2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-05-2**

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

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ABSTRACT

Carbon-supported metal nanoparticles were prepared for fuel cell applications by radiation-induced reduction of metal ions precursors. Pd/C and PdSn/C electrocatalysts (Pd:Sn atomic ratio 90:10), prepared by using electron beam irradiation, were tested for glycerol electro-oxidation in single alkaline direct glycerol fuel cell (ADGFC). EDX analysis showed that the Pd:Sn atomic ratio is very similar to the nominal one. X-ray diffractograms of PdSn/C electrocatalyst showed the presence of Pd (fcc) phase. Cyclic voltammetry (CV) indicated that Pd/C and PdSn/C electrocatalysts have good activity for glycerol electro-oxidation, at room temperature. Experiments with single ADGFC were carried out from 60 to 90 ºC, using Pd/C and PdSn/C electrocatalysts and glycerol 2.0 mol.L^{-1}, as fuel. The best performance was obtained at 85 ºC, for both electrocatalysts. The Pd/C and PdSn/C electrocatalysts showed similar performance (34 mW cm^{-2}), at 85 ºC.

1. INTRODUCTION

Fuel Cell has attracted considerable attention over the last decade as a sustainable technology for electricity generation due to their potential for use in mobile, portable and stationary applications [1]. These cells use metallic electrocatalyst for accelerating alcohols oxidation reactions.

In fuel cells employing alcohols directly (direct alcohol fuel cell, DAFC), the interest is greater because the use of liquid fuels simplifies the fuel delivery system, compared to hydrogen-fed fuel cells [2,3]. The use of glycerol, a non valued residue of biodiesel production as fuel may be an interesting alternative, because it is less toxic than methanol and displays relatively lower theoretical energy density, 5.0 kWh kg^{-1}, *versus* 6.1 kWh kg^{-1} for methanol [4].

The problem of catalysis is decisive when considering platinum-free anodic catalysts for the partial oxidation of alcohol, in alkaline medium. Palladium has proved to be an active metal for glycerol electro-oxidation [4,5]. PtSn/C electrocatalysts have been described to be more active for ethanol electro-oxidation in acid medium [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 [3]. The carbon-supported metal nanoparticles were prepared for fuel cell applications by radiation-induced reduction of metal ions precursors [6]. In a recent work, Silva et al [7] 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, while PtAuBi/C (50:40:10) demonstrated a superior performance for ethanol oxidation in alkaline medium.

In this context, the aim of this work was to prepare Pd/C and PdSn/C electrocatalysts (Pd:Sn atomic ratio 90:10), using electron beam irradiation. The obtained materials were tested for glycerol electro-oxidation in alkaline medium, using electrochemical techniques at room temperature and in single alkaline direct glycerol fuel cell (ADGFC), from 60 to 90 ^{o}C.

2. EXPERIMENTAL

Pd/C and PdSn/C (90:10) electrocatalysts (20 wt% of metal loading) were prepared using $Pd(NO_3)_2$. $2H_2O$ (Fluka) and $SnCl_2$. $2H_2O$ (Fluka), as metals 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). 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 PdSn/C electrocatalysts) were washed and dried at 70 ºC for 2 h [7,8].

The Pd:Sn 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 º with step size of 0.05 º and scan time of 2 s per step. The average crystallite size was calculated using Scherrer equation [9].

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [10]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate.

The membrane electrode assemblies (MEA) were prepared by hot pressing using 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 PdSn/C electrodes with 1 mg Pd.cm^{-2} catalyst loading, working as anode, and a 20 wt% Pd/C, wording as cathode. The temperature was set between 60 to 90 ºC for the fuel cell and 85 ºC for the oxygen humidifier. Glycerol (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) [11]:

$$H_2O + \xrightarrow{\text{Electron beam}} e^-_{aq}; H^+, H^\bullet, H_2, {}^\bullet OH, H_2O_2 \quad (1)$$

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)):

$$M^+ + e^-_{aq} \rightarrow M^0 \quad (2)$$

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

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)) [11]:

$$(CH_3)_2CHOH + {}^\bullet OH \rightarrow (CH_3)_2COH + H_2O \quad (4)$$

$$M^+ + (CH_3)_2COH \rightarrow M^0 + (CH_3)_2CO + H^+ \quad (5)$$

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 PdSn/C electrocatalyst prepared using electron beam irradiation showed that Pd:Sn atomic ratio was very similar to the nominal one (Table 1). This result suggests that the radiation-induced reduction of metal ions precursors method was efficient.

Table 1: Nominal Pd:Sn atomic ratio, EDX-obtained atomic ratio and the size of PdSn/C electrocatalyst prepared by electron beam irradiation.

Pd:Sn atomic ratio (nominal)	Pd:Sn atomic ratio (EDX)	Crystallite size (nm)
90:10	86:14	3.8

Fig. 1 shows the XRD diffractograms of Pd/C and PdSn/C (90:10) electrocatalysts.

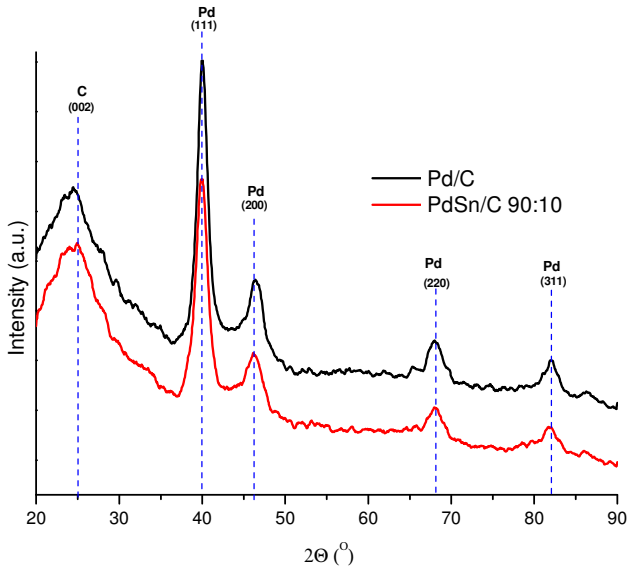


Figure 1: X-ray diffractograms of the Pd/C and PdSn/C (90:10).

A broad peak at about 25º, associated with the Vulcan XC72R support, can be clearly seen in all diffractograms. 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: these peaks are characteristic of the face-centered cubic (fcc) structure of Pd [12,13]. Although the EDX analysis confirmed the presence of tin (Pd:Sn 86:14), no diffraction peaks were observed for the SnO_2 (cassiterite phase), suggesting that element is in the amorphous phase or that it can be inserted in the crystalline structure of Pd. Displacements of the diffraction peaks, due to the proximity of diameter atoms (Pd (137 *p*m) and Sn (140 *p*m)) and/or owing to a small amount of Sn, present in the sample, were not observed either. The materials analyzed showed crystallite sizes, estimated by Scherrer equation, of around 4.0 nm.

Fig. 2 shows TEM micrographs of Pd/C and PdSn/C (90:10) electrocatalysts. The TEM micrographs of Pd/C electrocatalyst showed a wide distribution of nanoparticles over the carbon support and the PdSn/C 90:10 electrocatalyst showed some agglomeration of the nanoparticles on the carbon support.

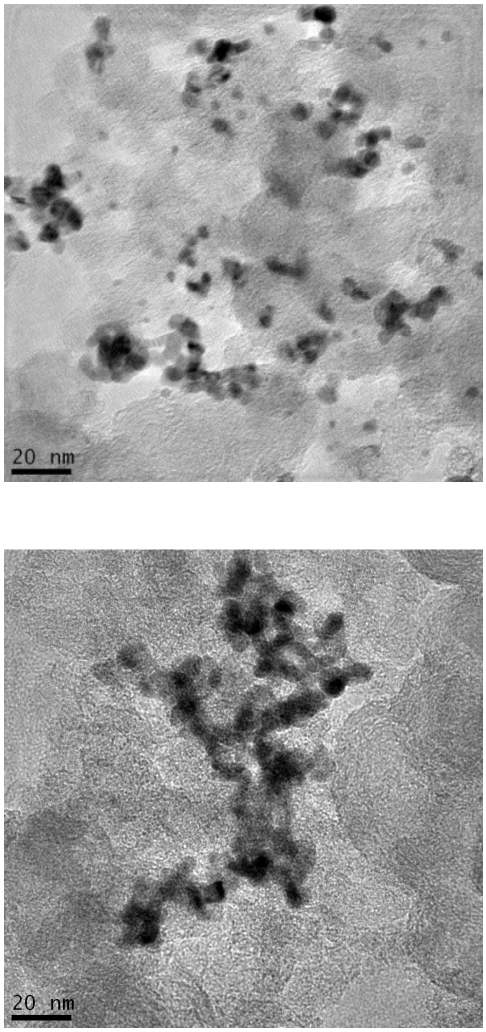


Figure 2: TEM micrographs of (a) Pd/C and (b) PdSn/C (90:10)/C electrocatalysts.

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 glycerol 1.0 mol L^{-1}, referring to the Pd/C and PdSn/C 90:10 electrocatalysts. The CV responses were normalized per gram of metal.

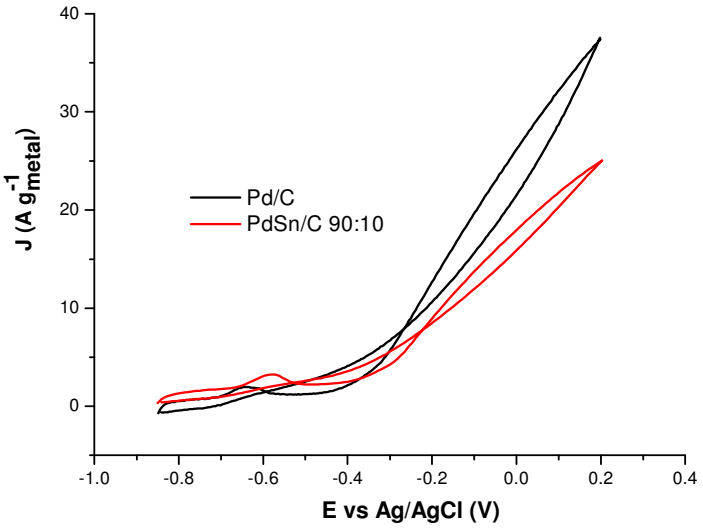


Figure 3: CV of Pd/C and PdSn/C 90:10 electrocatalysts in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} glycerol, in a potential range from -0.85 V to 0.20 V *vs.* Ag/AgCl, at a scan rate of 10 mV s^{-1}.

The voltammograms obtained from glycerol electro-oxidation on Pd/C electrocatalyst shows onset potential, -0.65 V *vs.* Ag/AgCl while the PdSn/C 90:10 electrocatalyst presented onset potential at -0.58 V *vs*. Ag/AgCl. The CV also showed that during the potential scan the maximum currents generated by electrocatalysts were alternated. Above -0.50 V *vs* Ag/AgCl the activity of Pd/C electrocatalyst overcomes PdSn/C electrocatalyst activity. Despite the PdSn/C electrocatalyst begin glycerol oxidation in greatest potential (-0.60 V *vs* Ag/AgCl), in the range between -0.90 V and -0.55 V *vs* Ag/AgCl its activity is higher for Pd/C, although in the interest potential region (-0.30 V *vs* Ag/AgCl) its activity is lower. This fact can be associated with the generation of intermediate having low activity (slow oxidation kinetics), or with strong affinity to Pd, or also may be associated with reduced active surface area of Pd due to the presence of Sn, which though oxophilic it is not acts on glycerol adsorption. The CV results showed that in the potential interest region for fuel cell the PdSn/C 90:10 electrocatalyst showed slightly lower activity than the Pd/C electrocatalyst when prepared by the method described above.

Fig. 4 displays the single fuel cell performances in the temperature range 60 to 90 ºC of Pd/C and PdSn/C (90:10) electrocatalysts fed with 2.0 mol L^{-1} glycerol in 2.0 mol L^{-1} KOH.

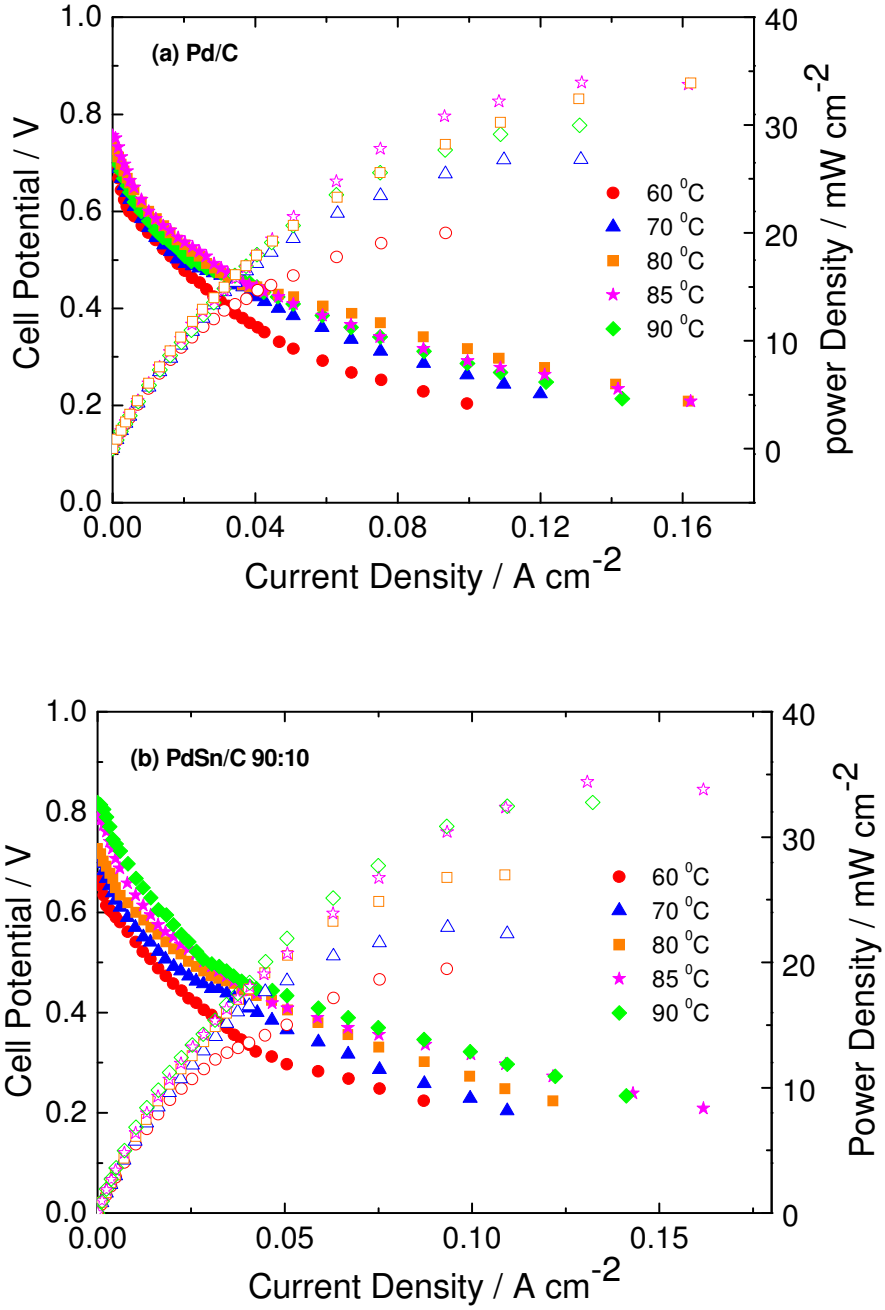


Figure 4: Polarization and power density curves of a 5 cm^2 ADGFC operating from 60 to 90 ºC and using a (a) Pd/C and (b) PdSn/C 90:10 anodic electrocatalyst and a Pd/C cathodic electrocatalyst fed with 2.0 mol L^{-1} glycerol in 2.0 mol L^{-1} KOH solution.

The performance of each electrode was significantly improved as temperature increased, indicating that the glycerol electro-oxidation processes are thermally activated. The highest current and power densities were obtained at 85 ºC. Above this temperature, water

management and membrane dryness began to interfere with electrode performance, most likely due to an increase in cell resistance. At 85 ºC, both of electrocatalysts had similar maximum power densities (see Table 2).

Table 2: Maximum power density Pd and PdSn/C electrocatalysts achieved at 60 to 90 ºC range.

	P_{max} / mW.cm^{-2}	
T_{cell} / °C	Pd/C	PdSn(90:10)/C
60	20	19
70	27	22
80	32	27
85	34	34
90	30	32

The single-cell tests demonstrate that the addition up to 10 parts of Sn into PdSn/C catalyst may promote similar activity to Pd/C for glycerol oxidation, depending on operating temperature.

4. CONCLUSION

Pd/C and PdSn/C 90:10 electrocatalysts were prepared. The electron bean irradiation showed to be an effective method to produce active electrocatalysts for glycerol oxidation in alkaline medium. The best operating temperature in ADGFC tests was found to be 85 ºC, toward the glycerol electro-oxidation in Pd-based electrocatalysts. It is assumed that the best proportion depends on the operation temperature. These results indicate that part of the palladium may be replaced by tin, without compromising the ADGFC performance towards glycerol electro-oxidation. At 85 ºC and in the potential interest for fuel cell applications, the electrocatalysts Pd/C and PdSn/C showed similar activities. The performance of each electrode was significantly improved as temperature increased, indicating that the glycerol electro-oxidation processes are thermally activated.

ACKNOWLEDGMENTS

The authors thank FAPESP (10/16511-6), CNPq (160057/2012-4), INCT Energia e Meio Ambiente (573.783/2008-0) and Capes for the financial support. CTR and CCCH from IPEN/CNEN-SP for electron beam irradiations and single fuel cell measurements.

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