ETHANOL ELECTRO-OXIDATION IN ALKALINE MEDIUM USING Pd/C AND PdRh/C ELECTROCATALYSTS PREPARED BY ELECTRON BEAM IRRADIATION

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ABSTRACT

In this study, carbon-supported Pd (Pd/C) and bimetallic PdRh (Pd:Rh 90:10 atomic ratio) (PdRh/C) electrocatalysts were prepared using electron beam irradiation. The morphology and composition of the obtained materials were characterized by Cyclic voltammetry (VC), Chronoamperometry (CA), Energy dispersive X-ray (EDX), X-ray Diffraction (XRD) and Thermo-gravimetric analysis (TGA). The catalytic activities of the electrocatalysts toward the ethanol electro-oxidation were evaluated in alkaline medium in a single alkaline direct ethanol fuel cell (ADEFC), in a range temperature of 50 to 85 ^{o}C. The best performances were obtained at 85 ^{o}C (25 mW.cm^{-2}) and 75 ^{o}C (38 mW.cm^{-2}) for Pd/C and PdRh/C electrocatalysts, respectively. The XRD of the PdRh/C electrocatalyst showed the presence of Pd-rich (fcc) phase. CV and CA experiments showed that PdRh/C electrocatalyst demonstrated superior activity toward ethanol electro-oxidation at room temperature, compared to Pd/C electrocatalyst.

1. INTRODUCTION

Environmental problems and the world growing demand for energy has mobilized the scientific community to find clean and renewable energy sources. In this context, fuel cells appear as an appropriate technology for generating electricity through alcohols electro-oxidation [1]. Fuel cells employing alcohols directly (direct alcohol fuel cell, DAFC) are attractive as power sources for mobile, stationary and portable applications, since the use of liquid fuels simplifies the fuel delivery system, compared to hydrogen-fed fuel cells [2]. Methanol has been considered the most promising fuel in acid fuel cells, due to the fact that it is more efficiently oxidized than other alcohols; however, a slow anode kinetics is observed and, besides, methanol is also toxic [2]. An alternative to methanol is the use of ethanol for DAFC, because it could be produced in large scale from renewable sources and it is also less toxic than methanol [2]. There are two fuel cells types, acid and alkaline, which use proton exchange membrane and anion exchange membrane, respectively. The problem of catalysis is also important when considering the alcohol electro-oxidation. The ethanol electro-oxidation is more sluggish than methanol electro-oxidation by Pt-based electrocatalysts in

acidic cells [2]. Pd-based electrocatalysts have no activity for alcohol electro-oxidation in acidic solution: nevertheless, their activity towards ethanol electro-oxidation was higher compared to methanol electro-oxidation in alkaline media, indicating improved reaction kinetics of ethanol electro-oxidation [3,4]. In order to improve the activity of these electrocatalysts, a common practice found in the literature consists by replacing part of the metal by another, in search of a synergistic effect that enhances the activity of the whole catalyst. Rhodium is known to activate the C-H bonds and cleavage C-C bonds, necessary for the decomposition of ethanol, a very important stage for fuel cells performance. The combination of these metals may produce a synergistic beneficial effect to ethanol electro-oxidation by improving the selectivity of ethanol electro-oxidation to CO_2 [5,6].

The nature, structure and composition of multi-metallic catalysts have, then, an important effect on the alcohol electro-oxidation, in terms of activity (energy generation) and selectivity. Considering that the chemical and physical characteristics of these electrocatalysts depend on the preparation procedure, this becomes a key factor regarding their electrochemical activity [7]. The carbon-supported metal nanoparticles were prepared for fuel cell applications by radiation-induced reduction of metal ions precursors [8]. In a recent work, Silva et al [9] studied the activity of the electrocatalysts for alcohol oxidation in alkaline medium and showed that PtAu/C electrocatalysts had a better performance for methanol oxidation, compared to other electrocatalysts prepared; on the other hand, PtAuBi/C (50:40:10) demonstrated a superior performance for ethanol oxidation in alkaline medium.

Hence, the aim of this work was to prepare Pd/C and PdRh/C electrocatalysts (Pd:Rh atomic ratio 90:10), using electron beam irradiation. The obtained materials were tested for ethanol electro-oxidation in alkaline medium, using electrochemical techniques at room temperature and in single alkaline direct ethanol fuel cell (ADEFC), from 50 to 85 ^{o}C.


2. EXPERIMENTAL

Pd/C and PdRh/C (90:10) electrocatalysts (20 wt% of metal loading) were prepared using $Pd(NO_3)_2$. $2H_2O$ (Fluka) and $Rh(NO_3)_3$.H_2O- Aldrich Chemical as metal sources, dissolved in water/2-propanol solution 50/50 (v/v). Thereafter Carbon Vulcan® XC72R was added and the mixture was placed in ultrasonic bath to improve the dispersion of the components. 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}, time 3 min). After electron beam irradiation, the mixtures were filtered and the solids (Pd/C and PdRh/C electrocatalysts) were washed with water and dried at 70 ºC for 2 h [9,10].

The Pd:Rh atomic ratio was obtained by energy-dispersive X-ray analysis (EDX) using a Philips XL30 scanning electron microscope with a 20 keV electron beam and provided with EDAX DX-4 microanalyzer. The X-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using CuKα (λ=1.54056 Å). 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 [11]. Thermogravimetric measurement (TG) was recorded with a SETARAM TG/DTA LabSysTM. in nitrogen atmosphere, from 25 up to 800 °C at a heating rate of 10 °C min^{-1}.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [12]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate. The chronoamperometry curves of the Pd/C and PdRh/C (90:10) electrocatalysts were performed holding the cell potential at -0.40 V vs Ag/AgCl electrode (0.50 V vs RHE) in 1.0 mol L^{-1} KOH solution containing 1.0 mol L^{-1} ethanol at room temperature. The membrane electrode assemblies (MEA) were prepared by hot pressing a Fumasep-FAA-PEEK membrane (Fumasep FAA reinforced with PEEK - pretreated in KOH 1.0 mol L^{-1} for 24 h) placed between either a Pd/C or PdRh/C prepared in this work as anode (1 mg Pd.cm^{-2} catalyst loading) and a 20 wt% Pd/C (prepared in this work). The temperature was set between 50 to 85 ºC for the fuel cell and 85 ºC for the oxygen humidifier. Ethanol (2.0 mol L^{-1}) was fed at room temperature.
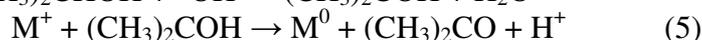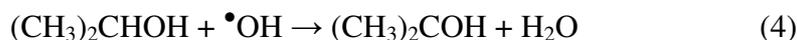
3. RESULTS AND DISCUSSION

Electron beam irradiation of water solution causes the ionization and excitation of water molecules, producing the species shown in Eq. (1) [13]:

$$H_2O + \xrightarrow{\text{Electron beam}} e_{aq}^-; H^+, H^\bullet, H_2, {}^\bullet OH, H_2O_2 \qquad (1)$$
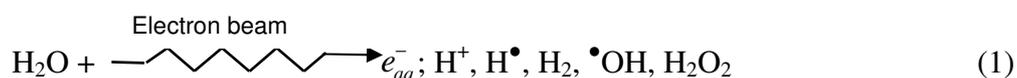
The solvated electrons, e_{aq}^-, and $H^\bullet$ radicals are strong reducing agents and are able to reduce metal ions down to their zero-valent states (Eqs. (2) and (3)):

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

$$M^+ + H^\bullet \rightarrow M^0 + H^+ \qquad (3)$$

However, ${}^\bullet OH$ radicals can oxidize ions or atoms into a higher oxidation state and thus counterbalance reduction reactions (2) and (3). Thus, an ${}^\bullet OH$ radical scavenger, in this case 2-propanol, is added to the above solution and reacts with these radicals, leading to the formation of radicals that are able to reduce metal ions (Eqs. (4) and (5)) [13]:

$$(CH_3)_2CHOH + {}^\bullet OH \rightarrow (CH_3)_2COH + H_2O \qquad (4)$$
$$M^+ + (CH_3)_2COH \rightarrow M^0 + (CH_3)_2CO + H^+ \qquad (5)$$

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

The EDX analysis of PdRh/C electrocatalyst prepared using electron beam irradiation showed that Pd:Rh atomic ratio was very similar to the nominal ones (Table 1). This result suggesting the radiation-induced reduction of metal ions precursors method was efficient.

Table 1: Nominal Pd:Rh atomic ratio, those obtained by EDX and size of PdRh/C electrocatalyst prepared using electron beam irradiation.

Pd:Rh atomic ratio (nominal)	Pd:Rh atomic ratio (EDX)	Crystallite size (nm)
90:10	85:15	3.8

Fig. 1 shows the XRD diffractograms of Pd/C and PdRh/C (90:10) electrocatalysts.
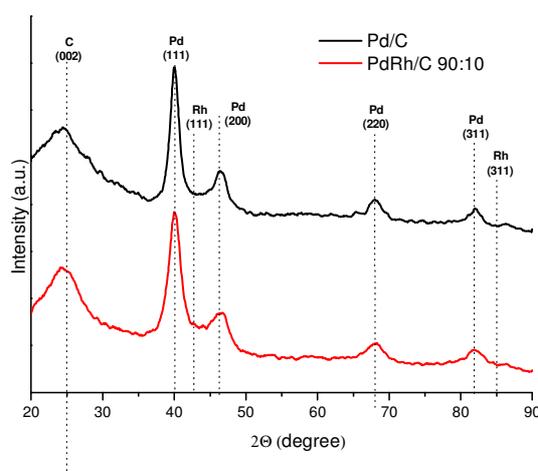
Figure 1: X-ray diffractograms of the Pd/C and PdRh/C (90:10).

In all diffractograms can be clearly seen a broad peak at about 25º associated with the Vulcan XC72R support. Pd/C electrocatalyst showed four diffraction peaks at about 2Θ = 40º, 46º, 68º and 82º that are associated to the (111), (200), (220) and (311) planes, respectively, which are characteristic of the face-centered cubic (fcc) structure of Pd [14,15]. Although EDX analysis confirmed the presence of Rh (Pd:Rh 85:15), no diffraction peaks were observed for Rh suggesting that this element can be inserted in the amorphous phase or in the crystalline structure of Pd, in this case were not observed displacements of the diffraction peaks due to the proximity of diameter atoms - Pd (137 pm) and Rh (134 pm) - and small amount of Rh present in the sample. The materials analyzed showed crystallite sizes, estimated by Scherrer equation, around 3.5 nm.

The EDX results suggest the occurrence of the reduction of ions contained in the solution. This assumption is corroborated by the results of TG analysis (Fig. 2) indicating the beginning of a weight loss profile similar to Pd/C and PdRh/C 90:10 electrocatalyst.
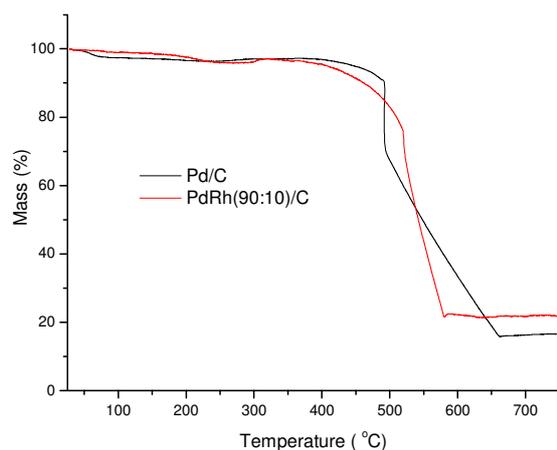
Figure 2: TG curves of Pd/C and PdRh/C 90:10 electrocatalyst.

The thermal stability electrocatalysts was determined by TG, Fig. 2. The results of Pd/C and PdRh/C 90:10 electrocatalyst were similar. There are two decomposition steps: the first one between until 200 °C is attributed to loss of water and the second is attributed to carbon oxidation. The T_{onset} of electrocatalysts was 400 and 370 ºC to Pd/C and PdRh/C 90:10, respectively. Above 600 °C the samples achieves a constant mass and it is corresponding to metal mass percentage contained in electrocatalysts (around 20%).

Fig. 3 shows the CV obtained at room temperature in 1.0 mol L^{-1} KOH, with a scan rate of 10 mV s $^{-1}$ in the presence of 1.0 mol L $^{-1}$ ethanol, referring to the Pd/C and PdRh/C 90:10 electrocatalysts. The CV responses were normalized per gram of metal.
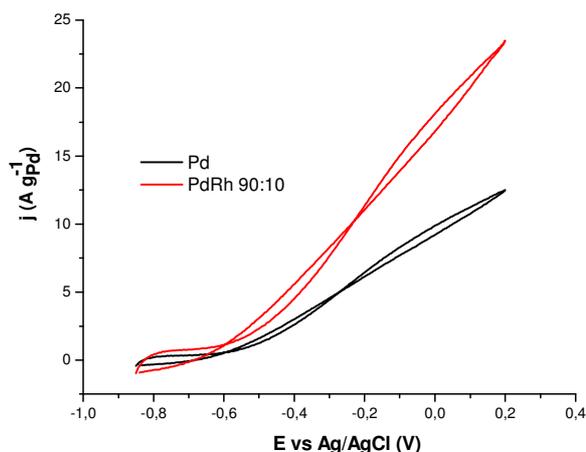

Figure 3: CV of Pd/C and PdRh/C 90:10 electrocatalysts in 1.0 mol L^{-1}, KOH in 1.0 mol L^{-1} ethanol, in a potential range from -0.85 V to 0.20 V *vs*. Ag/AgCl, at a scan rate of 10 mV s^{-1}.

In all voltammograms, the region of hydrogen adsorption/desorption is significantly suppressed by the presence of ethanol. The voltammogram obtained from ethanol electro-oxidation of Pd/C and PdRh/C (90:10) electrocatalysts shows onset potentials at -0.58 and -0.60 V *vs*. Ag/AgCl respectively.

The CV to PdRh/C 90:10 electrocatalyst showed superior performance when compared to Pd/C. This observation is confirmed by chronoamperometry curves at -0.40 V in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} ethanol for Pd/C, PdRh/C (90:10) (Fig. 4).
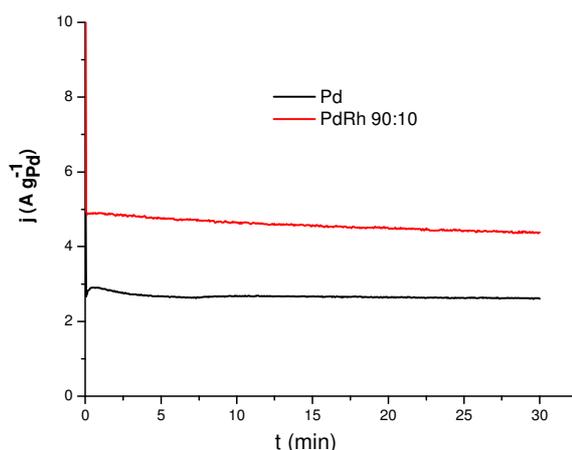

Figure 4. Current–time curves at -0.40 V in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} ethanol for Pd/C, PdRh/C (90:10) electrocatalysts.

The addition of Rh to PdRh/C electrocatalyst enhanced the performance of these electrocatalyst, however the addition of small quantity of Rh (10 at.%) was necessary to obtain good performances.

Fig. 5 displays the single fuel cell performances in the temperature range 50 to 85 ºC of Pd/C and PdRh/C (90:10) electrocatalysts fed with 2.0 mol L^{-1} ethanol in 2.0 mol L^{-1} KOH.
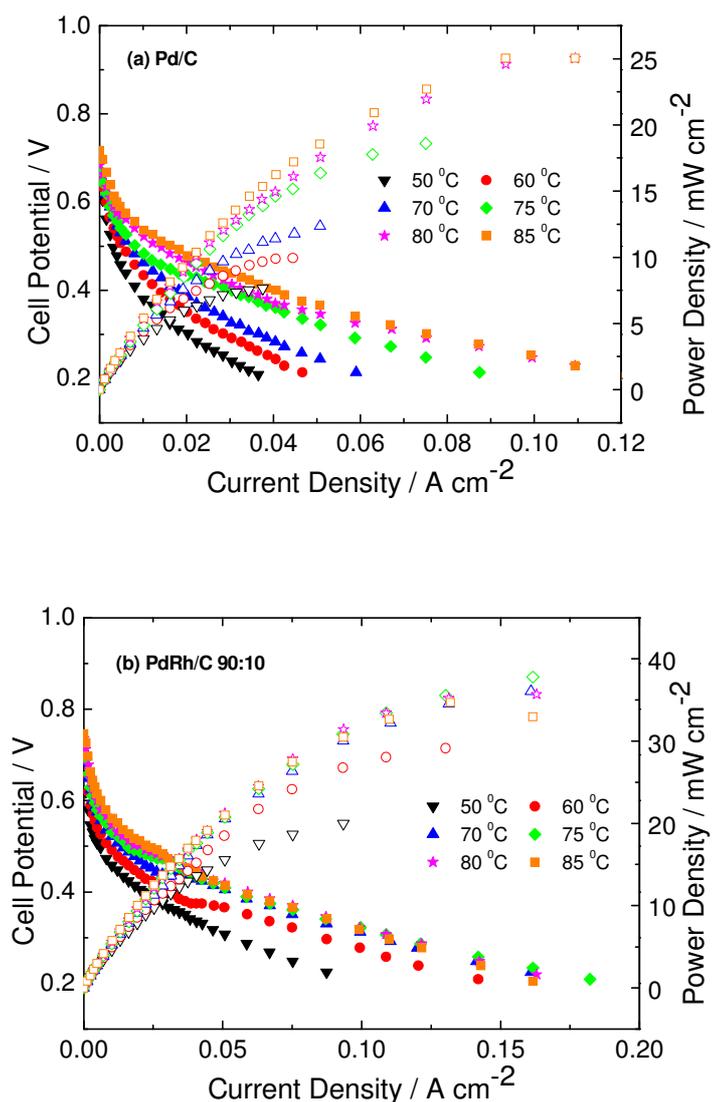
Figure 5: Polarization and power density curves of a 5 cm^2 ADEFC operating from 50 to 85 ºC and using a (a) Pd/C and (b) PdRh/C 90:10 anodic electrocatalyst and Pd/C cathodic electrocatalyst fed with 2.0 mol L^{-1} ethanol in 2.0 mol L^{-1} KOH solution.

The performance of each electrode was significantly improved as temperature increased, indicating that the ethanol electro-oxidation processes are thermally activated. The highest current and power densities were obtained at 85 ºC (25 mW.cm^{-2}) and 75 ºC (38 mW.cm^{-2}) for Pd/C and PdRh/C, respectively (see Table 2).

Table 2: Maximum power density Pd and PdRh/C electrocatalysts achieved at 50 to 85 ºC range.

T_{cell} / °C	Pmax / mW.cm^{-2}	
	Pd/C	PdSn(90:10)/C
50	9	20
60	11	29
70	14	36
75	19	38
80	25	35
85	25	33

The single-cell tests demonstrate that the addition up to 10 parts of Rh into PdRh/C catalyst may promote enhanced the performance of these electrocatalysts. Probably due to the rhodium ability to break the C-C bond more easily [16], making the ethanol electro-oxidation reaction more selective to CO_2. This fact increases the electrocatalytic efficiency whereas the complete ethanol oxidation generates larger number of electrons [7].

4. CONCLUSIONS

The electrocatalysts of Pd/C and PdRh/C 90:10 atomic ratio were prepared. The electron bean irradiation showed to be an effective method for producing active electrocatalysts for ethanol electro-oxidation in alkaline medium. The best operating temperature in ADEFC tests was evaluated to be 85 ºC and 75 ºC for Pd/C and PdRh/C, respectively, toward the ethanol electro-oxidation in Pd-based electrocatalysts. The addition of up to 10% Rh is supposed to improve the activity and stability of binary PdRh/C electrocatalyst; however, it is assumed that the best performance depends on the operating temperature. These results indicate that part of the palladium can be replaced by rhodium, causing an improved ADEFC performance towards ethanol electro-oxidation. The performance enhancement in the catalyst PdRh/C seems to be associated to the facility that Rh has to break the C-C bond more easily. This facility promotes the formation of a large amount of CO_2, improving the activity of PdRh binary electrocatalyst.

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