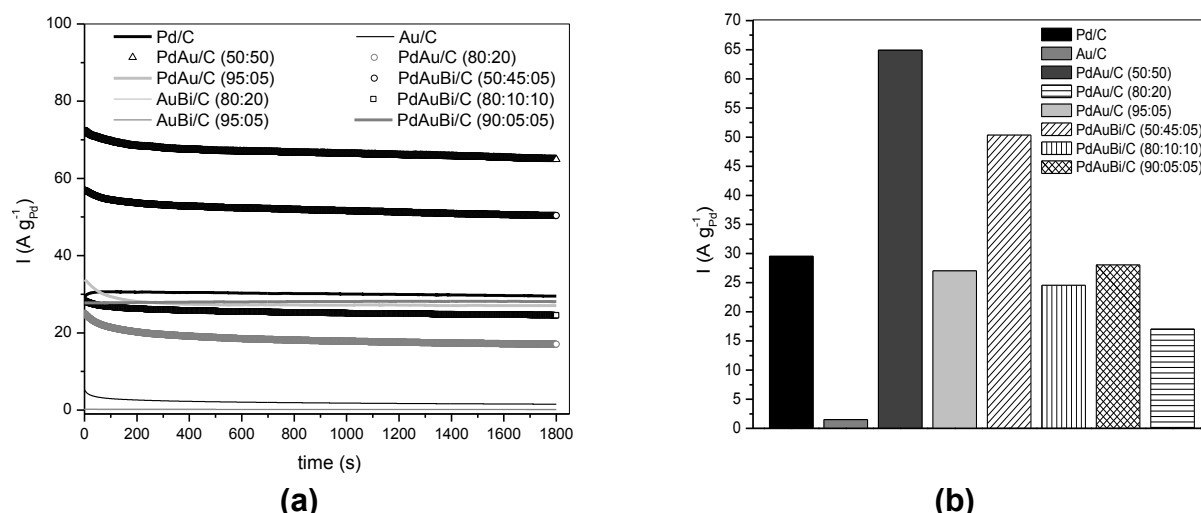


Fig. 2. (a) Chronoamperometry of ethanol electro-oxidation on Pd/C, PdAu/C, Au/C, AuBi/C and PdAuBi/C electrocatalysts at -0,4 V versus Ag/AgCl during 30 min at room temperature. **(b)** Final currents at -0.4 V versus Ag/AgCl after 30 min for ethanol electro-oxidation on Pd/C, Au/C, PdAu/C and PdAuBi/C electrocatalysts.

The current-time curves showed that all electrocatalysts are stable during the 1800 s of operation. The final current values indicate that the electroactivity of the Pd/C electrocatalyst for ethanol electro-oxidation is higher than the ones observed for methanol electro-oxidation. As observed for methanol electro-oxidation, the PdAu/C (50:50) electrocatalyst also showed an increase of activity compared to Pd/C showing that the presence of Pd and Au sites are essential to obtain high current values for ethanol electro-oxidation. In fact, the mechanism of action of Au in Pd-based electrocatalysts is not well understood. An hypothesis is the Pd sites acting as a primary site to the alcohol dehydrogenation, while the Au oxidize the adsorbed intermediates on catalyst surface, releasing the active sites [29,30]. Comparing the activity of the PtAuBi/C electrocatalysts with the PtAu/C electrocatalysts with similar compositions it was observed that the presence of Bi practically does not affect or decrease of activity. The final current values (Fig. 2a and b) after 1800 s of operation at -0,4 V versus Ag/AgCl showed the follow order: PdAu/C (50:50) > PdAuBi/C (50:45:05) > Pd/C > PdAuBi/C (90:05:05) \approx PdAu/C (95:05) > PdAuBi/C (80:10:10) > PdAu/C (80:20) > Au/C > AuBi/C (95:05) > AuBi (80:20).

Conclusions

Au/C and BiAu/C electrocatalysts do not have activity for methanol and ethanol electro-oxidation. The presence of Pd was essential to obtain good activity. The obtained current values of the Pd/C electrocatalyst for ethanol electro-oxidation are higher than the ones observed for methanol electro-oxidation. PdAu/C electrocatalyst with Pd: Au atomic ratio of 50:50 showed a significantly increase of activity for methanol and ethanol electro-oxidation when compared to Pd/C and Au/C electrocatalysts. This probably occurs by the presence of Pd and Au sites facilitating the dehydrogenation of the alcohol molecules and the oxidation of the adsorbed intermediates formed during the reaction. The addition of small quantities of Bi to PdAu/C electrocatalysts practically does not affect the activity.

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