

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

**Methanol Electrooxidation on Au-Pd/C in Alkaline Media:
The Dissolution of Palladium in the Bimetallic Alloy - A Case Scenario**

V-H Ramos-Sánchez¹, Diana Brito-Picciotto², Ramón Gómez-Vargas³, and Edgar Valenzuela^{4,*}

¹Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus Universitario, Circuito Universitario, Chihuahua, Chih., México. C.P. 31125

²Unidad de Energía Renovable, Centro de Investigación Científica de Yucatán, A.C., Calle 43 #130, Col. Chuburná de Hidalgo, Mérida Yuc., México. C.P. 97200

³Energías Renovables y Protección del Medio Ambiente, Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes #120, Complejo Industrial Chihuahua, Chihuahua, Chih., México. C.P. 31109

⁴Cuerpo Académico de Energía y Sustentabilidad, Universidad Politécnica de Chiapas, Calle Eduardo J. Selvas S/N, Col. Magisterial, Tuxtla Gutiérrez, Chis., México. C.P. 29010

*Tel: (961)6120484, fax 6120499, mail: edgarvm@gmail.com

ABSTRACT

Among the familiar types of fuel cells, a new technology is emerging. Alkaline direct alcohol fuel cells (ADAFC) have attracted much attention, since they overcome many of the major issues of its predecessors, such as carbonation and alcohol crossover. Historically, either in acid or alkaline media, Pt has shown the best catalytic activity for methanol electrooxidation. Unfortunately, the high price and limited supply of Pt make it prohibitive for large scale production. In ADAFC, the weaker specific adsorption of spectator ions in basic media; and higher coverage of adsorbed OH at low potential permit superior catalytic performance of other noble catalysts for methanol electrooxidation.

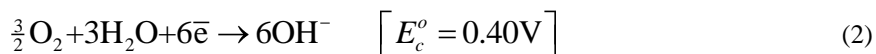
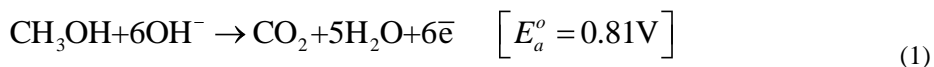
In this context, the present work is concerned with two different carbon supported alloys, AuPd and Au₂Pd. These alloy compositions were chosen for comparison, but also, in the case of the latter, to set a scenario where Pd is depleted due to its unavoidable dissolution during continuous operation of an alkaline direct methanol fuel cell (ADMFC). Thus, the bimetallic catalysts were synthesized by chemical reduction with NaBH₄; supported in commercial carbon black; and later fully characterized to obtain parameters such as chemical composition, alloying degree, particle size, and electrocatalytic activity. Exclusively, the AuPd/C demonstrated capability to promote the electrooxidation of methanol. This proved that, within these bimetallic alloys, in conditions of dissolution of Pd and ensuing enrichment of Au, a null catalytic activity is attained.



1. Introduction

Among the familiar types of fuel cells, a new technology is emerging, which is not quite an alkaline fuel cell (AFC) nor a direct alcohol fuel cell (DAFC), but a hybrid. These alkaline direct alcohol fuel cells, ADAFC hereinafter, have recently attracted much attention, since they overcome many of the major issues encountered in the two abovementioned parent technological approaches. As a matter of fact, the exploitation of alkaline anion exchange membranes (AAEM) as electrolyte in ADAFC brings with it inherent benefits, such as carbonation prevention and reduced alcohol crossover. Besides, a basic medium, on the other hand, eases both alcohol oxidation and oxygen reduction.[1,2]

Either in acid or alkaline media, platinum (Pt) has shown the best catalytic activity for methanol electrooxidation. Therefore, Pt and Pt-based catalysts have been traditionally used in direct methanol fuel cells (DMFC).[3] However, the high price and limited supply of Pt make it prohibitive for large scale production. Here, alkaline direct methanol fuel cells (ADMFC) become the obvious choice due to their weaker specific adsorption of spectator ions in basic media; and higher coverage of adsorbed OH at low potential, necessary for methanol electrooxidation. These two characteristics even permit superior catalytic performance of other noble catalysts in alkaline media, according to the following reactions:



Despite its slightly larger particle size, when compared to Pt, palladium (Pd) can be a suitable catalyst for ADMFC. Actually, it has been shown that Pd exhibits an outstanding synergistic effect in combination with gold (Au) in bimetallic alloys, [4] which make acceptable the use of Au, a precious metal twice more expensive than Pd.[5,6] This improvement in catalytic activity and chemical stability is almost certainly due to the suppression of Pd dissolution in a highly oxidizing medium [7] that in turn results of the capacity of Au to withdraw electrons within the bimetallic alloy, as the most electronegative metal in the periodic chart. Thus, it is not surprising that since 1960s Au-Pd had been investigated mainly as an alternative catalyst for hydrocarbon refining. [8]

Overall, among the key factors that affect the activity of a bimetallic catalyst during the electrooxidation process in an ADAFC are the components arrangement, surface structure, particle size, and alloying degree. For instance, it has been demonstrated that Pd particles in the range between 5 and 7 nm show an enhanced catalytic performance. [9] Added to this, and even more important are the particular geometric effects exhibited by Au-Pd at various alloy homogeneities.[10] At this last point, the catalyst synthesis route plays an important role in controlling metal deposition and ultimately the alloying degree in bimetallic particles.

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Indeed, incomplete alloying of Au-Pd can be originated due to a faster reduction of Au, when employing sodium borohydride (NaBH_4), particularly if both catalyst precursors are dissolved in tandem.[8] Thus, if the aforesaid occurs, it is expected to encounter both Au and Au-Pd particles, rather than isolated Pd particles; such chemical behaviour, it is understood in terms of the redox potentials of Au (1.00 V) and Pd (0.62 V), which do not allow a galvanic reaction to occur for the electrodeposition of Pd, through the reduction of the PdCl_4^- ion, on the surface of Au.

In this context, the present paper is concerned with the synthesis and characterization of a low metal loading catalyst: Au-Pd/C. Data from two different carbon supported alloys, AuPd and Au_2Pd , is discussed. These alloy compositions were chosen for comparison, but also, in the case of the latter, to set a scenario where palladium is depleted due to its unavoidable dissolution during continuous operation of an ADMFC. To our knowledge, the electrocatalytic performance of such bimetallic alloy for methanol oxidation has not yet been investigated.

2. Experimental

Preparation of Au-Pd/C electrocatalysts

Carbon-supported AuPd nanoparticles with two different compositions [3:1] and [1:1], Au_2Pd and AuPd hereinafter, were synthesized by simultaneous chemical reduction of HAuCl_4 and Na_2PdCl_4 in presence of NaBH_4 as a reducing agent.

The Au_2Pd and AuPd nanoalloys were prepared by dissolving appropriate amounts of HAuCl_4 and Na_2PdCl_4 in 50 mL of deionized water, as summarized in **Table 1**. The two resulting aqueous solutions were then heated at 50°C under air atmosphere. In tandem, a protective agent was obtained by dissolving 300 mg of Polyvinylpyrrolidone (PVP40) in 100 mL of methanol. Afterwards, each of the two aqueous solutions containing the precursors were mixed, separately, with 50 mL of the solution containing PVP40 and kept under stirring under air atmosphere. These metallic admixtures were then chemically reduced by the drop-wise incorporation of 6 mL of a 66 mM NaBH_4 solution. All reagents were high purity, 99.99% or better, from Sigma Aldrich, except for NaBH_4 which was obtained from Fluka.

Table 1. The amounts of precursors weighed and expected compositions of Au-Pd particles synthesized in this study.

Sample	System	mmol Au	mmol Pd	mg HAuCl_4	mg Na_2PdCl_4
Au_2Pd	[3:1]	0.99	0.33	33.63	9.70
AuPd	[1:1]	0.66	0.66	22.42	19.41

The aforesaid procedure yielded two colloidal dispersions, AuPd and Au_2Pd . In order to obtain either of the supported bimetallic catalysts, AuPd/C or $\text{Au}_2\text{Pd}/\text{C}$, 1 g of carbon black (Vulcan XC72) were oxidized with 500 mL

of H_2O_2 (30wt%) at 40°C, and just before the carbon paste got dry, 1 mL of the corresponding colloidal dispersion was added, and then treated at 330°C under nitrogen atmosphere for 20 minutes.

Characterization Methods

X-ray diffraction (XRD) was carried out directly on the supported electrocatalysts using a Siemens D5000 diffractometer with a step of 0.1° from 5° to 90° 2θ , 5s/step; and employing a Cu $K\alpha$ radiation's wavelength of 1.541877 Å. Thermogravimetric analysis (TGA) was performed within a TGA Q500 from TA Instruments. The sample (*ca.* 20 mg) was heated in a platinum pan from room temperature up to 950°C at a temperature slope of $10^\circ\text{C}/\text{min}$ and with a constant flow of 50 mL/min of N_2 . X-ray fluorescence (XRF) measurements were made in a Horiba XGT-1000WR spectrometer equipped with a Rh X-ray source and a high purity Si detector. A Jeol 100 CX was used for transmission electron microscopy (TEM) analysis of the bimetallic particles. For this purpose, a drop of each of the nanoparticle colloidal dispersions was placed separately on a copper grid and later dried for its observation under the microscope.

Electrochemical Measurements

Electrochemical characterization of the supported catalysts was conducted at room temperature ($20 \pm 0.5^\circ\text{C}$) in a three-electrode glass cell consisting of a platinum rod as counter electrode; a saturated calomel electrode (SCE) serving as reference; and carbon paper with an area of 1 cm^2 acting as working electrode. The reference electrode was fixed close to the working electrode through a Luggin capillary. The working electrode was produced by dropping a suitable amount of alcoholic sol containing the catalyst onto the carbon paper; such sol was prepared dispersing ultrasonically 20 mg of the carbon supported electrocatalyst in 0.5 mL of isopropanol to which 25 μL of 5wt% Nafion solution were added, during 20 minutes.

Cyclic voltammetry (CV) and electrochemical impedance (EIS) measurements were performed in 0.5 M NaOH in absence and presence of 1.0 M methanol, using a Voltalab Potentiostat/Galvanostat model PGZ 301. In both experimental scenarios, the electrolyte (0.5 M NaOH) was bubbled with high purity nitrogen gas for deaeration during one hour before initiating any electrochemical analysis. Whereas voltammogram curves were acquired at 50, 25 and 10 mV/s; impedance spectra were recorded at open circuit potential within the frequency range between 100 kHz to 10 mHz and the amplitude of the AC signal at 10 mV.

3. Results and discussion

Catalyst Characterization

Figure 1 shows the micrographs of the Au_2Pd and AuPd colloidal dispersions. A qualitative interpretation of TEM analysis through the micrographs (insets in **Fig. 1A** and **1B**) obtained from high angle annular dark field scanning transmission electron microscopy (Z-contrast) revealed that there was not just one single phase occurring in the colloidal dispersions, as would be expected; which is likely to result of an incomplete alloying process between Au and Pd during simultaneous chemical reduction. All of the above derived from the fact that under Z-contrast conditions, the micrographs exhibited several dots within the specimens in which the brightness was not similar.



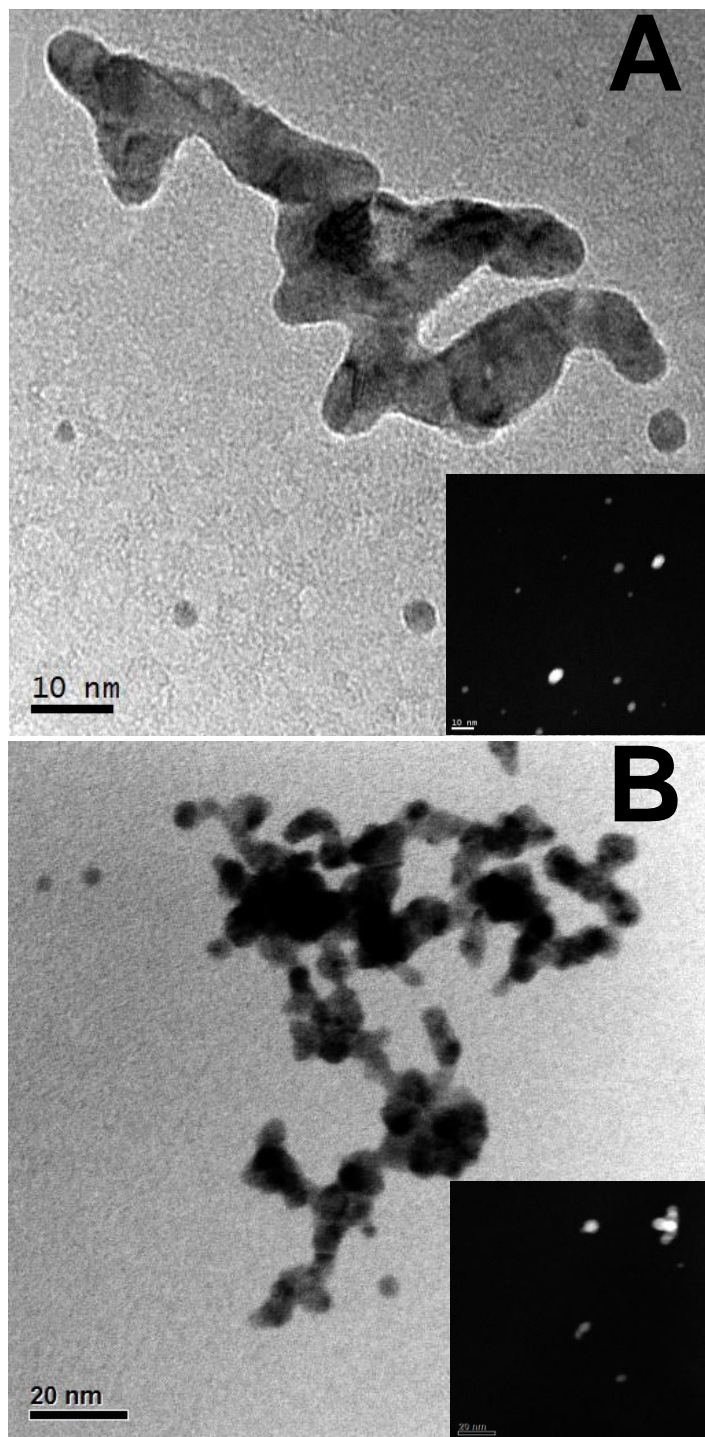


Figure 1. TEM images of the colloidal dispersions of: A) Au_2Pd ; and B) AuPd . Inset in each figure displays a HAADF-STEM micrograph of its corresponding system.



Since it was, therefore, important to verify the alloying degree in both bimetallic systems, XRD and XRF were exploited. **Figure 2** displays the XRD patterns of $\text{Au}_2\text{Pd/C}$ and AuPd/C . In both cases, the diffractograms revealed peaks that relate to the (111), (200), (220) and (311) planes indexed for Au (JCPDS 04-0784) and Pd (JCPDS 05-0681) in their face centered cubic structures. Although all of these XRD features observed in the diffractograms result of the sum of two single diffraction peaks, it was remarkable to notice an isolated reflection for tetragonal PdO, evolving from the convolution of its facets (002) and (101); such observation made clear that the asymmetric peak *ca.* 45° should also include a significant contribution from the (110) plane of PdO (JCPDS 75-0584). The unexpected occurrence of PdO is evidence of an inadequate catalyst supporting process, which did not avoid oxidation of the free metallic Pd, produced due to an incomplete alloying process. With respect to the carbonaceous catalyst support, the diffractograms allowed to identify unequivocally a broad band *ca.* 25° , attributed to the (002) plane of turbostratic carbon, which is clearly evident in both XRD patterns. Isolated reflections for Au-Pd (alloy) and PdO, *ca.* 39° and 32° respectively, were chosen to estimate the mean crystallite size according to the Debye-Scherrer equation. Peak fitting analysis correspondingly indicated crystallite sizes of about 5 nm and 19 nm for Au-Pd and PdO. Also using the results of the peak fitting analysis of the XRD patterns, the alloying degree in both catalysts was calculated using Vegard's law, based particularly on the position of the (111) peak for Au-Pd; since that is one of the two Au-Pd reflections free of contribution from PdO. According to the above, the atomic percent of alloying Au in $\text{Au}_2\text{Pd/C}$ was 77% and 64% in AuPd/C . These values were, however, in discrepancy with the XRF atomic compositions, as shown in **Table 2**. This provides further support to the abovementioned argument that sustains that oxidation of free metallic Pd gives rise to PdO; as a matter of fact, such difference among atomic compositions yields that 33% and 50% of the Pd within $\text{Au}_2\text{Pd/C}$ and AuPd/C , respectively, is in the form of PdO.

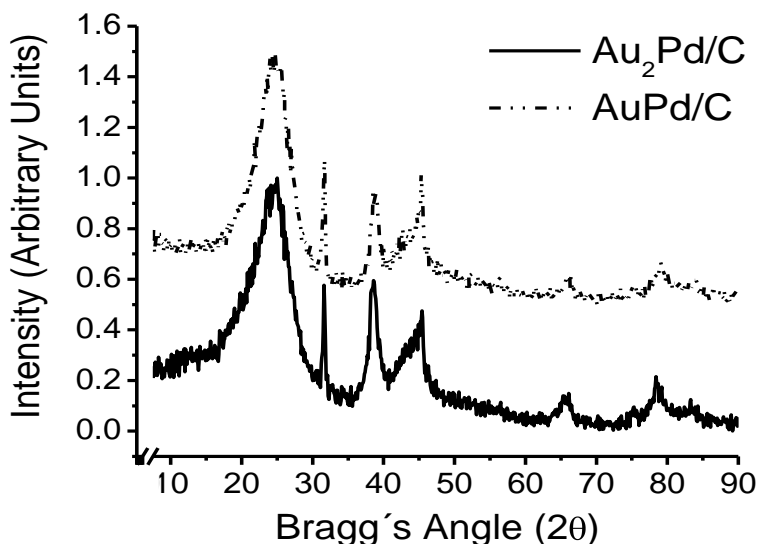


Figure 2. X-ray diffractograms of the bimetallic supported catalysts.



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

In order to determine the metal loadings of the two supported catalysts TGA was exploited. **Figure 3** presents the analytical thermograms of Au₂Pd/C and AuPd/C. Several insights were inferred through simple observation. In the case of Au₂Pd/C, it is evident an early weight loss that stabilizes around 100°C that, accordingly, it has been associated with water evaporation. Another drop, *ca.* 300°C, solely observed in Au₂Pd/C was attributed to a palladium hydride (PdH_x) that decomposes at such temperature, releasing hydrogen. Despite not being apparent in **Figure 2**, PdH_x was considered, since its corresponding XRD reflections could easily be obscured by the (111) and (200) peaks of Au-Pd. Besides, PdH_x could be feasibly produced *via* dissociation of BH₄⁻ ions and later absorption of chemisorbed hydrogen atoms into its lattice.[11] Then, a uniform behavior was observed for both catalysts, where full thermal decomposition of the carbonaceous support was achieved at 550°C; followed by the melting and ultimate conversion of PdO to Pd starting at 750°C.[12] Thus, based on the analytical thermograms, the actual metal loadings in Au₂Pd/C and AuPd/C were 4.56% and 5.56%, respectively. Note that, in virtue of the above, metal loadings were determined in the flat region situated between 550°C to 750°C with the aim of incorporating the mass contribution of PdO within the metal loadings of both catalysts.

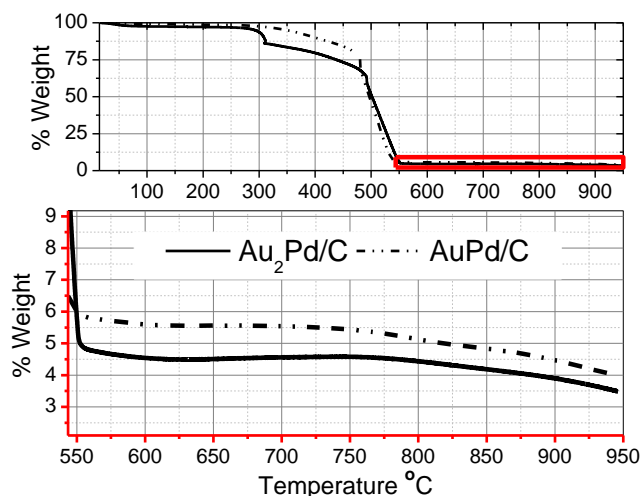


Figure 3. *Top*: Thermograms of Au₂Pd/C and AuPd/C. *Bottom*: Zoom in on the PdO decomposition region.

Table 2. Summary of relevant characterization results of the supported catalysts prepared in this study.

Sample	Composition		Components	Crystallite sizes (nm)		Metal loading
	Alloy	Atomic		Au-Pd	PdO	
Au ₂ Pd/C	Au _{0.77} Pd _{0.23}	Au _{0.67} Pd _{0.33}	Au-Pd, PdO; PdH _x ; H ₂ O; C	4.8	16.9	4.56%
AuPd/C	Au _{0.64} Pd _{0.36}	Au _{0.48} Pd _{0.52}	Au-Pd; PdO; C	5.6	21.6	5.56%



Electrochemical Performance

The cyclic voltammograms for the Au₂Pd/C and AuPd/C in alkaline media are shown in **Figure 4**. Whereas the main plot in **Figure 4** is intended to observe methanol electrooxidation; the inset within should display the characteristic hydroxyl (OH⁻) adsorption/desorption process.

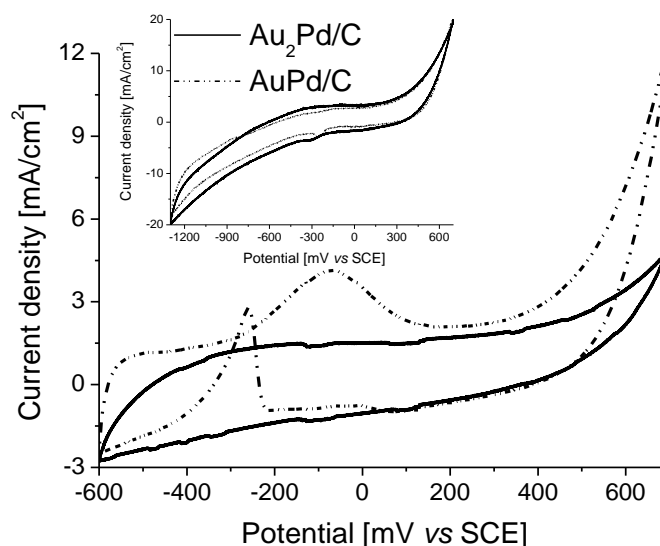
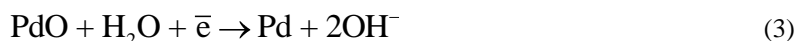


Figure 4. Cyclic voltammograms of methanol electrooxidation on the Au-Pd electrodes in 0.5 M NaOH solution containing 1.0 M methanol with a scan rate of 10 mV/s. *Inset*: Cyclic voltammetry of hydroxyl (OH⁻) adsorption/desorption in 0.5 M NaOH solution at 10 mV/s.

Although similar, both voltammograms presented in the inset in **Figure 4** revealed two distinct cathodic peaks *ca.* -300 mV, which were attributed to the reduction of PdO (**Reaction 3**), already present in both catalysts, as demonstrated by the XRD patterns. It is noteworthy that no clear evidence of sorption processes was found. Even though, the electrochemically active surface area (ECSA) was calculated for AuPd/C (434.9 cm²/mg) based on the PdO reduction peak; subsequently the electrocatalytic activity was only qualitatively assessed due to the significant uncertainty derived of the occurrence of PdO in the original composition of both catalysts and therefore the abovementioned value for ECSA of AuPd/C should be taken with caution.



At this point, and despite the lack of adsorption and desorption peaks; it was outstanding to observe in **Figure 4**, only for AuPd/C, the capability of promoting electrooxidation of methanol in alkaline media, even if it is at a higher onset potential (-437 mV) with respect to Pd/C (-590 mV).[13] Methanol oxidation in alkaline media has been characterized by two anodic peaks obtained during the forward and reverse scan. The former is usually related to the oxidation of freshly chemisorbed species from methanol adsorption; whereas the latter is fundamentally associated to removal of the carbonaceous species originated during the aforesaid chemisorption process.[13] It should be noted

that during cyclic voltammetries the forward sweep was restrained in order to avoid water oxidation that could lead to oxygen production, which ultimately would interfere. Therefore it was suffice to observe just one of the anodic peaks to verify the electrocatalytic activity of AuPd/C. Finishing with a detailed description of the cyclic voltammogram of methanol oxidation on the surface of AuPd/C, there is a broad anodic peak centred at -75 mV caused by the formation of an oxide of the alloy. The complementary cathodic peak corresponding to the reduction of the oxide of the alloy is diffuse, and roughly centred at 70 mV.

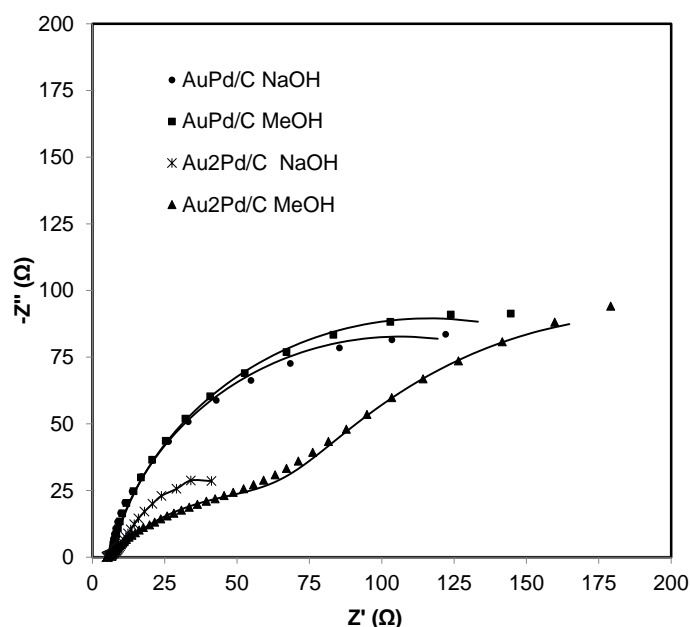
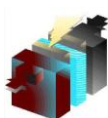


Figure 5. Nyquist plots of the EIS results obtained for Au₂Pd/C and AuPd/C in alkaline media, whether in presence or absence of methanol. Whereas experimental data is represented by dots; simulations are presented as solid lines.

Impedance results are shown in **Figures 5**. The EIS experimental data was simulated using ZPLOT software. The values obtained for the Charge Transfer Resistances (R_{CT}) and Constant Phase Elements (CPE) are summarized in **Table 3**, and the electric equivalent circuits used for the simulation are presented in **Figure 6**.

Table 3. Electrical elements and their values employed during simulations of the electrochemical data.

Sample	MeOH	R_{CT1} (Ω)	CPE_1 (F)	n	R_{CT2} (Ω)	CPE_2 (F)	n
Au ₂ Pd/C	(-)	109.60	0.0074	0.52	245	0.039	0.80
Au ₂ Pd/C	(+)	6	0.04	0.70	80	0.15	0.87
AuPd/C	(-)	200	0.057	0.87			
AuPd/C	(+)	220	0.042	0.87			



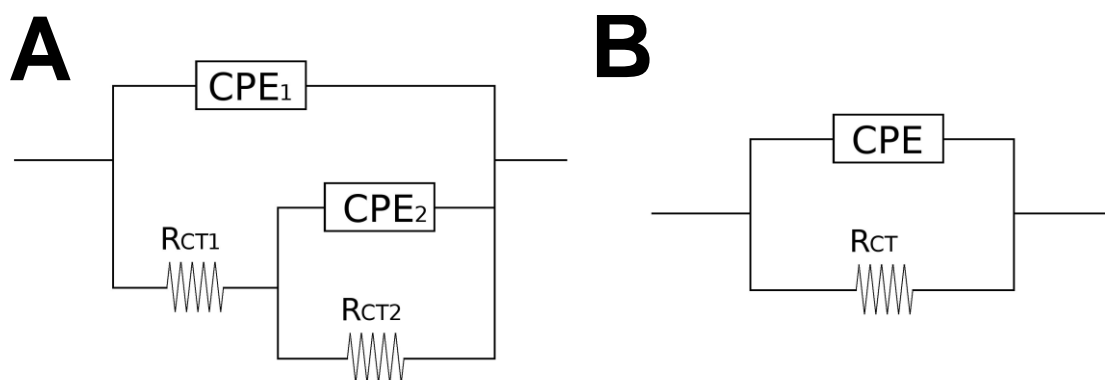


Figure 6. Electrical equivalent circuits used during simulations of the EIS results. A) $\text{Au}_2\text{Pd/C}$; and B) AuPd/C .

In both materials, a response controlled by a Faradaic process was observed. For the AuPd/C sample, the Nyquist diagrams in presence and absence of methanol were represented with a single semicircle slightly depressed. This response is typical for an electrode/electrolyte interface, where the charge transference between the catalyst and the chemical species in the electrolyte is accomplished in one single step. [14]. This behaviour is highly desirable in a catalyst, since as the number of steps involved in the oxidation/reduction of species diminishes, the overall kinetics of the process is increased.

A complete different scenario was observed in the $\text{Au}_2\text{Pd/C}$ sample where two overlapped semicircles were obtained. This response is attributed to two different processes associated to an additional interface comparable to the AuPd/C system. According to the TGA and XRD results of $\text{Au}_2\text{Pd/C}$, PdH_x is also occurring within the catalyst. As a matter of fact, PdH_x contributes to the EIS analysis, and is represented by the second semicircle present solely in $\text{Au}_2\text{Pd/C}$ impedances. This additional interface provides an additional opposition to the charge transference between the chemical species and the catalyst. This observation is in agreement with the voltamperometric analysis that shows a higher catalytic activity of AuPd/C with respect to $\text{Au}_2\text{Pd/C}$.

4. Conclusions

A complete characterization of $\text{Au}_2\text{Pd/C}$ and AuPd/C , prepared by co-reduction in aqueous solution, revealed that an inadequate thermal treatment during catalyst supporting process coupled to an incomplete alloying process yielded a significant amount of PdO in both systems. Nevertheless, and contrary to what it would be expected, AuPd/C demonstrated electrocatalytic activity to promote methanol oxidation in alkaline media, although at higher potentials than Pd/C on its own. In fact, cyclic voltammetry put forward nanostructured PdO , as the active phase in AuPd/C , rather than the bimetallic nanoalloy.

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

On the other hand, there was an implicit suggestion that the deficiency of palladium in Au₂Pd/C could be associated to a preferential reaction pathway, in which the occurrence of PdH_x is benefited over the reduction reaction, and ultimately the alloying process.

5. Acknowledgements

The authors would like to thank Jorge Ivan Carrillo Flores, Daniel Lardizábal Gutiérrez and Enrique Torres Moya from CIMAV, S.C. for the technical assistance provided throughout the present study.

This research was funded by the Public Education Ministry (SEP, México) through the PROMEP program under grant PROMEP/103.5/09/0424.

6. References

- [1] Bidault, F., et al., Review of gas diffusion cathodes for alkaline fuel cells. *Journal of Power Sources*, 2009. 187(1): p. 39-48.
- [2] Tripković, A.V., et al., Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions. *Electrochimica Acta*, 2002. 47(22-23): p. 3707-3714.
- [3] Antolini, E. and E.R. Gonzalez, Alkaline direct alcohol fuel cells. *Journal of Power Sources*, 2010. 195(11): p. 3431-3450.
- [4] Nutt, M.O. et al., Improved Pd-on-Au bimetallic nanoparticle catalysts for aqueous-phase trichloroethene hydrodechlorination. *Applied Catalysis B: Environmental*, 2006. 69(1-2): p. 115-125.
- [5] Palladiumprice. 06/02/2012]; Available from: <http://palladiumprice.org/>.
- [6] Goldprice. 06/02/2012]; Available from: <http://goldprice.org>.
- [7] Zhang, J. et al., Stabilization of platinum oxygen-reduction electrocatalysts using gold clusters. *Science*, 2007. 315: p. 220-222.
- [8] Park, S.Y. et al., The effective bimetallic component of Pd-Au/C for electrochemical oxidation of borohydrides. *Current Applied Physics*, 2010. 10(2): p. S40-S43
- [9] Zhou, W. and J.Y. Lee, Particle Size Effects in Pd-Catalyzed Electrooxidation of Formic Acid. *The Journal of Physical Chemistry C*, 2008. 112(10): p. 3789-3793.
- [10] Venezia, A.M. et al., Activity of SiO₂ supported gold-palladium catalysts in CO oxidation. *Applied Catalysis A: General*, 2003. 251(2): p. 359-368.
- [11] Phan, T-H and R.E. Schaak, Polyol synthesis of palladium hydride: bulk powders vs. nanocrystals. *Chemical Communications*, 2009. 45(21): p.3026-3028
- [12] Greenwood, N.N. and A. Earnshaw, *Chemistry of the Elements*, 1997. Butterworth-Heinemann, Oxford, UK.
- [13] S. S. Mahapatra and J. Datta, Characterization of Pt-Pd/C Electrocatalyst for Methanol Oxidation in Alkaline Medium, *International Journal of Electrochemistry*, 2011, Article ID 563495, 16 pages.
- [14] Zhang, J. et al., EIS-assisted performance analysis of non-noble metal electrocatalyst (Fe-N/C)-based PEM fuel cells in the temperature range of 23–80°C. *Electrochimica Acta*, 2009. 54(6): p. 1737-1743.

