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# Improved methanol electro-oxidation reaction on PdRh-PVP/C electrodes

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## ABSTRACT

Here we report on the organometallic synthesis of polyvinylpyrrolidone (PVP)-stabilized palladium-rhodium nanostructures that display high electrochemical properties when used as carbon-supported electrodes (Pd<sub>x</sub>Rh<sub>1-x</sub>-PVP/C) for methanol oxidation reaction (MOR). These nanostructures were synthesized by hydrogenation of the tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) and tris(allyl) rhodium (Rh(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>3</sub>)

complexes, in tetrahydrofuran (THF) under mild reaction conditions (room temperature and 3 bar H<sub>2</sub>) and in the presence of PVP as stabilizer. The influence of methanol concentration (0.5, 1.0 and 2.0 M) as well as different scan rates (5-100 mV s<sup>-1</sup>) was evaluated to determine changes in the stability and catalytic activity. The organometallic approach and the use of PVP for the preparation of PdRh electrode materials promoted the formation of highly dispersed nanostructures, that led to a remarkably enhanced methanol electro-oxidation in alkaline medium. This high catalytic behavior can reasonably arise from a synergistic effect between Pd and Rh metals as, under the applied conditions, Rh is expected to enhance the Pd ability to oxidize methanol to CO<sub>2</sub> (oxophilic character) as well as the catalyst stability. From all the evaluated electrode materials, Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C electrode showed the highest mass activity at high methanol concentration (2.0 M) and low scan rate (10 mV s<sup>-1</sup>). This catalyst showed a performance up to 26 times higher than that of Pd-PVP/C and interestingly an electroactivity superior to that of previously reported PdRh catalysts.

Keywords: Nanoparticles, palladium-rhodium, methanol electro-oxidation, electrocatalysis, organometallic compounds.

## 1. Introduction

Stabilized metal-based nanoparticles (MNPs; nanocrystalline metal cores surrounded by a protecting shell, namely organic ligand or polymers) have attracted considerable attention due to their unusual chemical and physical properties that can lead to various applications in different areas such as nanocatalysis, biolabeling, sensing, biomedicine, and solar energy [1-6]. Chemical or *bottom-up* synthesis methods have been widely used due to their advantage for controlling the primary structures than physical or *top-down* methods [7]. Transition metal nanoparticles are frequently synthesized by the reduction of metal salts in aqueous solution, although other methods like thermal decomposition (conventional or microwave heating), sonochemistry,

electrochemistry, reduction or displacement of ligands from organometallic precursors have been also successfully used [8-12]. Well-defined metal nanoparticles, namely with homogeneous size, shape or composition, are highly demanded but the nature of the stabilizer is also a key-point not only for stabilization reason but also because the interaction of the stabilizer with the NP surface may govern their final chemical, physical or physicochemical properties [13-16]. The synthesis of MNPs from organometallic precursors can be easily performed in organic solvents in the presence of organic stabilizers. These latter limit agglomeration and aggregation of the particles, thus leading to size-controlled metal nanostructures with good stability and dispersion [17, 18]. Among a variety of stabilizers, polyvinylpyrrolidone (PVP) has been widely used for two main reasons: i) to prevent the aggregation of metallic nanoparticles through repulsive forces as a result of their hydrophobic carbon chains that will extend into the solvent [19]; and ii) to be used as a flexible membrane or polymer to stabilize metallic nanoparticles of different sizes and shapes[20]. In recent years, stable colloids have been obtained from PVP-coated Rh nanoparticles in organic solvent with potential electrochemical activity [21].

The activity of Pd for methanol oxidation reaction in alkaline media can be enhanced by the presence of a second metal that forms Pd alloys[22]. Pd alloys with different transition metals and carbon-free nanoparticles are used as electrodes in direct methanol fuel cells (DMFCs). These materials have revealed the ability of these new materials to overcome CO poisoning and promote the oxidation of other intermediates generated during the methanol oxidation [23]. Specifically, PdRh alloys have been studied with promising results in DMFCs and other catalytic reactions. Therefore, Rh nanomaterials and their combinations to form solid solutions are interesting from the point of view of catalysis and/or electrocatalysis [24]. In particular, Rh plays a key role in the DMFC, namely for the over oxidation of CO produced during methanol dehydrogenation [25]. Rh

is an oxyphilic metal that absorbs easily  $\text{OH}^-$  groups that is essential to the production of clean energy systems. Also, RhM nanoparticles have proven to be alternative catalytic materials due to the selectivity and conversion that can be significantly improved by using bimetallic instead of monometallic catalysts [26, 27]. For example, the combination of Rh with Pd can greatly improve the catalytic performance, due to a synergistic interaction between them and similar redox potentials assuring the alloy formation which in turn results in a promotion of the active surface sites.

PdRh nanostructures for catalytic applications have been prepared by different methods. For example, Querejeta and co-workers synthesized PdRh nanoparticles (ca. 113 to 385 nm) by sequential electrodeposition from  $\text{PdCl}_2$  and  $\text{Na}_3\text{RhCl}_6$  onto glassy carbon substrates. These NPs displayed a core-shell type structure and an improved electrocatalytic behavior on the hydrogen evolution reaction (HER) [28]. Baeza et al. reported used  $\text{RhCl}_3$  and  $\text{PdCl}_2$  to prepare PdRh nanoparticles *via* co-reduction and successive reduction, and compared the influence of the synthesis method and the Pd/Rh molar ratio onto their activity in the hydrodechlorination of 4-chlorophenol [27]. Polyol method also allowed to produce controlled alloyed PdRh nanoparticles with excellent results as hydrogen storage materials [29].

Three dimensional net-like PdRh NPs (2-8 nm) have been obtained *via* a wet chemical route using triblockpluronic copolymer as stabilizer with and without adding KBr [26]. The presence of  $\text{Br}^-$  ions favored the formation of well-defined structures and the activity on methanol oxidation reaction. An one-pot alkaline hydrothermal synthesis with urea led to hollow and porous PdRh nanobowls with enhanced electrocatalytic activity on ethanol oxidation reaction [30]. Almeida et al. prepared Ni@PdRh/C exhibiting enhanced electrocatalytic activity towards the oxidation of ethanol in alkaline media [31] whereas PdRh nanoparticles (4.4 - 7.7 nm) synthesized by one-pot

hydrothermal method using triblock pluronic copolymers produced hollow structure NPs having excellent electrocatalytic performance towards MOR [32]. Open 3D structures made of ultrathin PdRh nanosheets were synthesized via a seed-mediated growth method that showed enhanced electrocatalytic activity and stability toward MOR in KOH solution [33].

In this work, we explore an alternative synthesis method to access well-controlled and well-dispersed PdRh nanostructures in order to improve the electrocatalytic performance when used as electrode material in proton-exchange fuel cells. Semispherical PdRh NPs below 5 nm were synthesized starting from organometallic precursors and using polyvinylpyrrolidone (PVP) as a stabilizer. Their electrochemical performance on the methanol electro-oxidation reaction (MOR) in alkaline media has been evaluated according to the Rh amount in the bimetallic PdRh materials. Systematic electrocatalytic studies using different scan rates (5, 10 and 100 mV s<sup>-1</sup>) and CH<sub>3</sub>OH concentrations (0.5, 1.0 and 2.0 M) have been performed in order to achieve a fundamental understanding of the effect of the Rh addition.

## 2. Materials and Methods

Tris(allyl)rhodium, Rh( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub>, precursor was synthesized from rhodium (III) chloride (Johnson Matthey, 99.9 % purity) and allylmagnesium chloride (Sigma-Aldrich; solution 2.0 M in THF) using the procedure previously reported [34, 35]. Tris(dibenzylideneacetone)dipalladium(0), Pd<sub>2</sub>(dba)<sub>3</sub> was purchased from Strem Chemicals (99.9% purity); Polyvinylpyrrolidone (PVP) molar wt. 40,000 (Sigma-Aldrich, 98% purity). Tetrahydrofuran (99.7 % purity) and pentane (99% purity) were acquired from Carlo Erba Co., and were dried and purified before use using a purification equipment MBraun (MB SPS-800). The reactive gas dihydrogen (99.999% purity) was purchased from Alphagaz 1.

## 2.1 Synthesis of Pd/PVP and Pd<sub>x</sub>Rh<sub>1-x</sub>/PVP nanoparticles

PdRh nanoparticles stabilized by polyvinylpyrrolidone (PdRh-PVP) were prepared in three different molar ratios (20:80, 50:50 and 80:20) using the following procedure: Pd<sub>2</sub>(dba)<sub>3</sub> and Rh( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> precursors and PVP as stabilizer were mixed in a Fischer-Porter bottle with proper amounts to reach a final metal:stabilizer weight ratio of 10:90 (Table 1). Thereafter, 40 mL of THF were slowly added under vigorous stirring and the reactor was pressurized with dihydrogen (3 bar). The system was maintained under pressure at room temperature during 20 h leading to a dark colloidal solution. Then, powders obtained by pentane addition, repeatedly washed with pentane and finally dried under vacuum. For comparison purpose, Pd PVP-stabilized NPs (Pd-PVP) were also synthesized following the same experimental procedure. A schematic representation of the organometallic synthesis of Pd-PVP and PdRh-PVP nanoparticles is given on Figure 1.

## 3. Characterization of Pd<sub>x</sub>Rh<sub>1-x</sub>/PVP stabilized bimetallic nanostructures

Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the metal composition of the PdRh nanostructures. The experiments were performed in a Thermo Scientific iCAP 6300 DUO couple with a Perkin Elmer 2400 Serie II analyzer. The samples were dissolved in a mixture of HCl and HNO<sub>3</sub> 1:1 at metal concentration of 5 ppm. Fourier-transform infrared (FT-IR) analyses were carried out to study the stabilization of the as-prepared PdRh nanostructures using a Nicolet spectrophotometer FT-IR spectrometer. For that purpose, powders of PdRh nanostructures were mixed with KBr to obtain pellet-shape samples. The measurements were implemented in the wavenumber range of 500 to 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

Structural characterization of the as-prepared PdRh nanostructures was carried out using an X-ray diffractometer (Bruker D8 Advance, equipped with a Lynxeye detector and Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å)). X-ray diffraction (XRD) patterns were recorded from 20 to 90° at 40 kV, 40 mA and at a scan rate of 0.021° min<sup>-1</sup>.

Hydrodynamic diameters of PdRh NPs were determined by dynamic light scattering (DLS) in a Malvern Zetasizer Nano ZSP, model ZEN5600 equipped with an Argon laser ( $\lambda= 633$  nm). DLS technique measures a diffusion coefficient of the sample that is inversely proportional to the particle size in a specific medium; i.e. a relaxation of the autocorrelation function of the scattered light. The analyses were performed at room temperature and a scattering angle of 90°. Previously, the as-prepared nanostructures were diluted in THF in a 1/100 ratio. The hydrodynamic diameters were calculated from the particle diameter moments (number-average diameter  $D_n$ ; weight-average diameter  $D_w$  and z-average diameter  $D_z$ ) and the polydispersity index (PDI) [36].

The dispersion and particle size of each Pd<sub>x</sub>Rh<sub>1-x</sub>-PVP system were also analyzed by transmission electron microscopy (TEM) using an EM-ARM200CF JEOL electron microscope operating at 200 kV. A drop of each colloidal solution was deposited onto a carbon covered copper grid for TEM analysis and then the solvent was evaporated at room temperature.

#### **4. Electrode preparation**

Monometallic and bimetallic carbon supported catalysts were prepared by mixing 2 g of graphite powder (Alfa Aesar, 99.9995%), 0.5 g of the as-prepared nanostructures and 200  $\mu$ L of silicone oil using to form a paste. Then, the paste was put in a plastic cylinder of 100 mm in length and 2



mm in diameter with an exposure area of 0.0314 cm<sup>2</sup>. A copper wire was used as electrical contact of the working electrode.

#### **4.1 Electrochemical measurements**

Electrochemical measurements were performed with a potentiostat-galvanostat Autolab PGSTAT30 using a conventional three-electrode cell. Saturated calomel electrode (SCE) and carbon rod electrode were used as a reference and counter-electrode (CE), respectively.

Cyclic voltammetry (CV) experiments were initially used to stabilize electrode materials. The experiments were performed in the potential interval ranging from 1.2 to 0.6 *vs* SCE using a 0.5 M KOH solution saturated with a gas (Ar, 99.99% purity). The activity of the electrode materials was measured on MOR. CV measurements were achieved at different scan rates (5, 10 and 100 mV s<sup>-1</sup>) in the potential range of -1.2 to 0.4 V *vs* SCE using as electrolyte a mixture of 0.5 M KOH + CH<sub>3</sub>OH (CH<sub>3</sub>OH = 0.5, 1.0 and 2.0 M) under argon atmosphere.

### **5. Results and discussion**

#### **5.1 Chemical and structural characterization of the Pd<sub>x</sub>Rh<sub>1-x</sub>-PVP nanoparticles**

Composition in metals of the as-prepared nanomaterials is shown in Table 1. Based on the calibration curves, final compositions appeared slightly different to the theoretical ones calculated from the quantities of reagents introduced. Such differences can be ascribed to the itself synthesis method because the dispersion of the NPs into the PVP matrix can vary from one synthesis to another and also because of the purification step. They are considered minor under the main goal of this study.

Figure 2 shows FT-IR spectra of the as-synthesized Pd-PVP, Pd<sub>8</sub>Rh<sub>2</sub>-PVP, Pd<sub>5</sub>Rh<sub>5</sub>-PVP and Pd<sub>2</sub>Rh<sub>8</sub>-PVP NPs together with that of pure PVP as a reference. FT-IR spectrum of PVP shows typical bands that can be assigned to the C-H asymmetric stretching vibration (2956 cm<sup>-1</sup>), CH<sub>2</sub> bending vibrations (1466 cm<sup>-1</sup>), C=O stretching vibration (1655 cm<sup>-1</sup>), N-OH (1294 cm<sup>-1</sup>) and C-N vibrations (1079 and 1015 cm<sup>-1</sup>) [19, 37]. FT-IR spectra of the series of PdRh nanostructures present slight differences in comparison to that of the pure PVP, that are attributable to the high weight of PVP in comparison to the metal content (ca. 1:10 ratio; theoretical value). The presence of PVP is visible in all samples and the obtained results are in good agreement with those previously reported for other nanostructures (Ni-Pd) stabilized by PVP [38]. The slight changes observed for the bands at 1079 and 1015 cm<sup>-1</sup> reflect the coordination between N and the metal surface of the particles, thus attesting of the stabilizing role of PVP [37].

Figure 3 presents the XRD patterns of the as-synthesized PdRh nanostructures. For comparison purpose, XRD pattern of PVP-stabilized Pd nanostructures is also given. Pd-PVP NPs showed reflections at 40.12° (111), 46.58° (200), 68.12° (220) and 82.12° (311) that matched well with the face-centered-cubic (fcc) structure of Pd (JCPDS 00-046-1043). The addition of Rh to Pd enforced a reduction in the crystallite size, as evidenced by the broader signals observed for the PdRh NPs. These broad signals are also accompanied with a slight shift towards higher 2θ degrees, thus indicating the formation of Pd<sub>x</sub>Rh<sub>1-x</sub> solid-solutions namely alloyed NPs. An approximation of the crystallite size was realized by Scherrer's equation (Table 2). Crystallite sizes for the PdRh alloys were found between 1.5 and 2.0 nm versus 4.3 nm for the Pd NPs. These data evidence that PdRh nanoparticles contain smaller crystallites than monometallic Pd ones.

The nanoparticle morphology and size distribution were evaluated by TEM analysis (Figure 4 a-d). Well-dispersed nanostructures that have a semispherical-shape can be observed on the TEM images which indicates that the PVP polymeric matrix acts as an efficient stabilizer and prevents the agglomeration of the NPs. Have well-dispersed and small NPs is a promising feature for catalysis due to high number of potential active catalytic sites [39, 40]. Size histograms are shown as inset of the TEM images for each system. They are quite large as revealed by the high standard deviation values. The average particle size was found to be in the range 2.5 and 3.3 nm and to increase in the following order  $2.5 \pm 0.9$  (Pd<sub>2</sub>Rh<sub>8</sub>-PVP) >  $2.8 \pm 1.2$  (Pd<sub>8</sub>Rh<sub>2</sub>-PVP) >  $3.0 \pm 1.5$  (Pd<sub>5</sub>Rh<sub>5</sub>-PVP) >  $3.3 \pm 1.4$  (Pd-PVP). This size order has to be taken with caution as the standard deviation is quite high which makes in turn the sizes very similar.

In agreement with XRD patterns, the average particle size is slightly reduced when the solid solution is formed compared to Pd monometallic system, indicating highly dispersed PdRh systems [30].

Colloidal solutions of NPs were also analyzed by DLS measurement and the results are shown in Figure 5. DLS is an optical technique for the characterization of species in solution that allows to evaluate the particle agglomeration and also provides information on size distribution [36]. The measurements were performed on 1/100 diluted solutions of nanoparticles in THF using a Millipore filter. DLS measurements revealed hydrodynamic diameters of ca. 35.9 nm (Pd<sub>8</sub>Rh<sub>2</sub>-PVP), 45.9 nm (Pd<sub>2</sub>Rh<sub>8</sub>-PVP), 52.6 nm (Pd-PVP) and 59.6 nm (Pd<sub>5</sub>Rh<sub>5</sub>-PVP). In opposition to XRD and TEM measurements that reflect only to the metal cores, DLS permits to determine the hydrodynamic diameters of the whole nanostructures that is the sum of the metal core and the stabilizing layer (here the PVP matrix). It is the reason why the obtained values are greater than those determined by XRD and TEM analyses. An important feature is that the compute

polydispersity index (PDI, also known as heterogeneity index) is lower than 0.7 for all NP samples, thus suggesting that the obtained nanoparticles are well-dispersed in the polymeric matrix (Table 2) [41].

## 5.2 Electrochemical measurements

Figures 6 a-d show the CV measurements of the as-prepared electrode materials after 20<sup>th</sup> potential cycles at four different scan rates (5, 10, 20 and 100 mV s<sup>-1</sup>). Note that the samples presented a steady-state after two potential cycles but we considered to verify the stability depending on scan rate. Cyclic voltammograms show a peak in the typical region for H<sub>2</sub> oxidation (A<sub>1</sub> y A<sub>2</sub>) which position varies depending on the Rh quantity and scan rate. The position range observed is from -1.1 to -0.70 V<sub>SCE</sub>. It can be correlated with the oxidation of the absorbed/adsorbed hydrogen on Pd and/or Rh ( $Pd - H_{abs/ads} + OH^- \rightarrow Pd + H_2O + e^-$ ). The low peak located above 0.1 V<sub>SCE</sub> (A<sub>3</sub>) is linked to the formation of an oxide layer of palladium or rhodium according to the following reactions  $Pd + OH^- \leftrightarrow Pd - OH_{ads} + e^-$  and  $Pd - OH_{ads} + OH^- \leftrightarrow Pd - O + H_2O + e^-$  or  $Pd - OH_{ads} + Pd - OH_{ads} \leftrightarrow Pd - O + H_2O$  [42-44]. The negative currents, observed in the backward scan, indicate the reduction processes of the oxygen (R<sub>1</sub>, 0.13 V<sub>SCE</sub>), of Pd(II) or Rh(II) oxide species (R<sub>2</sub>, -0.49 V<sub>SCE</sub>) and the absorption/adsorption process of hydrogen (R<sub>3</sub>, -0.97 V<sub>SCE</sub>). Electrochemically active surface area (ECSA) is commonly used to obtain a meaningful comparison between electrode materials. Thus, a number of different electrochemical methods have been used to estimate ECSA and all of them considers important estimations that can result in a lack of precision. In the case of Pd base catalysts, three methods can be used to obtain ECSA values. The first method is the integration of the hydrogen absorption-desorption charge related to the hydrogen underpotential deposition, H<sub>upd</sub>). This method, considers the following equation:

$ECSA_{Pd-M} = Q_H/|Pd| \times q_H$ . In this formula,  $Q_H$  represents the charge for hydrogen adsorption,  $|Pd|$  is the mass of metal on electrode and  $q_H$  is the charge required for a monolayer of adsorbed hydrogen on Pd surface (assuming that the reduction of PdO monolayer takes  $0.424 \text{ mC cm}^{-2}$ ) [45]. Finally, the active surface coverage  $\theta = ECSA_{Pd-M}/S_{g(Pd-M)}$  can be also computed using the palladium area. The geometric surface area can be obtained after knowing the mean diameter of the particles, commonly by TEM analysis, using the following equation  $S_{g(Pd-M)} = \frac{6000}{d\rho}$ ; where  $S_g$  is the palladium surface area ( $\text{m}^2 \text{ g}^{-1}$ ),  $d$  is the mean diameter of the particles (nm) and  $\rho$  is the average density (for this study,  $12.0 \text{ g cm}^{-3}$  (Pd) and  $8.9 \text{ g cm}^{-3}$  (Rh)).

The second method involves the required charge to oxidize a potentiostatically adsorbed carbon monoxide monolayer (CO stripping method) [46]. This technique requires the CO-coverage ( $\theta_c$ ) and adsorption mode; i.e the dependency of the CO-dosing potential and the crystallographic composition. The third common method is through charging under the peak associated with the reduction of palladium oxide/hydroxide in the CVs using positive reversal potentials, defining an integration baseline free of pseudo-capacitive contributions. Then, the ECSA were initially calculated from the first method and compared with the third mentioned method; and finally it was analyzed the CO stripping method for a specific case was revised in acid media to confirm activity of the materials; the results are summarized in Tables 3-4 and in the supplementary material.

In general, the ECSA and active surface coverage values, computed from the first method, showed an increase at low scan rates ( $5$  and  $10 \text{ mV s}^{-1}$ ), but reduced with high scan rates values. From all evaluated conditions, the highest ECSA value was observed for the electrode material with a 8:2 ratio (Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C),  $17.64 \text{ m}^2 \text{ g}^{-1}$  suggesting that this composition provided better electroactivity for methanol oxidation reaction than the counterparts (Table 3). It is also clear that ECSA values were quite affected by the applied scan rate. Taking into account the conditions at

which the electrode materials presented the high ECSA values, the following order was obtained:  $17.64 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_8\text{Rh}_2\text{-PVP/C @ } 10 \text{ mV s}^{-1}) > 11.29 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_5\text{Rh}_5\text{-PVP/C @ } 10 \text{ mV s}^{-1}) > 11.28 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_2\text{Rh}_8\text{-PVP/C @ } 10 \text{ mV s}^{-1}) > 3.75 \text{ m}^2 \text{ g}^{-1} (\text{Pd-PVP/C @ } 20 \text{ mV s}^{-1})$ .

ECSA values were also calculated from the charge under the peak associated with the reduction of Pd oxide/hydroxide compounds (table 4). The obtained values showed a similar trend compared to the method using the hydrogen absorption-desorption region; that is., the maximum ECSA values were obtained in samples with a ratio of 8:2 ( $\text{Pd}_8\text{Rh}_2\text{-PVP/C}$ ) at low scan rates. ECSA values (in the second evaluated method) were found in the following order:  $15.06 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_8\text{Rh}_2\text{-PVP/C @ } 5 \text{ mV s}^{-1}) > 8.82 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_2\text{Rh}_8\text{-PVP/C @ } 10 \text{ mV s}^{-1}) > 7.91 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_5\text{Rh}_5\text{-PVP/C @ } 10 \text{ mV s}^{-1}) \cong 7.74 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_5\text{Rh}_5\text{-PVP/C @ } 5 \text{ mV s}^{-1}) \cong (\text{Pd}_8\text{Rh}_2\text{-PVP/C @ } 10 \text{ mV s}^{-1}) > 6.75 \text{ m}^2 \text{ g}^{-1} (\text{Pd}_8\text{Rh}_2\text{-PVP/C @ } 5 \text{ mV s}^{-1})$ . In summary, under the experimental conditions, the charges associated with the reduction surfaces of the palladium oxide/hydroxide compounds and the hydrogen absorption-desorption region are very similar, correlating in good way the catalytic activity. These results suggested that by controlling the scan rate, the insertion of small Rh amounts to form a PdRh alloys, enhanced the current peak and reduced the onset potential for the hydrogen adsorption; which in turn, improve the ECSA in the electrode materials.

In the supplementary material (Figure S1), it can be seen that electrode materials are also more active in acid media in comparison with commercial Pt/C catalysts. In this case, the catalysts were evaluated from switching potential of CVs in the Pd-oxide adsorption-desorption region recorded in 0.5 M  $\text{H}_2\text{SO}_4$  and a scan rate of 20  $\text{mV s}^{-1}$ .

From these plots, the calculated ECSA values were in the order  $\text{Pd}_2\text{Rh}_8\text{-PVP/C (45)} > \text{Pd}_8\text{Rh}_2\text{-PVP/C (34.5)} > \text{Pd/C}_{\text{commercial}} (6.0) > \text{Pd-PVP/C (3.8)}$ , in  $\text{m}^2/\text{g}_{\text{cat}}$ . Notice that ECSA is in the same order of magnitude for the synthesized bi-metallic materials; whereas, the mono-metallic

electrodes are one order of magnitude lower. It is also clear, that in acid media the electro-activity of PdRh alloy enhanced with the quantity of Rh. An analysis of CO-stripping was also realized in acid media and added in the supplementary material (Figure S2). CO-stripping voltammetry is recognized as a surface structure-sensitive process [47]; thus, the electrochemical performance of the catalysts stabilized with PVP present low affinity-poisoning to CO (curves marked (1) in Figure S2) as can be deduced during the second cycle (curves marked with (2)); possibly due to the presence of Rh and/or stabilizer employed or both. Conversely, CO-stripping in the sample from commercial source, present a major current difference between cycle 1 and cycle 2, and two oxidation-peaks that can be attributed to two types of active sites for reaction. In addition, during cycle 2, it is evident that some adsorbed-traces of CO are again oxidized to CO<sub>2</sub>, indication of a poisoning-surface state in Pd-commercial. These results highlight that the MOR-mechanism is, within experimental error, similar for PVP-based catalysts and with better activity with lower Rh-content, avoiding interfacial interaction of CO to produce carbon dioxide, which is in good agreement with the ECSA values calculated from the other two methods. Thus, the calculations of ECSA showed a high resistance to the poisoning with low Rh amounts, when are proposed this experimental conditions (PVP as stabilizer and an organometallic approach).

On the other hand, it is well-stated that the methanol crossover negatively affects the fuel cells performance. Methanol concentration, among other key parameters, is critical to avoid methanol crossover. For this reason, an initial evaluation of MOR on the Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C catalysts was experimentally carried out in order to determinate the adequate methanol concentration. The cyclic voltammograms were recorded at relatively high (100 mV s<sup>-1</sup>) scan rates and different KOH + CH<sub>3</sub>OH electrolytes varying methanol concentration (0.0, 0.5, 1.0 and 2 M), as has been previously suggested [48, 49]. The CV profiles after 20 potential cycles show that the current density of the

oxidation peaks increased with the amount of methanol (Figure 7a), which is accompanied by a shift towards lower potentials in the main oxidation peak. Comparing this electrode material (Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C) with Pd-PVP/C monometallic catalysts, it can be observed a significant improvement in the electroactivity for MOR, thus corroborating that the formed alloy presents a typical oxophilic character due to Rh is promoting Pd ability to oxidize methanol → CO<sub>2</sub> [50]. Actually, a gradual loss of this mass activity is observed with the PdRh-PVP/C electrodes as increases the Rh amount; highlighting that oxophilic character in the PdRh alloys is more promoted at low Rh concentrations, which may explain the observed results. Such oxophilic character is enhanced at high methanol concentrations (2.0 M) reaching specific activities about 198 mA mg<sup>-1</sup><sub>Pd</sub> which inhibit in a well-manner the undesired side products during the reaction. In order to confirm, this trend, the mass activity of the as-prepared materials vs. the methanol concentration at a scan rate of 100 mV s<sup>-1</sup> is shown in Figure 7b. The Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C electrode also showed the highest mass activity for all evaluated methanol concentrations with a linear tendency, thus ratifying a typical diffusion-controlled process with an improved in the electrode kinetic with low Rh additions [51-53].

The dependence of the MOR activity at different scan rates (5, 10, 20, 40, 60, 80 and 100 mV s<sup>-1</sup>) was also studied in a KOH + CH<sub>3</sub>OH (2.0 M) solutions. Figure 8a-b shows typical cyclic voltammograms of the electrodes at low scan rates and after 20<sup>th</sup> potential cycles. Cyclic voltammograms show typical catalytic active sites for MOR which are associated with two apparent activation energies and pathways [25, 50, 54].

The synergistic effect between both metals in dependence of the weight ratio has been relied as the main cause of the reactions involved on the active surface for MOR. The addition of Rh in the Pd matrix enhances noticeably the electro-catalytic activity on MOR in comparison with Pd-



PVP/C catalyst, but the highest electrochemical performance was found for the 8:2 (Pd:Rh) ratio, with peak currents about  $166 \text{ mA mg}^{-1}_{\text{Pd}}$ . Other ratios (5:5 and 2:4) experimented a decrease in the activity of MOR, which is in good agreement with the ECSA values along with a probable agglomeration of the nanostructures during the catalysis that may result from a release of PVP due its solubility in the reaction medium. In the potential window of  $-1.0$  to  $0.6 \text{ V}_{\text{SCE}}$ , the onset potential for oxidation of methanol starts between  $-0.52$  to  $-0.45 \text{ V}_{\text{SCE}}$  ( $5 \text{ mV s}^{-1}$ ) and in the range from  $-0.48$  to  $-0.41 \text{ V}_{\text{SCE}}$  ( $10 \text{ mV s}^{-1}$ ); i.e., all PdRh catalysts exhibit lower onset potentials in comparison with the Pd-PVP/C catalysts ( $\sim -0.32 \text{ V}_{\text{SCE}}$  at both scan rates). Differences in the onset potential are correlated with the mentioned oxophilic character of the PdRh alloy, which seems to be favorable at low Rh amount. On reversing the scan, the reduction of the PdRh-PVP/C systems, essential to obtain renewable surface [55-57], is also modified with the Rh quantity, i.e. it occurs at a higher potential as increases the Rh amount in the PdRh compounds. The dependence of peak current density on MOR with the applied scan rate was again observed in the PdRh catalysts. The peak current densities for Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C, Pd<sub>5</sub>Rh<sub>5</sub>-PVP/C and Pd<sub>2</sub>Rh<sub>8</sub>-PVP/C catalysts were found about  $164.10$ ,  $56.25$ , and  $27.63 \text{ mA mg}^{-1}_{\text{Pd}}$  at  $5 \text{ mV s}^{-1}$ . These values augmented to  $166.51$ ,  $43.28$ , and  $30.63 \text{ mA mg}^{-1}_{\text{Pd}}$  when at  $10 \text{ mV s}^{-1}$ , respectively. Thus, in the best case, the catalytic activity was up to 26 times higher than that of pure Pd-PVP/C catalyst. It is well established that rhodium plays an important role in the oxidation reactions of methanol and ethanol in both acid and alkaline environments [25, 58, 59]. In addition, it has been demonstrated that the presence of rhodium could improve the CO-tolerance, increasing the oxidation kinetics of some alcohols [25, 60, 61]. Thus, the observed electrochemical yield in the CO-stripping reaction and the MOR activity for the prepared bimetallic materials confirm that the stabilization of Rh with PVP during the synthesis

of this organometallic method improves CO-tolerance increasing MOR in comparison with the mono-metallic catalysts (Pd/C-PVP and Pd/C from commercial source).

Figure 8 c-d show the obtained current density and peak potential vs. square root of scan rates (5, 10, 20, 40, 60, 80 and 100  $\text{mV s}^{-1}$ ) confirming that high current densities accompanied with lower chemical potential of the reaction (main oxidation peak) were obtained in the stabilized bimetallic electrocatalysts in comparison with pure Pd-PVP/C electrode. The data displayed a quasi-linear dependence in both parameters which is congruent with the ECSA values and the number of available active-sites for the methanol electro-oxidation reaction.

Charge transfer and mass transport limitation were also elucidated in selected samples using electrochemical impedance measurements (EIS) during methanol oxidation reaction in KOH 0.5 M and CH<sub>3</sub>OH 2.0 M solution. Selected samples were those that in previous characterizations showed the high electrochemical performance; i.e.; Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C and Pd<sub>2</sub>Rh<sub>8</sub>-PVP/C. Comparison of EIS performance for monometallic catalyst (Pd-PVP/C) including commercial sample (Pd<sub>commercial</sub>/C) was also showed in the Nyquist Plots (Figure 10a). The electrode-electrolyte interphase was adjusted using nonlinear least-squares analysis of the complex impedance. The electrodes were adjusted using a simple Randles circuit, substituting the double-layer capacitance with a constant phase element. CPE was used to compensate the non-ideal performance of the capacitive behavior of the electrode materials due to the roughness, surface impurities, porosity and dislocations. In the scheme of Figure 10a, R<sub>1</sub> is correlated with the solution resistance (R<sub>s</sub>), CPE is the constant phase element that simulates the capacitance of the double-layer (C<sub>dl</sub>) and is in parallel with the charge transfer resistance (R<sub>2</sub>=R<sub>ct</sub>). The impedance magnitude can be represented through the following equation  $Z_{CPE} = \frac{1}{Y_0(j\omega)^n}$ ; with n that represents the resistive or capacitive behavior ( $0 \leq n \leq 1$ ),  $\omega$  the angular frequency and Y<sub>0</sub> the pseudo-capacitance,

which in turn depends of the following formula;  $Y_o = C_{dl}^n (R_s^{-1} - R_{ct}^{-1})^{1-n}$ . The parameters obtained from EIS analysis are shown in Table 5. From these values, it can be notice that polarization resistance ( $R_p$ ) presented the following order  $Pd_8Rh_2/PVP < Pd_2Rh_8/PVP < Pd/PVP < Pd/C$ , which is in good agreement with previous electrochemical analysis. It is also evident that free-rhodium catalysts, synthesized and commercial, showed a lower activity for MOR under the experimental conditions which in turn are correlated with the obtained electrochemical surface area.

On the other hand, electrochemical stability of the prepared and commercial catalysts was monitored using chronoamperometry at an applied potential of  $-0.25 V_{SCE}$  during 1750s, in a solution containing 2 M MeOH and 0.5 M KOH, Figure 10b. The results showed that the stability (or durability) during MOR, obtained as a function of time, is acceptable for the all binary catalysts in study. Nevertheless, the electrode material with the high current density (insignificant current deviation) and good stability was  $Pd_8Rh_2/PVP$  as demonstrated previously cyclic voltammetry and EIS measurements.

In summary, the obtained results suggest that the combination of the organometallic approach and the use of PVP as stabilizing agent allowed to enhance the MOR electrocatalytic performance of the PdRh nanocatalysts. In this way, it is known that synthesis method impacts the activity of the final product through the reduction of charge transfer resistance [31, 62, 63]. Thus, the use of an organic stabilizer during the preparation could modulated the distribution and size of the particles, helping to improve the electrochemical catalytic activity through synergistic effect between the components of the alloy and stability. Thus, the present study demonstrates that this method allows the in-situ interaction of the support matrix and the stabilizer with the metallic-precursors, promoting a homogeneous reaction-environment, and a better modulation of the obtained catalyst

properties. In this context, the mass-transport limitations are best reduced at the interface of PdRh-PVP/C catalysts, with low Rh amounts. Complementary results, obtained from the CO-stripping reaction and the ECSA values in both acid and alkaline media, show that, in general, PVP-stabilized rhodium containing catalysts have a higher tolerance to CO compared to commercial Pd/C catalysts.

Finally, high activity and stability for MOR in alkaline medium were achieved for Pd<sub>8</sub>Rh<sub>2</sub>-stabilized nanostructures produced with organometallic approach. Results are superior or comparable to other reported bimetallic or ternary electrode materials [25, 31-33, 61, 64].

## 6. CONCLUSIONS

In summary, a series of PdRh alloyed nanostructures (Pd<sub>8</sub>Rh<sub>2</sub>-PVP, Pd<sub>5</sub>Rh<sub>5</sub>-PVP, Pd<sub>2</sub>Rh<sub>8</sub>-PVP) were successfully prepared from organometallic complexes as metal precursors and PVP as stabilizer, in THF as a solvent. This preparation method led to the formation of monodisperse, semispherical and well-dispersed nanostructures of mean size < 5 nm. Acceptable differences in the final composition of the nanocatalysts was achieved, thus allowing a comparative study of their electrocatalytic performance in MOR after deposition onto carbon support. Cyclic voltammograms show a shift in the oxidation peak potential towards negative values with the increasing of Rh amount. All the carbon supported nanocatalysts (Pd<sub>8</sub>Rh<sub>2</sub>-PVP/C, Pd<sub>5</sub>Rh<sub>5</sub>-PVP/C, Pd<sub>2</sub>Rh<sub>8</sub>-PVP/C) presented superior catalytic activity when compared to Pd-PVP/C catalyst, up to 1.5 orders in magnitude higher than that of pure electrode material.

Comparison of the electrochemical performance of the PdRh catalysts in MOR showed the highest activity at methanol concentration of 2.0 M (198 mA mg<sup>-1</sup><sub>Pd</sub>) and at scan rate of 10 mV s<sup>-1</sup>. In these conditions, a superior electrocatalytic performance was found for the PdRh catalyst with the lowest

amount of rhodium ( $\text{Pd}_8\text{Rh}_2\text{-PVP/C}$ ). The  $\text{Pd}_8\text{Rh}_2\text{-PVP/C}$  catalyst showed an enhanced performance, up to 26 times higher than that of  $\text{Pd-PVP/C}$  and also, a superior electroactivity compared to previous reports for  $\text{PdRh}$  catalysts. The improved catalytic activity is correlated with a less transport limitation due to the combination of synthesis and reaction parameters (PVP as stabilizer, organometallic method, methanol concentration and scan rate) with a low rhodium amount, thus inducing a better charge-transfer on MOR by favoring adsorption-desorption process at the electrode-electrolyte interface. Then, oxophilic character in the  $\text{PdRh}$  alloys is favored at low Rh quantities. The results reached with  $\text{Pd}_8\text{Rh}_2\text{/PVP}$  material highlighted the role of the PVP stabilizer which promoted in an important manner, the synergistic effect by facilitating the methanol dehydrogenation.

Finally, this study demonstrates that select a proper synthesis method and a suitable stabilizing agent can be a valuable strategy to produce nanocatalysts in order to improve the electrochemical performance in MOR with a low content of noble metals.

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