

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

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ABSTRACT

Environmental problems and the world growing demand for energy has mobilized the scientific community in finding of clean and renewable energy sources. In this context, fuel cells appear as appropriate technology for generating electricity through alcohols electro-oxidation. Multi Wall Carbon Nanotubes (MWCNT)-supported Pd and trimetallic PdAuSn (Pd:Au:Sn 50:10:40 atomic ratio) electrocatalysts were prepared using electron beam irradiation. The obtained materials were characterized by VC, Chronoamperometry, EDX, TEM and XRD. The catalytic activities of electrocatalysts toward ethanol electro-oxidation were evaluated in alkaline medium in a single alkaline direct ethanol fuel cell (ADEFC) in a range temperature 60 to 90 °C. The best performances were obtained at 85 °C: 33 mW.cm⁻² and 31 mW.cm⁻² for Pd/ MWCNT and PdAuSn/MWCNT electrocatalysts, respectively. X-ray diffractograms of electrocatalysts showed the presence of Pd-rich (fcc) and Au-rich (fcc) phases. Cyclic voltammetry and chronoamperometry experiments showed that PdAuSn/MWCNT electrocatalyst demonstrated similar activity toward ethanol electro-oxidation at room temperature, compared to electrocatalyst Pd/MWCNT.

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. 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. The fastest kinetic of the alcohol oxidation reaction in alkaline direct alcohol fuel cell (ADAFCS) provides the possibility of using less expensive metal catalysts, such as palladium, tin, silver, and nickel that make the alkaline direct alcohol fuel cells a potentially low-cost technology, compared to acid direct alcohol fuel cells, which employ based-platinum electrocatalysts [5,6]. Another point to be considered for the development of fuel cell technology is the choice of support. The high crystalline status of carbon nanotubes (CNT) makes these materials highly conductive, while the high surface area and the great number of mesopores can lead to high metal dispersion and a good reactant flux in the tubular graphite structure [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, Geraldes et al [9] prepared Pd and PdSn (Pd:Sn atomic ratios of 90:10), supported on Multi Wall Carbon Nanotubes (MWCNT) or Carbon (C). CV analysis finds that Pd/MWCNT and PdSn/MWCNT present onset potentials changing to negative values and high current values, compared to Pd/C and PdSn/C electrocatalysts. In single fuel cell tests, at 85 °C, using 2.0 mol.L⁻¹ ethanol in 2.0 mol.L⁻¹ KOH solutions, the electrocatalysts supported on MWCNT, showed higher power densities, compared to the materials supported on carbon: PdSn/MWCNT presented the best result (36 mW.cm⁻²). The results demonstrated that the use of MWCNT improves the electrocatalytic activity for Ethanol Oxidation Reaction (EOR).

In this context, the aim of this work was to prepare Multi Wall Carbon Nanotubes (MWCNT)-supported Pd and trimetallic PdAuSn (Pd:Au:Sn 50:10:40 atomic ratio) electrocatalysts 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 60 to 90 °C.

2. EXPERIMENTAL

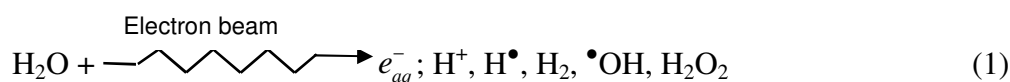
Pd/MWCNT and trimetallic PdAuSn/MWCNT (Pd:Au:Sn 50:10:40 atomic ratio) electrocatalysts (20 wt% of metal loading) were prepared using Pd(NO₃)₂ · 2H₂O (Fluka), SnCl₂ · 2H₂O (Fluka) and HAuCl₄ · 3H₂O (Fluka) as metal sources, dissolved in water/2-propanol solution 50/50 (v/v). Thereafter MWCNT was added 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 were washed with water and dried at 70 °C for 2 h [10,11].

The Pd:Au: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 CuK α ($\lambda=1.54056$ 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 [12]. Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [13]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate. The chronoamperometry curves of 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/MWCNT or PdAuSn/ MWCNT prepared in this work as anode (1 mg catalyst loading) and a 20 wt% Pd/ MWCNT (prepared in this work). The temperature was set between 50 to 85 °C for the fuel cell and 85 °C for the oxygen humidifier. Ethanol (2.0 mol L $^{-1}$) was fed at room temperature.

3. RESULTS AND DISCUSSION

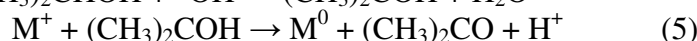
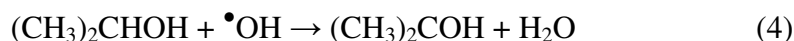
Electron beam irradiation of water solution causes the ionization and excitation of water molecules, producing the species shown in Eq. (1) [14]:



The solvated electrons, e_{aq}^- , and $\text{H}^\bullet$ radicals are strong reducing agents and are able to reduce metal ions down to their zero-valent states (Eqs. (2) and (3)):



However, $\bullet\text{OH}$ radicals can oxidize ions or atoms into a higher oxidation state and thus counterbalance reduction reactions (2) and (3). Thus, an $\bullet\text{OH}$ 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)) [14]:



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 PdAuSn/MWCNT electrocatalyst prepared using electron beam irradiation showed that Pd:Au:Sn atomic ratio was 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:Au:Sn atomic ratio, those obtained by EDX and size of PdAuSn/MWCNT electrocatalyst prepared using electron beam irradiation.

Pd:Au:Sn atomic ratio (nominal)	Pd:Au:Sn atomic ratio (EDX)	Crystallite size (nm)
50:10:40	44:21:35	5.1

Fig. 1 shows the XRD diffractograms of Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts.

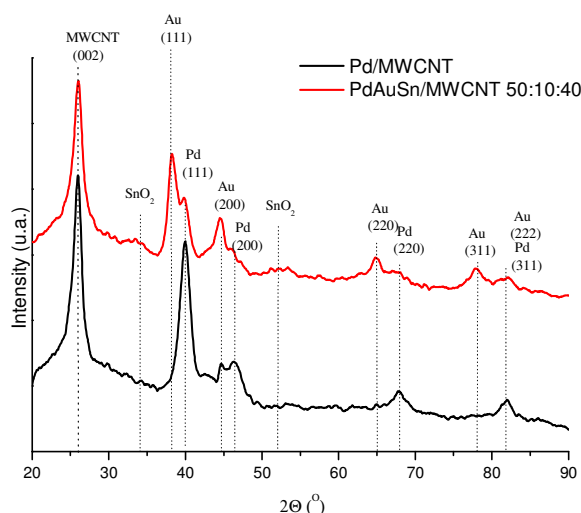


Figure 1: X-ray diffractograms of the Pd/MWCNT and PdAuSn/MWCNT (50:10:40).

The X-ray diffractograms displayed in Fig. 1 showed a broad peak centered at about $2\theta=26^\circ$ (Bragg angle) that was attributed to reflection plane (002) of the hexagonal structure of MWCNT support. The four diffraction peaks related to the Pd are showed at 2θ , approximately, 40° , 46° , 68° and 82° , associated with the reflection planes (111), (200), (220) and (311), respectively, which are characteristic of the face-centered cubic (fcc) structure of Pd [14-17]. Five peaks related to Au were observed at about $2\theta = 38^\circ$, 45° , 65° , 78° and 82° , attributed to the (111), (200), (220), (311) and (222) planes, respectively, which are characteristic of the fcc structure of Au [18]. In the diffractograms the position of the peaks of Pt (fcc) and Au (fcc) are not shifted indicating no alloy formation between them. For PdAuSn/MWCNT electrocatalyst it could be also observed two peaks at about $2\theta = 38^\circ$ and 52° that were attributed to a SnO_2 phase [8,11,19,20]. Our previous study of PtSn/C electrocatalysts prepared by electron beam irradiation reduction [8], showed that Pt exists as Pt(fcc) phase and Sn as an SnO_2 phase, which was identified using ^{119}Sn Mössbauer

spectroscopy. Based on these results, we could infer that Pd (fcc), Au (fcc) and a SnO_2 phase coexist on PdAuSn/MWCNT electrocatalysts.

TEM micrographs of electrocatalysts studied show morphology, particle size and their distribution histograms in Fig. 2.

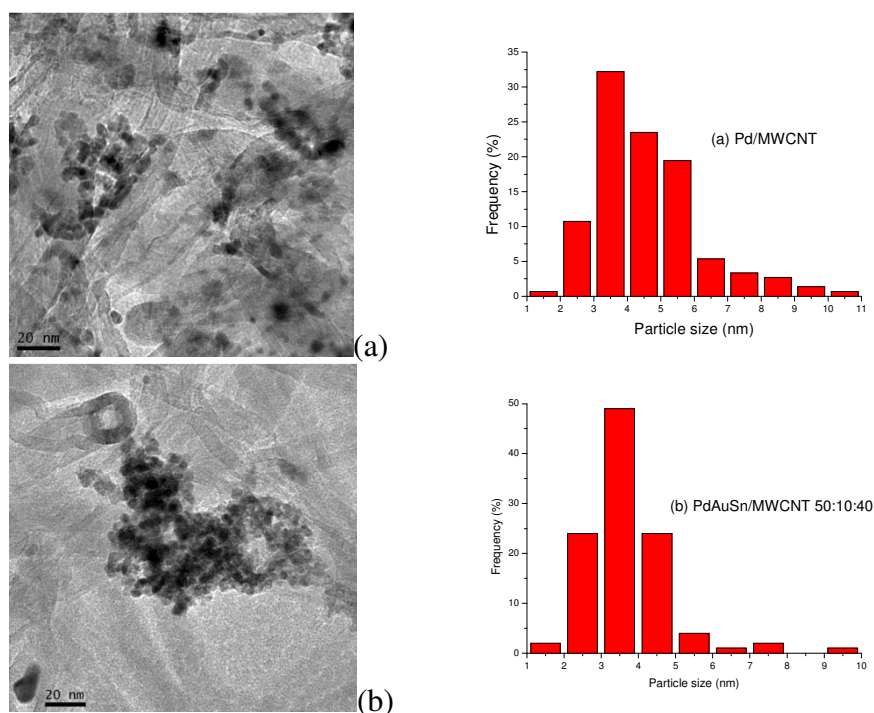


Figure 2: TEM micrographs and particle size distribution histograms of (a) Pd/MWCNT and (b) PdAuSn/MWCNT (50:10:40).

The micrographs of Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts showed few agglomerates. TEM micrographs, also, show that MWCNT-supported electrocatalysts present reduced particle sizes.

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/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts. The CV responses were normalized per gram of metal.

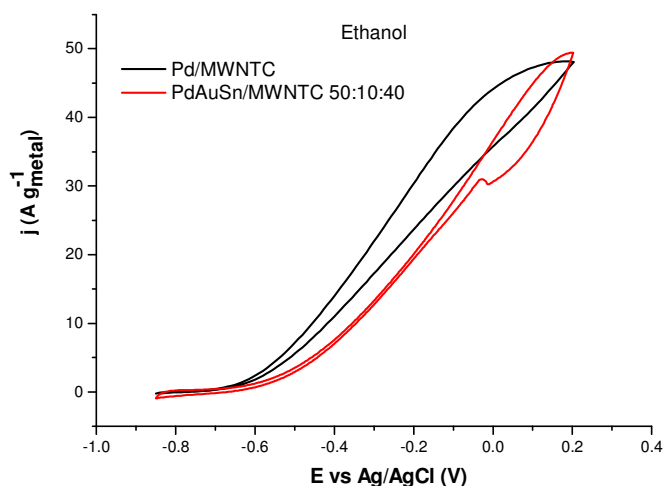


Figure 3: CV of Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts in 1.0 mol L⁻¹, KOH in 1.0 mol L⁻¹ ethanol, in a potential range from -0.85 V to 0.20 V vs. Ag/AgCl, at a scan rate of 10 mV s⁻¹.

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/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts shows onset potentials at -0.69 and -0.66 V vs. Ag/AgCl respectively.

The CV to Pd/MWCNT electrocatalyst showed superior performance when compared to PdAuSn/MWCNT (50:10:40). 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/MWCNT and PdAuSn/MWCNT (50:10:40) (Fig. 4).

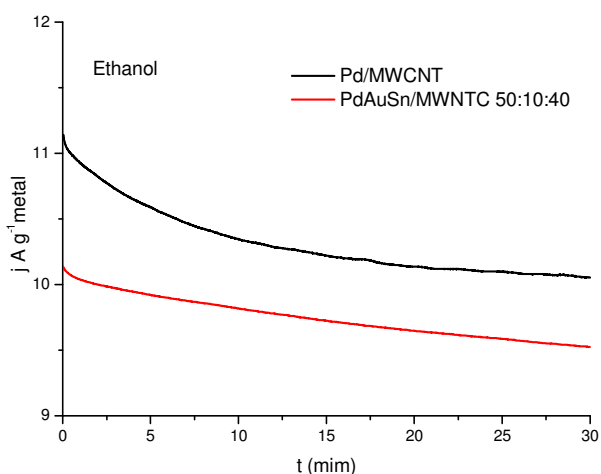


Figure 4. Current–time curves at -0.40 V in 1.0 mol L⁻¹ KOH containing 1.0 mol L⁻¹ ethanol for Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts.

Fig. 5 displays the single fuel cell performances in the temperature range 60 to 90 °C of Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts fed with 2.0 mol L⁻¹ ethanol in 2.0 mol L⁻¹ KOH.

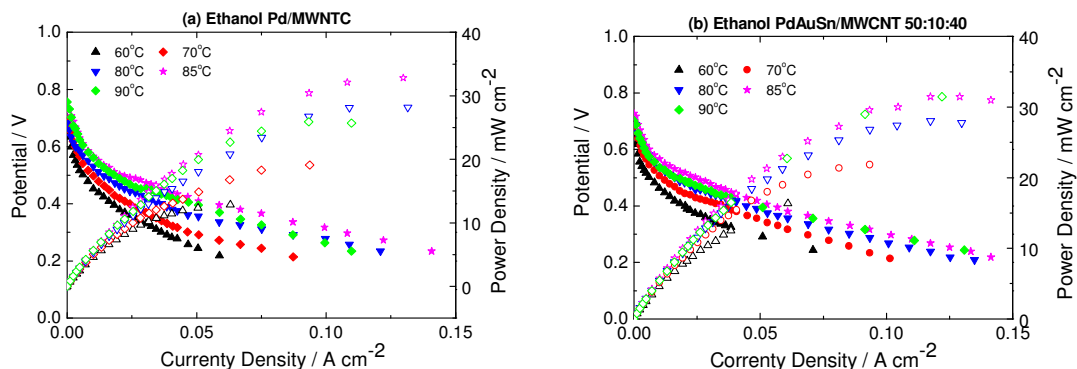


Figure 5: Polarization and power density curves of a 5 cm² ADEFC operating from 60 to 90 °C and using a (a) Pd/MWCNT and (b) PdAuSn/MWCNT (50:10:40) anodic electrocatalyst and Pd/MWCNT cathodic electrocatalyst fed with 2.0 mol L⁻¹ ethanol in 2.0 mol L⁻¹ KOH solution.

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 °C: 33 mW.cm⁻² and 31 mW.cm⁻² for Pd/MWCNT and PdAuSn/MWCNT (50:10:40), respectively (see Table 2).

Table 2: Maximum power density Pd/MWCNT and PdAuSn/MWCNT (50:10:40) electrocatalysts achieved at 60 to 90 °C range.

T _{cell} / °C	P _{max} / mW.cm ⁻²	
	Pd/MWCNT	PdAuSn/MWCNT (50:10:40)
60	13	16
70	19	22
80	28	28
85	33	31
90	26	31

The single-cell tests demonstrate that the addition Au and Sn into PdAuSn/MWCNT catalyst may promote similar performance of this electrocatalyst when compared to Pd/MWCNT. Probably due to the gold and tin ability to break the C-C bond more easily [21], making the ethanol electro-oxidation reaction more selective to CO₂. This fact increases the electrocatalytic efficiency whereas the complete ethanol oxidation generates larger number of electrons [7].

4. CONCLUSIONS

The electrocatalysts of Pd/MWCNT and PdAuSn/MWCNT (50:10:40) atomic ratio were prepared. The electron beam 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 °C toward the ethanol electro-oxidation in Pd-based electrocatalysts. These results indicate that part of the palladium may be replaced by gold and tin, without compromising the ADEFC performance towards ethanol electro-oxidation. At 85 °C and in the potential interest for fuel cell applications, the electrocatalysts Pd/MWCNT and PdAuSn/MWCNT (50:10:40) showed similar activities. The performance of each electrode was significantly improved as temperature increased, indicating that the ethanol electro-oxidation processes are thermally activated.

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