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Employing iron and nickel to enhance ethanol oxidation of Pd-based anodes in alkaline medium

T.S. Almeida^{a,b,c}, Y. Yu^b, A.R. de Andrade^{c*}, H.D. Abruña^b

^{*a*} Departament of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850,USA.

^b Universidade Federal do Triângulo Mineiro, *Campus* Universitário de Iturama. Iturama, MG, 38280-000, Brazil

^c Departamento de Química, Faculdade de Filosofia Ciências e Letras de Ribeirão Preto,

Universidade de São Paulo, Ribeirão Preto, SP, 14040-901, Brazil

*Corresponding author: A. R. de Andrade (ardandra@ffclrp.usp.br)

Abstract: We report the addition of Fe or Ni to Pd:M electrocatalysts supported on Vulcan carbon XC-72 with 20 wt.% metal loading to activate ethanol electrooxidation reaction in alkaline medium. Experimental bulk compositions of nanoparticles were very close to the nominal one. All the catalysts display the fcc crystalline structure of palladium with crystallite sizes ranging from 2.5 nm to 5.4 nm. Electrochemical tests in the presence of ethanol shows that the addition of Fe and Ni to Pd catalysts enhances ethanol electrooxidation. Ni-containing compositions such as Pd(56)Ni(44) and Pd(71)Ni(29) exhibit excellent catalytic mass activity (30 A g_{Pd}^{-1}) at 0.5 V vs. RHE showing that they are promising anode electrocatalysts for direct ethanol alkaline fuel cells.

Keywords: Electrocatalysis, ethanol oxidation, Pd-based catalyst, iron and nickel

1. Introduction

Ethanol is an attractive potential fuel for low-temperature fuel cell systems [1] due to its high theoretical energy density and production from biomass. However, it is a difficult to release all 12 electrons from the ethanol molecule in order to achieve its full energy density [2]. During the past years many researchers have investigated ethanol electrooxidation in acidic media using the proton exchange membrane fuel cell (PEM-FC) with different Pt-based materials as catalysts [3-6]. Also, a number of techniques have been employed in an attempt to understand the phenomena occurring at the interface and the electrooxidation mechanism. These include Fourier transform infrared spectroscopy (FTIR) [7-8], differential electrochemical mass spectrometry (DEMS) [9,10], and high performance liquid chromatography (HPLC) [11,12]. So far, these techniques have shown that ethanol electrooxidation affords acetaldehyde and acetic acid as the major products, releasing between two and four electrons, respectively.

Scientists have gathered significant information about the phenomena occurring at the electrode/solution interface and the reaction mechanism during ethanol electrooxidation in acidic media. However, this same reaction still had been less investigated in alkaline media due to difficulties inherent to alkaline fuel cells [13].

From a thermodynamic point of view, the alkaline exchange membrane direct ethanol fuel cell (AEM-DEFC) system offers numerous advantages: (1) It presents a global reaction potential of 1.24 V, which corresponds to a gain of 100 mV when compared with the proton exchange membrane direct ethanol fuel cell (PEM-DEFC), reaction potential of 1.14V. (2) In addition electrocatalytic reactions in alkaline media can be more efficient than in acidic media [14]. (3) At an anion exchange membrane (AEM), the OH⁻ species that conducts ions in the system, presents a reverse ionic flow

and corresponding electroosmotic flow; i.e., from the cathode side to the anode side, largely inhibiting ethanol crossover [15].

Ethanol electrooxidation in alkaline media opens the possibility of using new catalytic materials and lower the production cost of noble-based catalysts. The use of alkaline electrolytes is of interest because alcohol oxidation generally does not strongly depend on catalyst composition in this medium, enabling the use of non-platinum based materials, such as Pd, Ag, Ni, and perovskite-type oxides [16-19]. While most of the Ptbased catalysts used in acidic media could find application in alkaline media, Pd displays the best performance due its higher oxophilicity and relatively inert nature [20]. Among Pd-based catalysts, PdFe and PdNi perform well in ORR [21-23] and could catalyze alcohol electrooxidation in alkaline media. Shen and Xu [18,24] studied the oxidation of alcohols such as methanol, ethanol, glycerol, and ethylene glycol on Pdbased catalysts containing Ce, Ni, Mn, or Co oxides and showed that transition metal oxides affect the activity of the catalyst. These authors observed that the Pd-NiO/C catalyst presented the highest catalytic activity and the lowest rate of poisoning by intermediates, because -OH_{ads} species could be readily generated on the oxide surface. Indeed, the generation of OH_{ads} species at lower potentials can convert CO-like poisoning species on Pt and Pd to CO₂ or other products that dissolve in water, liberating the Pt and Pd active sites for further electrochemical reaction. Fe₃O₄ also improved the catalytic performance of Pt and Pd based materials towards organic reactions [25].

In this context, we report how the addition of different amounts of Fe and Ni to a Pd/C catalyst enhances ethanol electrooxidation activity.

2. Experimental

2.1 Catalyst Preparation

Pd and Pd-M (M = Fe or Ni) containing 50, 30 or 10 wt. % of M were prepared by the microwave assisted method. 50.0 mg of each catalysts with 20 wt. % metal loading and different Pd:M metal ratios were obtained by mixing a calculated volume of PdCl₂ (Aldrich); NiCl₂.6H₂O (Mallinckrodt) or FeCl₃.6H₂O (Mallinckrodt) aqueous solution 0.05 mol L⁻¹ with 20 mL of ethylene glycol in a 200 mL becker, and the pH was adjusted to 10, dropwise, with 3.0 mol L⁻¹ NaOH. The mixture was stirred in an ultrasonic bath for 10 minutes, followed by the addition of 40.0 mg of Vulcan Carbon XC-72 powder. After was added 80 µL of hydrazine (Aldrich) as reducing agent and the mixture was kept under magnetic stirring for 30 min to obtain a homogeneous suspension. This suspension was placed in a common household microwave oven (Sonny Caroussell R-220 BW, 2450 Hz) operating at a power of 100 W for 5 min. The suspension was centrifuged and washed with water and the resulting solid product was dried in a vacuum oven at 50°C overnight.

2.2 Physical Characterization

Diffraction patterns were acquired on a Rigaku diffractometer operating with Cu K α radiation ($\lambda = 1.5406$ Å) generated at 40 kV and 40 mA. Scans were recorded at 5° min⁻¹ for 2 θ values between 20 and 90°. Particle bulk and surface composition were analyzed by energy dispersive X-ray spectroscopy (EDX) using a Leica microscope Zeiss LEO 440 model SEM coupled to an Oxford 7060 model analyzer and X-ray Photoelectron Spectroscopy (XPS) using Surface Science Instrument SSX-100, respectively. Catalyst morphology was also investigated by electron microscopy imaging using a Schottky-field-emission-gun Tecnai F20 scanning transmission

electron microscope (STEM) operating at 200 keV. The STEM image was acquired with a high angle annular dark field detector (HAADF. Energy dispersive x-ray (EDX) analysis was performed on the F20 using an Oxford detector, at a beam current of about 1 nA; an EDX resolution of 1-5 nm was achieved with this setup. The Pd-L, Fe-K, Ni-K edges were used to represent the EDX mapping or line scan data.

2.3 Electrochemical characterization

The cyclic voltammetric (CV) profile of the catalysts was obtained in N₂-purged 1.0 M NaOH (Mallinckrodt) solution. CVs were acquired on a PAR model 273 potentiostat. A conventional electrochemical cell was employed with a reversible hydrogen electrode (RHE) and a platinum wire as the reference and counter electrodes, respectively. To perform the electrochemical measurements, calculated amount of the catalyst powder were dispersed into a solution (100 μ L) consisting of isopropanol (95 μ L) and Nafion® (5 μ L). The mixture was homogenized in ultrasonic bath for 10 minutes. After homogenization, 10 μ L of the catalysts ink were deposited onto a previously polished glassy carbon disk electrode (0.196 cm²). In all cases, the catalyst layer had a metal loading of 0.1 mg_{Pd} cm⁻². Activity and stability tests were carried out by cyclic voltammetry in the range of +0.05 V to 0.80 V vs. RHE and chronoamperometry in the presence of 1.0 M ethanol in 1.0 M NaOH at 0.5 V vs. RHE.

Electrochemical Active Surface Area (EASA) was determined as described in [48,49] by recording cyclic voltammogram in 1.0 M NaOH in the range of +0.05 V to 1.2V vs RHE and integrating the cathodic peak for Pd(II)-oxide reduction.

3. Results and Discussion

3.1 Physical characterization

EDX analysis yielded the bulk composition of the nanoparticles. Table I summarizes the results for the Pd:M (M= Fe and Ni) catalysts. While the Pd(50)M(50) and Pd(70)M(30) catalysts had experimental molar compositions near their nominal values, Pd(90)M(10) presented much lower Ni (1%) and Fe (3%) percentages. Nevertheless, it should be noted that EDX just provides semi-quantitative data, and sometimes comparing metal compositions can lead to erroneous conclusions.

Catalyst	Lattice Constant (Å)	Crystallite Size (nm) ^a	Particle Size (nm) ^b	Pd:M (EDX)	Pd:M (XPS)
Pd	3.888	3.8	, –	-	-
Pd(90)Fe(10)	3.895	5.4	-	97:03	-
Pd(70)Fe(30)	3.884	2.6	-	71:29	69:31
Pd(50)Fe(50)	3.915	2.5	1.8	59:41	53:47
Pd(90)Ni(10)	3.920	3.1	-	99:01	-
Pd(70)Ni(30)	3.880	2.6	-	71:29	71:29
Pd(50)Ni(50)	3.886	2.8	2.4	56:44	54:46

 Table 1. Physical characteristics of Pd:M/C catalysts

^a from XRD analysis; ^b from TEM analysis

Fig.1 presents the diffraction patterns of the catalysts. We calculated the crystallite size using the Scherrer's equation and using the (220) reflection. We employed equation (1) to obtain the lattice parameter using the (220) reflection as well (Table 1).

$$a = \sqrt{2}\,\lambda/\sin\theta\tag{1}$$

Single Column



Fig. 1. XRD patterns of the carbon supported Pd-based materials prepared by the microwave method. (A) Pd:Fe and (B) Pd:Ni catalysts.

All the compositions displayed the typical face-centered cubic (fcc) structure of Pd (space group Fm-3m) corresponding to the (111), (200), (220), (311), and (222) reflections (PDF Card No.: 04-001-0111) with crystallite sizes around 3.0 nm for the binary compositions. Only Pd(97)Fe(03) presented crystallite size (5.4 nm) larger than pure Pd (3.8 nm). Despite being low, the amounts of Ni and Fe on the Pd(90)M(10)catalysts modified the diffraction patterns (Fig. 1A-B) and caused peaks shift to lower 20 values, resulting in larger apparent lattice parameters than that of pure Pd (3.898 Å) (Table I). Such behavior has been reported before for Pd:M (M = Co, Ni and Fe) catalysts and the increased of the lattice parameter is explained due the addition of the second metal to an interstitial position in the cell eliciting an isotropic expansion [26]. Increasing the molar ratio of the second metal (70:30 and 50:50) displaced 2θ to slightly higher values, yielding smaller lattice parameters when compared with pure Pd. This behavior can be attributed to the atomic radii of Fe (126 pm) and Ni (124 pm), which have smaller atomic radii than Pd (137 pm), so the lattice contracted when a nickel or iron replaced Pd. Particle and crystallite size are equal for the catalysts investigated, the difference observed are within the experimental error (Table 1).

XPS analyses were used to estimate the surface atomic composition and to analyze the electronic structure of the components in the synthesized catalysts. Palladium, carbon oxygen and were the main elements in all cases. We were able to detect iron and nickel only for the compositions containing higher amounts of these metals (30 and 50 at. %). It was not possible to determine the surface compositions of Pd(97)Fe(03) and Pd(99)Ni(01) because the concentration of the second metal on the surface was too low to yield reliable results. Table 1 presents the XPS compositions of the different materials. In the case of nanoparticles of 2-3 nm in diameter, as found in this work, XPS is between bulk and surface technique, so the

same compositions obtained by XPS and EDS only suggest that there is no great inhomogeneity of the compositions between bulk and catalyst surface.

By recording XPS over narrow energy ranges corresponding to the Pd 3d, Fe 2p, and Ni 2p core levels, we obtained the electronic structure of the catalyst particles (Fig. 2). For this analysis, we corrected all the spectra to the carbon 1s peak at a binding energy (BE) of 284.8 eV. Fig. 2A shows a representative spectrum of the Pd 3d core levels obtained from a pure Pd sample. We resolved the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks into three sets of spin-orbit doublets fitted by constraining the 5.2 eV spin-orbit separation. The Pd (3d_{5/2,3/2}) peaks at 335.7 and 340.9 eV corresponded to metallic Pd only, whereas the peaks at 336.7 and 342.1 eV and the peaks at 338.0 and 344.0 in the deconvolved spectrum referred to Pd(3d_{5/2,3/2}) peaks of Pd²⁺ (PdO) and Pd⁴⁺ (PdO₂) species, respectively. The values obtained for Pd metal, and the Pd²⁺ and Pd⁴⁺ species were close to reported values [27]. We detected Pd^{0} , Pd^{2+} , and Pd^{4+} for pure Pd and Pd(97)Fe(03) and Pd(99)Ni(01) compositions. As for the materials containing 30% and 50 at.% of Fe and Ni, only Pd^0 and Pd^{2+} were present in the samples. Hence, increasing the atomic ratio of the second metal inhibited the formation of Pd at higher oxidation states; like Pd^{4+} . Table 2 presents the binding energies for the Pd $3d_{5/2,3/2}$ levels, the palladium species observed on the catalyst surface, and the relative intensity of the species. Metallic Pd is the major specie in all the compositions; the binding energy from the Pd $3d_{5/2,3/2}$ shifts slightly when Ni or Fe is added indicating a possible and moderate electronic effect of these metals over the d-band of palladium induced by the electron transfer between Pd and Ni or Fe [28,29]. Such electronic effect may be responsible to decrease the adsorption strength of the intermediate compounds over Pd catalyst sites speeding up ethanol oxidation [30,31].

Double Column



Fig. 2. Spectra of the core levels of (A) Pd 3d, (B) Fe 2p, (C) Ni 2p of the Pd/C, Pd(59)Fe(41), and Pd(56)Ni(44) catalysts, respectively.

Table 2. Distribution of Pd species in the Pd:M/C catalysts as determined by XPS

		Binding E			
Ċ	Catalyst	Pd Species	Pd 3d 3/2	Pd 3d 5/2	Rel. intensity (%)
		Pd^0	340.9	335.6	65.9
	Pd	Pd^{2+}	342.1	336.6	23.9
		Pd^{4+}	344.0	338.0	10.2
	Pd(97)Fe(03)	Pd^0	341,0	335.7	67.2
		Pd^{2+}	342.2	336.3	26.5
		Pd^{4+}	344.2	338.5	6.3
	Pd(70)Fe(30)	Pd^0	341.2	335.8	78.9
		Pd^{2+}	342.9	337.1	21.1
		Pd^{4+}	-	-	-

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	Pd^0	340.6	335.3	79.3	
Pd(59)Fe(41)	Pd^{2+}	342.2	337.5	20.7	
	Pd^{4+}	-	-	-	
Pd(99)Ni(01)	Pd^0	341.1	335.7	54.2	
	Pd^{2+}	342.2	336.2	32.8	
	Pd^{4+}	343.7	338.7	13.0	
	Pd^0	341.1	335.8	67.0	
Pd(71)Ni(29)	Pd^{2+}	342.3	337.1	33.0	
	Pd^{4+}	-	-	-	
	Pd^0	341.0	335.6	69.7	
Pd(56)Ni(44)	Pd^{2+}	342.1	336.7	30.3	
	Pd^{4+}	-	-	-	

We refined the chemical state of iron in the catalysts using the Fe 2p spectra (Fig. 2B). The XPS spectra can be split in two parts Fe $2p_{3/2}$ and Fe $2p_{1/2}$; where each part consists of a main line and a satellite. The Fe $2p_{3/2}$ main line is located at 711.3 eV with a satellite peak at 716.7 eV; and the Fe $2p_{1/2}$ main line is located at 724.5 eV with a satellite peak at 731.0 eV. The presence of a main line together with a satellite peak results from a ligand-to-metal charge transfer during the photoemission process [32]. This profile allowed us to conclude that the iron on the surface had a +3 formal oxidation state, indicating the presence of Fe₂O₃ [33]. Catalysts containing Ni had the same profile. The Ni 2p_{3/2} and Ni 2p_{1/2} spectrum presented two pairs of prominent peaks at 855.9 and 861.9 eV and 873.7 and 879.9 eV (Fig. 2C). We attributed the peaks at 855.9 and 873.7 eV to NiO and identified the peaks at 861.9 and 879.9 eV as a multielectron excitation satellite peak [34].

As we will discuss later, the Pd(59)Fe(41) and Pd(56)Ni(44) catalysts exhibited the best electrocatalytic activity towards ethanol oxidation. Hence, we analyzed these materials by TEM (Fig. 3 and Fig. 4). The TEM micrograph of Pd(59)Fe(41) (Fig. 3A) revealed well-distributed catalyst nanoparticles on the carbon support and an average particle size of 1.8 ± 0.8 nm (Fig. 3B). Particle distribution maps provided more

information about metal distribution on the nanoparticle (Fig. 3C). Images evidenced regions rich in Fe (green) and Pd (red) indicating segregation of the nanoparticle. Pd(56)Ni(44) also displayed a homogeneous particle distribution on the support, with an average particle size equal to 2.4 ± 0.7 nm (Fig. 4A-B). For EDX analysis, we selected a line through the nanoparticle instead of choosing an area as in the case of Pd(59)Fe(41). We analyzed metal distribution as a function of position (Fig. 4C-D). Both Pd and Ni appeared homogenous distributed on the nanoparticle.



Single Column

Fig. 3. (A) TEM micrograph of the Pd(59)Fe(41)/C catalyst. (B) Particle size distribution (count: 60 nanoparticles) (C) Composition map for Pd and Fe.

Single Column



Fig. 4. (A) TEM micrograph of the Pd(56)Ni(44)/C catalyst. (B) Particles size distribution (count: 116 nanoparticles) (C) and (D) composition of the PdNi nanoparticle.

In summary, TEM indicated the presence of small particles well distributed on the carbon support, but with some aggregates for both Pd(59)Fe(41) and Pd(56)Fe(44). Particle sizes were comparable with those obtained by XRD. The composition map confirmed a good homogenous mixture of the metals (Ni and Fe) with Pd, as suggested by EDX analysis.

3.2 Electrochemical characterization

Figure 5A presents the cyclic voltammograms (CVs) of different Pd:Fe anode catalysts recorded in 1.0 M NaOH over the potential range from +0.05 to +0.8 V vs

RHE. Three peaks were observed during the positive sweep corresponding to different electrochemical processes at the Pd electrode surface. Peak I, between +0.05 and +0.15 V, is ascribed to absorbed and adsorbed hydrogen oxidation [35]:

$$Pd-H_{abs}/_{ads} + OH^{-} \rightarrow Pd + H_2O + e^{-}$$
(3)
$$Pd + OH^{-} \leftrightarrow Pd-OH_{ads} + e^{-}$$
(4)

Peak II, attributed to OH⁻ adsorption (Eq. (4)), appeared in different potential ranges for each Pd:Fe catalyst: between +0.38 and +0.72 V for Pd(59)Fe(41) and Pd(71)Fe(29), and between +0.18 to +0.43V for Pd(97)Fe(03) and Pd. This shift resulted from the high Fe concentration and the presence of Fe₂O₃ in the Pd(59)Fe(41) and Pd(71)Fe(29) compositions, as evidenced by XPS analysis. Therefore, electron transfer from Fe to Pd may have modified the adsorption energy of OH⁻ ions and the concentration of this species on the catalyst surface [25].

Peaks III/III' were ascribed to redox process of Fe [36] and appeared just for Pd(59)Fe(41). PdO formation was not evident since its formation only arises at potentials higher than +0.8 V vs ERH [35].

When Ni was the co-catalyst, the behavior was similar (Fig. 6A). However, contrary to the Pd:Fe compositions, all the Pd:Ni catalysts displayed lower OH adsorption potentials (+0.3V vs RHE). This resulted in the formation of PdO at lower potentials as evidenced by peak IV. Due to high amount of Ni at this composition peak II can be ascribed not only due Pd-OH_{ads} formation (Eq. 4) but also by the transition between Ni and α -Ni(OH)₂ as described by Obradovic et al. [37]. Although XPS analysis indicated the presence of nickel oxides, the transition between Ni and α - $Ni(OH)_2$ is convoluted with the OH⁻ adsorption over Pd (peak II) and makes the voltammetric profile not clear.



double Column

Fig. 5. (A) Cyclic voltammograms of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} at 10 mV s⁻¹; (B) Cyclic voltammograms of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 10 mV s⁻¹; (C) Mass activities of Pd:Fe catalysts from their corresponding current-time curves and (D) Polarization curve of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 0.5 V for 30 min.



double Column

Fig. 6. (A) Cyclic voltammograms of the Pd:Ni catalysts recorded in NaOH 1.0 mol L⁻¹ at 10 mV s⁻¹; (B) Cyclic voltammograms of the Pd:Ni catalysts recorded in NaOH 1.0 mol L⁻¹ + EtOH 1.0 mol L⁻¹ at 10 mV s⁻¹; (C) Mass activities of Pd:Ni catalysts from their corresponding current-time curves and (D) Polarization curve of the Pd:Ni catalysts recorded in NaOH 1.0 mol L⁻¹ + EtOH 1.0 mol L⁻¹ + EtOH 1.0 mol L⁻¹ + EtOH 1.0 mol L⁻¹ at 0.5 V for 30 min.

The Electrochemical Active Surface Area (EASA) was determined by integrating the cathodic peak for PdO reduction when cyclic voltammetry was record at higher potential as 1.2 V vs. RHE. To determine the EASA we take as parameter the charge of 424 μ C per cm⁻², which correspond to the charge of two electrons to reduce the PdO to Pd [38]. The results listed in Table 3 show that the EASA of the catalysts remain between 7.0 to 12.0 m² g_{Pd}⁻¹.

We examined the electrocatalytic activity of Pd:M electrocatalysts for ethanol electrooxidation in alkaline media. Fig. 5B and 6B present the cyclic voltammograms of the Pd:Fe and Pd:Ni catalysts in 1.0 M NaOH and 1.0 M ethanol solution at a sweep

rate of 10 mV s⁻¹ (Table 3). We normalized by the equivalent mass of Pd deposited on the glassy carbon support electrode and by the electrochemical surface-active area (EASA).

Addition of different amounts of Fe to the Pd catalyst did not enhance significantly the ethanol oxidation current values nevertheless; the onset oxidation potential (E_{onset}) is shifted towards lower values when compared with pure Pd (Fig. 5B, inset). The double layer charges increase as a function of the iron content. Pd(59)Fe(41) and Pd(71)Fe(29) exhibited more positive E_{onset} values when compared with Pd(97)Fe(03). The addition of increasing amounts of Ni enhanced the ethanol electrooxidation current (Fig. 6B). The only exception was Pd(99)Ni(01), which was less active than pure Pd. Regarding E_{onset} , Pd(99)Ni(01) presented the most positive value, which resulted in its lower activity toward ethanol oxidation. The E_{onset} of the other catalysts shifted negatively (by 50 mV) when compared with pure Pd (+0.30 V).

 Table 3. Initial onset potential and catalytic activity for ethanol oxidation on Pd:M

 catalysts

Catalyst	$\frac{\text{EASA}}{(\text{m}^2 \text{g}_{\text{Pd}}^{-1})}$	E _{onset} (V vs RHE)	Mass Activity (A g_{Pd}^{-1})	Intrinsic Activity* (A m ⁻²)
Pd	7.0	0.30	2	0.28
Pd(97)Fe(03)	7.1	0.20	3	0.42
Pd(71)Fe(29)	8.1	0.25	11	1.36
Pd(59)Fe(41)	9.3	0.29	20	2.15
Pd(99)Ni(01)	10.7	0.38	1.5	0.14
Pd(71)Ni(29)	10.7	0.25	26	2.43
Pd(56)Ni(44)	12.1	0.25	30	2.48

* Intrinsic activity = mass activity/EASA

Chronoamperometric experiments at a fixed potential (+0.5 V) in the presence of 1.0 M NaOH and 1.0 M ethanol (Fig. 5D and 6D) showed sharply drop of the current until achieve a steady state thereafter. At the beginning of the experiment, the active sites are free of adsorbed/oxidized ethanol molecules, but the rate at which new ethanol molecules are adsorbed depends on the availability of active catalyst sites as the reaction proceeds [11]. Table 3 and Fig. 5C and 6C presents the mass activities (A g_{Pd}^{-1}) obtained from the current of the chronoamperometric curve at the end of the experiment (30 min). Pd(59)Fe(41) had the highest catalytic activity among all the investigated iron-containing compositions. It is also worth noting that this composition contained the lowest amount of Pd. The combination of Pd nanoparticles with metal oxides increased catalyst activity towards alcohol oxidation in alkaline media, accounting for the better results.

The generally accepted mechanism of the EOR on Pd surfaces in alkaline environments for DEFC applications has been reported by many authors [37,39,40].

$$Pd + CH_3CH_2OH \rightleftharpoons Pd - (CH_3CH_2OH)_{ads}$$
(5)

$$Pd-(CH_3CH_2OH)_{ads} + 3OH^- \rightarrow Pd-(CH_3CO)_{ads} + 3H_2O + 3e^-$$
(6)

$$Pd-(CH_{3}CO)_{ads} + PdOH_{ads} \rightarrow Pd-CH_{3}COOH + Pd$$
(7)

$$Pd-CH_{3}COOH + OH^{-} \rightarrow Pd + CH_{3}COO^{-} + H_{2}O$$
(8)

Initially, the ethanol molecules are adsorbed in the Pd surface by a dissociative process (Eq. 5) that leads to molecule dehydrogenation and formation of ethoxy intermediate (CH₃CO)ads (Eq. 6). This intermediate is removed from Pd surface by the -OH species (Eq. 4), also adsorbed on Pd sites, forming acetic acid (Eq. 7) that is quickly converted in acetate ions by simple acid-base equilibrium (Eq. 8). Different

from ethanol oxidation in acidic media where the mechanism passes through the -CO formation on the catalyst sites of Pt [11,20]. In alkaline media the mechanism predicts the formation of the Pd–(CH₃CO)_{ads} intermediate, not CO_{ads}. In this mechanism the rate determining step represents the oxidative removal of (CH₃CO)ads by adsorbed -OH species leading to acetate formation as the major product.

Addition of Ni to Pd presents higher catalytic activity (30 A g_{Pd}^{-1}) than when Fe is introduced (20 A g_{Pd}^{-1}). This is in line with the intrinsic activity of PtNi and PtFe compositions. Moreover, Ni is claimed to be a good co-catalyst for Pt and Pd in alkaline media [41,42] since can generate surplus OH⁻ through the auto-catalytic reaction (Eq. 9 and 10). Promoting, the increase of local OH⁻ concentration around the catalyst [29].

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

$$Ni(OH)_2 \rightarrow NiOOH + H^+ + e^-$$
(10)

The effect of iron addition over Pd or Pt towards small organics molecules oxidations in alkaline media still unclear. Nevertheless, it is claimed the beneficial effect of iron to improve ORR due to a significant electronic effect of iron over Pd or Pt d-band [43,44]. This effect was also observed for PtFe alloy on methanol oxidation [45,46]. Our XPS-data have shown a very fair electronic effect of iron addition on Pd-catalyst.

4. Conclusion

We have investigated the activity activity of Pd:M (M = Fe or Ni) catalysts towards ethanol electrooxidation in alkaline media. All the compositions investigated (10, 30 and 50 at. % M loading) displayed the Pd face centered cubic (fcc) structure and the experimentally determined compositions were close to the nominal ones. The only

exceptions were compositions containing 10 at. % of M, for which the second metal was actually presented at less than 5 at. %. XPS analysis revealed that the nanoparticle surface composition was close to the bulk composition found by EDX. Also, a more detailed analysis showed that while Pd existed in its oxidized form PdO and PdO₂, metallic Pd prevailed. XPS also detected Fe_2O_3 and Ni oxides for the compositions containing 30 and 50 at. % Fe and Ni, respectively. TEM analysis demonstrated that the nanoparticles as well as Pd and the added metals (Fe and Ni) were homogeneously distributed on the carbon support. Addition of Fe or Ni enhanced the catalytic activity of Pd nanoparticles. The current increased and the E_{onset} for ethanol oxidation shifts to less positive potential when compared with pure Pd, except for Pd(99)Ni(01). Pd(50)M(50) compositions yielded the highest catalytic activity, and Ni addition affected the activity towards ethanol electrooxidation more markedly than Fe. In conclusion, Pd(50)M(50) catalysts are easy and fast to prepare by microwave methods. The resulting catalyst represent a potential option for DAFCs.

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Figure Captions

Fig. 1. XRD patterns of the carbon supported Pd-based materials prepared by the microwave method. (A) Pd:Fe and (B) Pd:Ni catalysts.

Fig. 2. Spectra of the core levels of (A) Pd 3d, (B) Fe 2p, (C) Ni 2p of the Pd/C, Pd(59)Fe(41), and Pd(56)Ni(44) catalysts, respectively.

Fig. 3. (A) TEM micrograph of the Pd(59)Fe(41)/C catalyst. (B) Particle size distribution (count: 60 nanoparticles) (C) Composition map for Pd and Fe.

Fig. 4. (A) TEM micrograph of the Pd(56)Ni(44)/C catalyst. (B) Particles size distribution (count: 116 nanoparticles) (C) and (D) composition of the PdNi nanoparticle.

Fig. 5. (A) Cyclic voltammograms of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} at 10 mV s⁻¹; (B) Cyclic voltammograms of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 10 mV s⁻¹; (C) Mass activities of Pd:Fe catalysts from their corresponding current-time curves and (D) Polarization curve of the Pd:Fe catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 0.5 V for 30 min.

Fig. 6. (A) Cyclic voltammograms of the Pd:Ni catalysts recorded in NaOH 1.0 mol L^{-1} at 10 mV s⁻¹; (B) Cyclic voltammograms of the Pd:Ni catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 10 mV s⁻¹; (C) Mass activities of Pd:Ni catalysts from their corresponding current-time curves and (D) Polarization curve of the Pd:Ni catalysts recorded in NaOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} + EtOH 1.0 mol L^{-1} at 0.5 V for 30 min.

- Pd-M/C (M = Ni or Fe) catalysts were prepared by the microwave method.
- This method is advantageous because easy, fast and promotes small nanoparticles.
- Pd(50)M(50) compositions yielded the highest catalytic activity.
- Ni addition affected the activity towards ethanol electrooxidation more markedly than Fe.
- We obtained catalytic activity 30 mA g_{Pd}^{-1} for Pd(50)Ni(50) confirming the beneficial effect of adding Ni.