

Pd-based Catalysts for Ethanol Oxidation in Alkaline Electrolyte

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Received September 12, 2014; Revised September 24, 2014; Accepted September 29, 2014

Abstract Direct ethanol fuel cells (DEFCs) have received tremendous attention from academics recently since they can oxidize the liquid ethanol to produce electrical energy efficiently. In this work, five catalysts, which are single, binary, and ternary ones of Pd, Sn, and Ni respectively, are synthesized by the impregnation-reduction method to speed up the reaction kinetics of ethanol oxidation (EOR) in alkaline medium. The crystal structure is investigated by the X-ray diffraction (XRD) technique. The electrochemical performance is evaluated by the cyclic voltammetry (CV) and chronopotentiometry (CA) analyses. The best catalytic performance has been achieved by the bi-catalyst Pd₄₀Ni₆₀/C and the tri-catalyst Pd₄₀Ni₅₀Sn₁₀/C. The reason, for that high performance, could be exemplified that Ni could generate OH⁻ species at lower potentials.

Keywords: ethanol oxidation, Pd catalyst, alkaline electrolyte

Cite This Article: A. M. Sheikh, E. L. Silva, L. Moares, L. M. Antonini, Mohammed Y. Abellah, and C. F. Malfatti, "Pd-based Catalysts for Ethanol Oxidation in Alkaline Electrolyte." *American Journal of Mining and Metallurgy*, vol. 2, no. 4 (2014): 64-69. doi: 10.12691/ajmm-2-4-1.

1. Introduction

Fuel cells are electrochemical devices that could generate electrical energy by oxidation and reduction of the externally supplied fuel and oxidant respectively [1]. One recent system of fuel cells is the direct ethanol fuel cell (DEFCs) in which the liquid ethanol is supplied into the anode. There are other liquid alcohols that could be applied directly into the anode such as the traditionally used methanol, formic acid, ethylene glycol and glycerol. DEFCs have received tremendous attention from the academics and researchers for the high potential advantages that ethanol could offer as a fuel for the anodic oxidation [2]. For instance, ethanol is liquid; thus easy of transport and storage unlike the hydrogen fuel and has satisfying energy density [3]. Moreover, ethanol is produced from biomass products (corn and sugar cane), so that is renewable. And compared to methanol, ethanol is not toxic and has lower membrane crossover rate [4]. Unfortunately, however, ethanol oxidation has sluggish reaction kinetics due to the difficult-to-be-cleaved C-C bond in every molecule added to CH₃, and C-O bonds. Thus, there are many intermediate reaction products which are adsorbed strongly on the catalyst surface [5]. Moreover, the complete ethanol oxidation requires 12-electron release [6].

There are two DEFC systems according to the used solution; alkaline and acidic. The acidic ones have been applied extensively between the fuel cell anode and cathode, but the alkaline-electrolyte DEFC has proved

intrinsic advantages as compared to the acidic counterparts: faster reaction kinetics, the non-Pt metal catalyst possibility, better water management, higher degree of freedom in selecting fuels, and no need for fluorinated polymers are some of them [1,7,8].

Especially, the use of non-Pt metal catalyst (like Pd) gives a big advantage for the alkaline-medium DEFC due to the fact that Pt is a noble metal and would increase the cell construction cost highly [1]. Pd in alkaline electrolyte has shown higher activity for ethanol oxidation reaction (EOR) compared to Pt in acidic one as result of high reaction speed in which, the OH⁻ are the active species [5,6]. Moreover, Pd in alkaline electrolyte has been proven to have higher CO tolerance than Pt. CO-poisoning - the attachment of CO molecules into the catalyst surface - reduces the available surface for further fuel oxidation [7]. Thus, Pd-catalysts are currently the best metal alternative to Pt-ones for alcohol oxidation in alkaline solution [9,10].

The surface properties of the catalyst are important consideration for studying catalysis because the reaction takes place on the catalyst surface. Thus there is a vital relation between the activity and surface of the catalyst [9]. There are many research efforts that confirm the good effect of alloying Pd with other elements like Ni, and Sn to increase the catalyst activity. The bi-functional mechanism assumes the second element will form oxygenated species at lower applied potentials, and thus will save O₂ to oxidize CO species to CO₂ and therefore would facilitate the removal of other intermediate products from the catalyst surface. Furthermore, it supposes that, after CO oxidation, there will be more free

Pd-active sites for ethanol adsorption/oxidation. Z. Zhang *et al.* [10] have prepared PdNi catalysts supported on carbon and have found that Ni addition refreshes the Pd active sites and increases the activity. Like Zhang, Yu-Chen Wei *et al.* [9] have shown that PdNi/C has achieved better performance than Pd/C and the further CeO₂ addition has improved the PdNi activity. Moreover, T. Maiyalagan *et al.* [11] have supported PdNi on carbon nanofibers (PdNi/CNF) and concluded that the onset EOR potential for the CNF supported catalyst is 200 mV lower than the carbon-supported one. Moreover, the EOR exchange current density for PdNi/CNF was 4 times higher than that for Pd/C [11].

Preparing bi-PdNi catalyst is still in need for further research, so that the endeavors continue to find better results for developing DEFC performance by using PdNi alloy. Zhen Qi *et al.* have fabricated nanocrystalline Pd₄₀Ni₆₀ by dealloying the ternary Al₇₅Pd₁₀Ni₁₅ alloy [12]. Although they have noticed enhanced amorphous zones and lattice distortions for Pd₄₀Ni₆₀, the Pd₄₀Ni₆₀ catalytic performance was higher than nano-porous Pd for ethanol and methanol oxidation in alkaline solution [12]. C. Qiu *et al.* have found that the electrocatalytic activity of PdNi thin films depends on the composition, structure and surface morphology obtained under different deposition conditions [13]. In addition to Ni, Sn is known as having improving catalytic effect for Pd for ethanol oxidation in alkaline medium because it could form a *ligand* modifying the electronic structure of Pd and by recovering the active sites, it could change the geometric structure [14]. Wenxin Du *et al.* have formed different-composition PdSn/C catalysts and deduced that Pd₈₆Sn₁₄/C achieved the best performance [15]. Furthermore, PdSn/C has been proved more active and stable for EOR than PdRuSn/C in alkaline solution [2]. In this study, R. Modibedi *et al.* have used different ethanol concentrations and found that increasing the concentration up to 3M results in higher current density [2]. A similar conclusion has been drawn by Qinggang He *et al.* [7], although some times the Tafel slopes in this study shows the charge transfer for Pt faster than for Pd, yet the Pd has higher poison tolerance making it more stable [7].

In this work, single, bi-, and tri-catalysts of Pd, Ni, and Sn are synthesized by the impregnation-reduction method to improve the catalytic activity of Pd for ethanol oxidation reaction EOR in alkaline medium. Based on the literature review, it should be obvious the improving effects that Sn and Ni would introduce if alloyed with Pd for the catalyst structure and activity. Besides, adding both Ni and Sn, in a ternary alloy, would have further better results on the catalytic activity.

2. Experimental

2.1. Catalyst Preparation

The impregnation-reduction method was used to synthesize the five catalysts reported in this work. The carbon support is functionalized with nitric acid. The metal loading was 40% in every catalyst. The weights of respective three element precursors (PdCl₂, NiCl₂, and SnCl₂) were first calculated according to their respective weight percentage (Table 1), and then they were mixed in

a solution of ethylene glycol, which is a reducing agent, and deionized water; the percentage of ethylene glycol to deionized water was 75/25 (v/v). Then, the complete solution was dispersed in ultrasonic bath followed by adding the carbon support (0.14 mg) for 30 minutes. The total solution was then agitated in ultrasonic bath for the salts are impregnated. Following, the pH was increased to 12 using a NaOH solution. After that, it was stirred for 3 hours at 130°C followed by washing and centrifuging the catalyst materials. The final step was to dry the catalyst at 80 C.

Table 1. The impregnated weights of metal precursors for respective catalysts

Catalyst	PdCl ₂ (mg)	SnCl ₂ (mg)	NiCl ₂ (mg)
Pd/C	0.156	0.000	0
Pd ₈₆ Sn ₁₄ /C	0.131	0.028	0
Pd ₆₀ Ni ₄₀ /C	0.100	0	0.073
Pd ₄₀ Ni ₆₀ /C	0.085	0	0.093
Pd ₄₀ Ni ₅₀ Sn ₁₀ /C	0.079	0.025	0.072

2.2. Structure Characterization

To characterize the surface structure and the chemical composition of the catalyst, the techniques of X-ray diffraction (XRD) is used. XRD is carried out by a Philips, Brucker-Axe-Simens diffractometer; model D5000, year 1992 with wave length 0.154 nm of a Cu-K α radiation generated at 40 kV and 40 mA and the objective is to find the chemical composition and the characterize the crystal structure of the catalyst.

2.3. Electrochemical Evaluation

The electrochemical activity of the five prepared catalysts was evaluated using the techniques of cyclic voltammetry (CV), and chronopotentiometry (CA). A three-electrode half-cell was prepared used for both the CV and CA experiments. This cell is constituted of the reference electrode (RE), which is a saturated calomel electrode (SCE), the counter electrode (CE), which was a platinum wire, and the working electrode (WE). WE is a graphite disc with an area of 0.29 cm². It was prepared as it follows: 5 mg of the catalyst powder were mixed with 2 mL of ethanol (Merck) and 25 μ L of Nafion (5%, Aldrich). The mixture was ultrasonically suspended to obtain ink slurry. Then, 136 mL of the slurry was spread on the working electrode to form a thin layer. The three-electrode half-cell was used both in the CV and CA analyses and the scan rate was 50 mV/s. The solution concentration, applied in both CV and CA, was 1.0 M ethanol + 1.0 M NaOH.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD diffraction patterns for the five synthesized catalysts by the impregnation-reduction method in this work. It is shown the clear diffraction peaks of *fcc* facets of Pd (111), Pd (200), Pd (220), and Pd (311) are at 40.5°, 46.9°, 68.47°, and 82.43° respectively. From the same figure, it should be clear the largest peak shift noticed from the Pd/C is for Pd₆₈Sn₁₄/C catalysts for which Pd peaks (111), (200), (220), and (311) have been shifted about of 0.6° (Figure 1, right), which means Pd and

Sn have been alloyed together. Also, it is clear from the XRD pattern of Pd₈₆Sn₁₄/C the formation of SnO₂ (101), and (211) peaks at 33.4° and 51.3° respectively. This result agrees with the findings of [2,15]. On the contrary, Q. He *et al.* [7] has noticed intense peaks of Sn (311) and (211) at nearly 42.5° and 75.5° on their catalyst diffractogram Pd_{2.5}Sn/C. About the Ni addition effect on the Pd structure, after adding the smallest Ni amount (40% in Pd₆₀Ni₄₀/C), the new PdNi peaks were closer to the original Pd peaks with a smaller shift (about 0.3° to the left) than that of Pd₈₆Sn₁₄/C ones. Furthermore, with increasing the Ni amount (to 60% in Pd₄₀Ni₆₀/C), the new PdNi peaks get even closer to the original Pd peaks and the shift in this case was even smaller about 0.2° to the left. It is clear also for Pd₆₀Ni₄₀/C and Pd₄₀Ni₆₀/C from XRD (Figure1, left), there are two separate Ni(OH)₂ peaks of (100) and (110) at 34.7° and 60.5°. These two Ni(OH)₂ have been noticed in the study of S. Y. Shen *et al.* [6] and also Z. Zhang *et al.* [10] have noticed them for Pd₁Ni₁/C they synthesized using NaBH₄ reduction. Furthermore, NiO (220) at peak at 60° had been reported [11]. The smaller peak shift and the clear formation of Ni(OH)₂ could be revised to the less homogeneous dispersion among the PdNi nanoparticles, although Pd and Ni form solid solutions in all elemental proportions as it is clear from their phase diagram (Figure 3). This can be declared by the study of Pai-Cheng Su *et al.* [8], who have argued that the degree of Ni and Pd alloying (36) is lower than that of Pd and Au revising this effect to the lower atomic radius difference between Pd and Au (7 pm) than that between Pd and Ni (13 pm). Other studies argue that the weak alloying between Pd and Ni is the result of low-temperature reduction synthesis [5,10] although adding Ni in high proportion to Pt produces very good alloys using similar methods [6]. In case of the ternary catalyst Pd₄₀Ni₅₀Sn₁₀/C, the Pd peaks are positioned nearly in the same diffraction angles of the binary Pd₄₀Ni₆₀/C ones.

Again in this one, the peaks of Ni(OH)₂ (110) and SnO₂(211) are noticed. There is one third peak at nearly 34 that may be revised to Ni(OH)₂ or SnO₂ formation or both of them. Conversely, adding a much greater quantity of Ni does not produce very homogeneous nano-alloy with Pd [6]. However, Pai-Cheng Su *et al.* have alloyed Pd with both Ni and Au with ratio (3:1) and found that for either the binary or the ternary Pd catalyst, the particle size will decrease after adding Ni or/and Au to Pd [8]. In this study they highlighted that the Ni and Au addition to the catalyst may suppress the grain growth of the Pd, and thus the particle size is decreased.

The Scherrer's equation (eq.1) is used to calculate the crystallite sizes for all catalysts. The palladium peak (220) is applied to deduce the crystallite sizes.

$$\tau = \frac{(k\lambda)}{\beta \cos(\theta)} \quad (1)$$

Where τ is the crystallite size nm, λ is the wave length (=0.154 nm for Cu-K α), β is the full width at half-maximum (FWHM) (in radians), k is a constant (0.94 to spherical crystallites) and θ is the diffraction angle. Depending on the XRD results, the interplanar distance d_{hkl} with Miller Indices (hkl) for the diverse catalysts could be estimated according to Bragg's equation (2):

$$n\lambda = 2d_{hkl} \cdot \sin \theta \quad (2)$$

Where, n is the reflection order (1 for first order), λ is the wave length (in nanometers), and θ is the half of 2θ diffraction angle for the different Pd (111), and (220) peaks. Thus, it is possible to calculate the lattice parameter a by equation (3).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

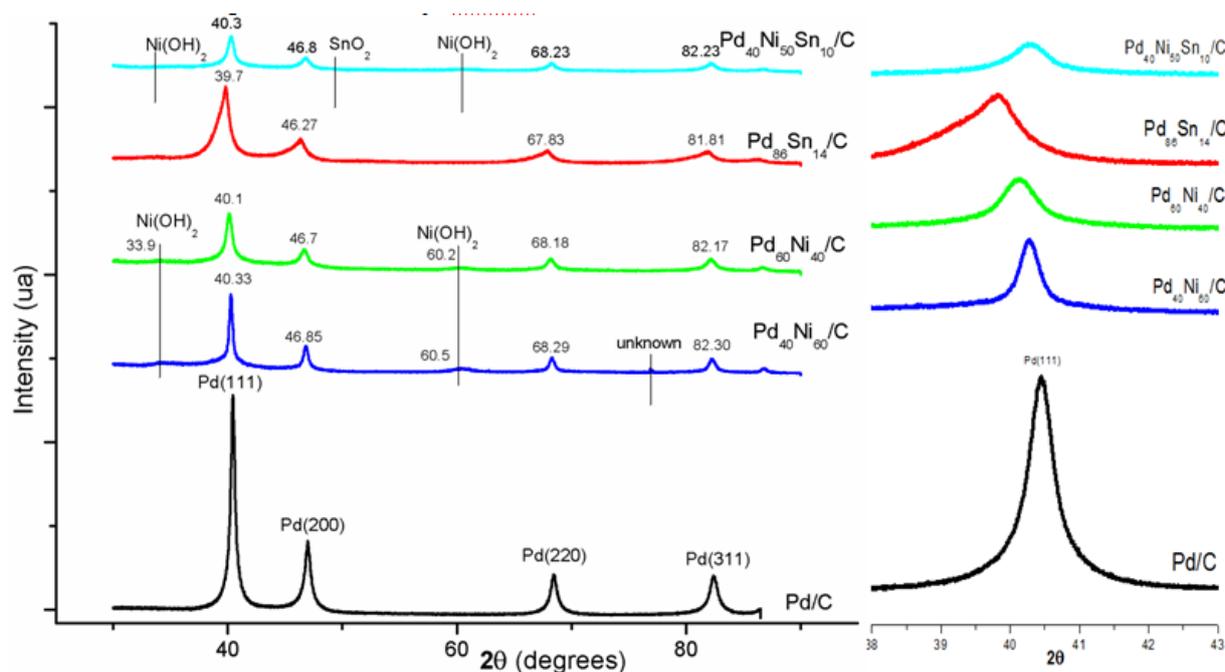


Figure 1. (left) XRD patterns of the prepared catalysts, (right) Enlarged Pd (111) peak

Table (2) shows the obtained crystallite sizes and lattice parameters for the different catalyst. According to this table, the Sn addition (Pd₈₆Sn₁₄/C and Pd₄₀Ni₅₀Sn₁₀/C)

results in increasing the lattice parameter although the inverse conclusion was drawn in ref [2], but more importantly the Sn presence clearly has reduced the Pd

crystallite size from about 13 to 5 nm (Table 2). The study of Q. He *et al.* [7] has ended out, after adding 25% of Sn to Pd/C, the Pd crystal lattice has become orthorhombic system having *Pnma* space group with different lattice constants ($a = 5.65 \text{ \AA}$, $b = 4.31 \text{ \AA}$, and $c = 8.12 \text{ \AA}$). This effect could be explained that the maximum Sn amount, to be added to Pd/C and yet produces solid solution, is 17% as it could be declared from the PdSn phase diagram (Figure 3). The same conclusion about the effect of higher Sn proportion on the Pd crystal lattice (orthorhombic one) was confirmed by the study of W. Du *et al.* [15] after adding 53% of Sn to Pd/C.

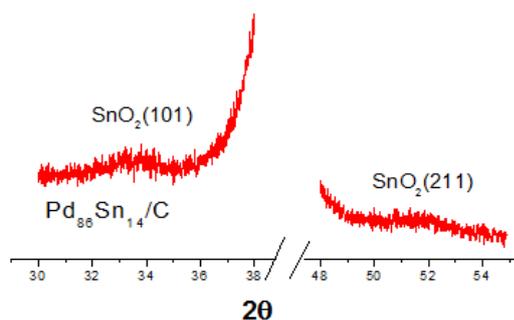


Figure 2. The XRD distinctive peaks for Pd₈₆Sn₁₄/C

Table 2. The XRD data results for the 5 prepared catalysts

Catalyst	τ (nm)	a (\AA)	β°
Pd/C	13,43	3,87	0,77
Pd ₈₆ Sn ₁₄ /C	5,38	3,92	1,75
Pd ₆₀ Ni ₄₀ /C	11,57	3,89	0,84
Pd ₄₀ Ni ₆₀ /C	15,25	3,88	0,57
Pd ₄₀ Ni ₅₀ Sn ₁₀ /C	10,40	3,88	0,94

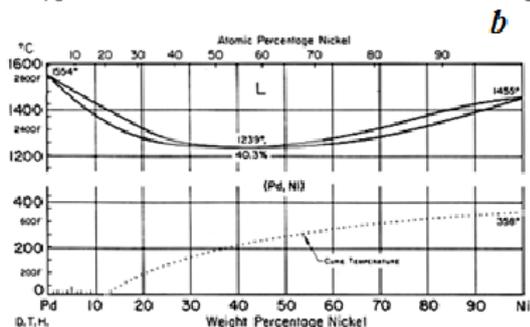
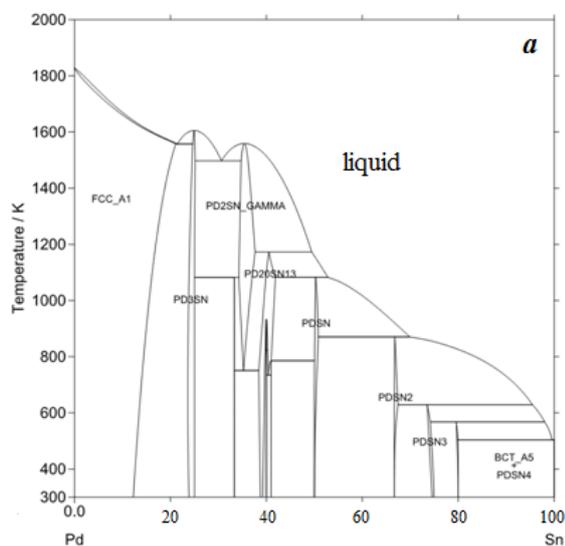


Figure 3. Phase diagrams of (a) Pd-Sn [16], (b) Pd-Ni [17]

On the other hand, the Ni addition (40%) and further Ni (60%) addition have caused the crystallite size to increase which may be explained by the poor alloying degree between Pd and Ni which is the same conclusion of [8]. From table (1) also, it can be observed for both Pd (200) and Pd (220) that the crystallite size of the ternary Pd₄₀Ni₅₀Sn₁₀/C catalyst has decreased less than those of Pd/C and Pd₈₆Sn₁₄/C to go suggest that the 10% Sn addition still plays a key role in formalizing the catalyst structure even though there are 50% of nickel which is expected to increase the crystallite size as what happened with the two binary PdNi/C catalysts. Since there is only one peak noticed for Ni(OH)₂, but not NiO, NiOOH, metallic Ni, it may be assumed that Ni, in the major part, exists in amorphous or little crystalline nature. This conclusion goes with [8].

3.2. Electrochemical Evaluation

The cyclic voltammetry (CV) technique is used to evaluate the electrochemical activity of the variable Pd catalysts. Figure 4 shows the CV performance for the prepared Pd catalysts supported on XC-72 Vulcan carbon. The CV voltamograms show that alloying Pd with other elements can enhance the electrochemical activity for ethanol oxidation in alkaline medium clearly. For instance, in case of Pd/C, the ethanol oxidation reaction (EOR) starts at 500 mV (E_{onset}) and the oxidation current peak is 48 mA, while using any other catalyst, the EOR starts at lower potential, and achieves higher current peak.

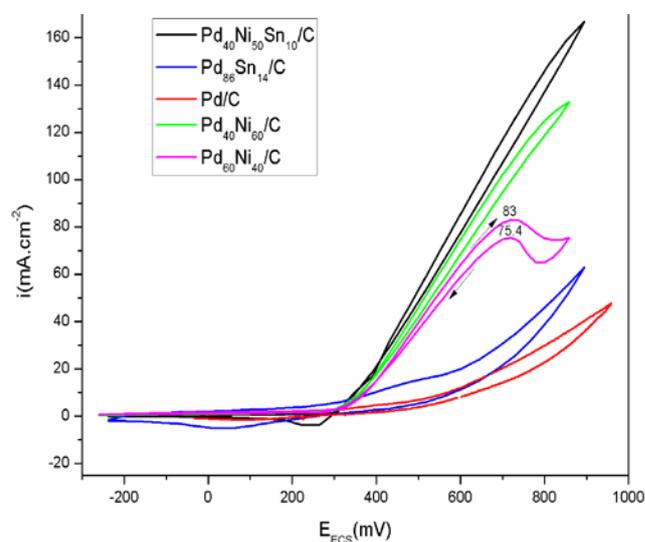


Figure 4. CV voltamograms for EOR for Pd catalysts in 1.0M Ethanol+1.0M NaOH (50 mV/s)

Thus, beneficial effects of adding Ni and Sn could be investigated. For example, adding Sn (Pd₈₆Sn₁₄/C) has decreased the E_{onset} and increased both the i_{peak} and ethanol diffusion in the pores of Pd/C. It is useful to consider the conclusion of Z. Liang *et al.* [5], who explained the CV analysis of Pd/C in 1M KOH + 1M ethanol. The presence of ethanol has led the H₂ peak suppression by the dissociative adsorption of ethanol. It results in the formation of (CH₃CO)_{ads} species at the catalyst surface. They explained that the (CH₃CO)_{ads} have blocked the Pd active sites, but due to the alkaline electrolyte, the OH⁻ species could be generated in lower potentials and facilitate the oxidation of them and thus

increasing the current density. By the further OH⁻ formation (in the forward scan), more Pd active sites are liberated for further ethanol oxidation and thus increasing the current density until it comes to the oxidation current peak at which the oxidation of Pd surface starts. By the further oxidation of Pd surface, the active sites of Pd are blocked and thus reducing the activity until the forward scan ends. Starting the inverse scan, the PdO is reduced, thus the active sites are recovered again and the current density increases.

Table 3. The catalytic activity data of the various catalysts

Catalyst	E _{onset} (mV)	i _{peak} (mA/cm ²)	D (cm ² .s ⁻¹)
Pd/C	500	47,5	3,53*10 ⁻¹⁰
Pd ₈₆ Sn ₁₄ /C	440	62,7	6,15*10 ⁻¹⁰
Pd ₆₀ Ni ₄₀ /C	330	83	1,1*10 ⁻⁹
Pd ₄₀ Ni ₆₀ /C	320	133,1	2,83*10 ⁻⁹
Pd ₄₀ Ni ₅₀ Sn ₁₀ /C	300	166,8	4,41*10 ⁻⁹

On the contrary of Liang findings [5], in this work there is no oxidation peak noticed in the forward scan, but directly after the maximum current value, the inverse scan starts. It means that the present catalyst surfaces are not oxidized during EOR. This is the case of all the catalysts in this study except Pd₆₀Ni₄₀/C which is oxidized partially and then reduced in the inverse scan. Although adding 14% of Sn has improved the Pd/C activity, adding Ni has a more prominent effect in increasing the activity. For example, adding 40% of Ni (Pd₆₀Ni₄₀/C) achieved even lower onset potential (330 mV) than Pd₈₆Sn₁₄/C for ethanol oxidation together with a noticed oxidation current peak, 83 mA/cm². This effect could be explained by the bi-functional mechanism that Ni can perform toward the catalytic Pd performance. According to [8], The Ni is capable to generate OH_{ads} at lower potentials to oxidize CO-like species into CO₂. Furthermore, with increasing the Ni content to 60% (Pd₄₀Ni₆₀/C), the catalytic performance was even developed with E_{onset} of 320 mV and the maximum current density was 133 mA.cm⁻². Thus, according to Figure 4 and Table 3, also the coefficient of diffusion has been sharpened more than Pd/C and Pd₈₆Sn₁₄/C. These promotional effects of Ni could be revised to its capacity to generate OH⁻ in lower potentials and thus help recover the Pd active sites by facilitating the oxidation of intermediate products [8,6,10,11,13].

Equation (4) is applied to evaluate the ethanol diffusion coefficient D (cm².s⁻¹).

$$D = \frac{I_{peak}}{\sqrt{(2.69 \times 10^5) n^{3/2} A \mu^{1/2} c}} \quad (4) \quad [18]$$

Where *D* is diffusion coefficient (cm².s⁻¹), *I_{peak}* is the peak current from CV graphs (A), *n* is number of electrons, *A*=surface area = 0.29 cm² in this study, *μ*= scan rate mV/s, and *C*= solution concentration (mol.cm⁻³). Thus, according to Figure 4 and Table 3, a catalytic comparison could be made among the five catalysts through the peak current density (i_{peak}), oxidation onset potential (E_{onset}) and the coefficient of diffusion (D cm².s⁻¹), which was calculated according to eq. 4 [18].

P.-Cheng Su *et al.* [8] have argued that the abundant surface Ni may block the Pd sites but is beneficial for catalyst stability through the bi-functional mechanism. In this work, being used the ethylene glycol as a reducing

agent has the same role noticed for NaBH₄ which can reduce PdO, and thus OH adsorption on Pd surface leads to the strip away the carbonaceous species and increases the current [8].

Having seen the developing effects of Ni and Sn if added into Pd/C to increase its activity for EOR in alkaline medium, it was sought to sharpen the activity by combining Pd, Ni, and Sn in one ternary catalyst. It was necessary for the Sn proportion to be small (less than 14%), but the Ni one is better to be high (50% or more). So that the nominal proportions of tri-catalyst were 40% Pd, 50% Ni, and Sn 10%. It is clear also for this ternary alloy catalyst that it has achieved the best catalytic activity proven by the least E_{onset} and the highest current peak (Figure 4). Furthermore, while using this catalyst, it was maintained the highest contact between ethanol and the Pd active sites which is based on the highest diffusion coefficient *D* (Table 3).

The chronopotentiometry test results are shown in Figure 5. It is obvious that Pd has zero activity for EOR if applied in acidic medium (red) while if the electrolyte is alkaline (black) the EOR activity is raised considerably. Furthermore, the 14% Sn addition (green) has improved the Pd stability sharply than Pd/C. The catalytic activity improvement continues with the addition of Ni (both 40 and 60%). Yet, while the current density achieved by the Ni-containing catalyst is higher than the rest of catalysts, there is a continuous fluctuation of the values up and down which may be revised the weak alloying degree between Pd and Ni on the catalyst surface.

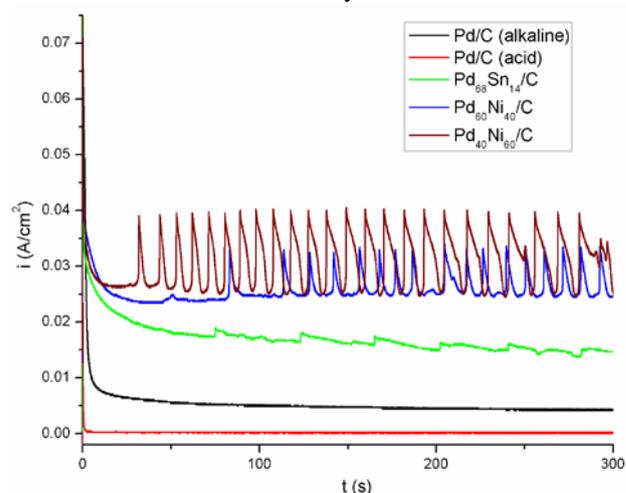


Figure 5. The CA results for the single and binary prepared catalysts in 1.0M EtOH + 1.0M NaOH (300 mV)

Unlike the binary catalysts, the time implemented for CA test in case of the tri catalysts was 1 hr (Figure 6). This time elongation was motivated by the conclusion of [8] who have argued that the ternary catalyst has shown low catalytic activity compared to the binary counterparts. However, when they applied long-term CA analysis they noted an obvious enhancement of the activity and they have revised it to the liberation of Pd active sites after intermediate product oxidation. On the other side, this conclusion is reinforced in this work since the catalytic activity of tri-catalyst is lower than the binary ones both in the onset of the analysis and it continues to be lower after long time.

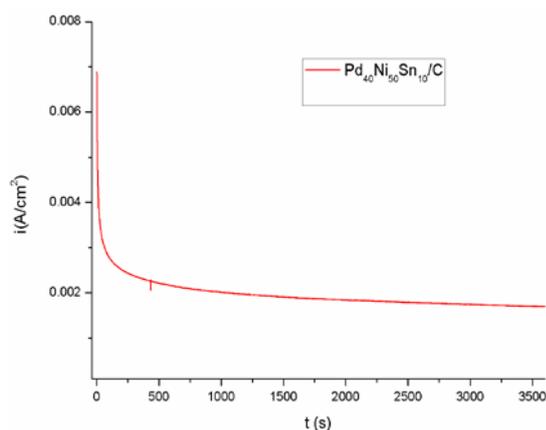


Figure 6. CA test result for the ternary catalyst Pd₄₀Ni₅₀Sn₁₀/C in 1.0M NaOH + 1.0M EtOH (300 mV)

It should be obvious from the CV and CA results that the best catalytic performance would result from the binary catalyst Pd₄₀Ni₆₀/C, which achieved the highest current density in the CA experiments. On the side, the ternary alloy, regardless of having the highest current densities in the CV experiments have very low current in CA analysis.

4. Conclusion

In this work, the impregnation-reduction technique was used to synthesize single, bi-, and tri-catalysts from Pd, Ni, and Sn for ethanol oxidation reaction EOR in alkaline-medium DEFC. Ni has enhanced the catalytic activity highly of Pd for EOR as it could generate OH⁻ species at lower potentials. Yet, the Ni does not have good alloying degree with Pd. On the other side, adding a small amount of Sn will result in a good alloy formation between Pd and Sn, and moreover, will develop the catalytic activity for EOR though less than Ni. Combining the three elements in one tri-catalyst, however, did not result in producing a well-dispersed alloy structure though there are not strange peaks noticed from XRD. Furthermore, the tri-catalyst has shown a slightly less onset potential for EOR than the Pd₄₀Ni₆₀/C which means the catalytic performance is improved by alloying the three elements.

Acknowledgements

The authors are grateful for the financial support of the agency Brazilian Government entity focused in human resources formation, (CAPES) for this work.

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