



OXYGEN REDUCTION KINETIC PATHWAY ON PT AND PD COMPOUNDS SYNTHETIZED BY DIFFERENT METHODS

P. González Puente¹, L. M. Leal Gámez¹, B. Ruiz Camacho², M. Valenzuela Zapata²,
R. Vargas García³, Omar Solorza Fera⁴, R. González Huerta^{1*}

¹ESIQIE-IPN, Laboratorio de Electrocatalisis, C.P. 07738, México D.F. UPALM.

²ESIQIE-IPN, Laboratorio de Catálisis y Materiales, C.P. 07738, México D.F. UPALM.

³ESIQIE-IPN, Departamento de Metalurgia y Materiales, C.P. 07738, México D.F. UPALM.

⁴CINVESTAV-IPN, Departamento de Química, Av. IPN 2508, C.P. 07360 México D.F.

* contact email: rosgonzalez_h@yahoo.com.mx

ABSTRACT

Proton exchange membrane fuel cells (PEMFCs) are electrochemical power sources with different applications where vehicular, portable devices and stationary systems are included. The oxygen reduction reaction (ORR) is a sluggish complex cathodic reaction that proceeds via consecutive or parallel elementary steps. The aim of this work is to study the kinetics of the ORR on carbon supported Pd and Pt electrocatalyst synthesized by borohydride reduction (Pd/C) and liquid phase photodeposition (Pt/C-photo) methods. Rotating ring-disk electrode (RRDE) technique was used to evaluate the kinetics and selectivity of the ORR and elucidate the pathway reaction in acid media. Results conducted to establish that the best electrocatalyst was Pt/C-Photo because favor 96.5 % conversion of O₂ to water formation instead of 95.3 % on Pd/C. In both cases the kinetics occurs via a multielectron charge transfer process, *i.e.*, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$.

Key words: Electrocatalyst synthesis, Oxygen reduction reaction, PEMFC.



1. INTRODUCTION

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are electrochemical devices that convert directly, clean and efficiently the energy stored in the hydrogen into electricity. PEMFC could be used to supply the world energetic necessities instead of the indiscriminate use of fossil fuels. There remain several challenges, technical and economical which need to be overcome prior to fuel cell commercialization in general associated to cost, electrocatalysts performance and stability of the membrane electrode assemblies (MEAs) [1]. The oxygen reduction reaction (ORR) is relevant in the energy conversion in a PEMFC because it implies the promotion of the dissociation of the O–O bond at the electrode/electrolyte interface enhancing the rate of the cathode reactions, maintaining stability of the catalyst. The ORR is a sluggish complex reaction that proceeds via several consecutive and parallel elementary steps. It has been accepted to occur in two principal pathways: the first is the direct reduction to water with the transference of four electrons; the second is the so called peroxide pathway which involves the transfer of two electrons to the formation of hydrogen peroxide (H_2O_2) as intermediate. The second pathway is not preferable, because H_2O_2 is a powerful oxidant agent, it reduces the life time of the PEMFC. The aim of this work is to elucidate the kinetic mechanism of the ORR by quantifying the percentage of the hydrogen peroxide produced by using carbon supported Pd and Pt compounds, produced by different routes of synthesis [2-5], recently developed by our group of research.

2. EXPERIMENTAL

2.1. Electrochemical Characterization

In a previous communication, we reported preliminary results concerning to the synthesis, physical and electrochemical characterization of Pt and Pd compounds described in this work [6-12]. Pd nanocatalyst has been synthesized by a NaBH_4 reduction of PdCl_2 in 50 ml H_2O , following the methodology reported in the literature [6-8]. Vulcan carbon supported Pt catalysts

(Pt/C) was prepared by liquid phase photo-deposition, LPPD, being $C_{10}H_{14}O_4Pt$ ($Pt(acac)_2$) the chemical platinum precursor (see Table 1) [9-12].

Table 1. Methodology for the synthesis of Pd and Pt electrocatalysts

Samples	Catalyst	Synthesized method
M1	Pd/C-400°C	Reduction of $PdCl_2$ supported in thermally-treated Vulcan carbon® at 400°C
M2	Pt/C-Photo	liquid phase photo-deposition

All electrochemical experiments were performed in a single, conventional three-electrode electrochemical cell in a 0.5M H_2SO_4 solution at 25°C. A platinum mesh was used as the counter electrode, and $Hg/Hg_2SO_4/0.5M H_2SO_4$ (MSE=0.680 V/NHE) as the reference electrode. Experiments were performed in a Potentiostat AutoLab PGSTAT12 and a Pine MSR-X rotation speed controller. The electrode potentials were referred to normal hydrogen electrode (NHE). Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques were employed for the purpose of determining the main reaction pathway and quantify the amount of hydrogen peroxide produced during the oxygen reduction reaction. For RDE experiments, 8 μl of a sonicated mixture of 1mg of catalyst, 60 μl of ethyl alcohol (spectrum grade), and 6 μl of 5wt% Nafion® solution (Du Pont, 1000EW) were deposited on a glassy carbon electrode (GC) with a cross-sectional area of 0.19 cm^2 . The estimated amount of catalyst on the GC surface was about 0.63 $mg cm^{-2}$. For RRDE experiments, a commercial RRDE-PAR glassy carbon disk (diam=4.57 mm), and platinum ring with $N=0.21$ of nominal collection efficiency. The catalytic ink was prepared with 1mg of catalyst, 8 μl of 5 wt% Nafion® solution (Du Pont, 1100 EW), 100 μl of water and 100 μl of ethyl alcohol (spectrum grade). 8 μl of this suspension were deposited on the disk of working electrode surface. The estimated amount of catalyst on the electrode surface was about 0.20 $mg cm^{-2}$.

Before the ORR measurements, cyclic voltammetry (CV) was performed from 0.1 to 1.25 V at 50 $mV s^{-1}$ in a nitrogen-saturated electrolyte, to activate the electrode surface. Forty cycles were necessary to stabilize the current–potential signal. Thereafter, the acid electrolyte was

saturated with pure oxygen and the flux maintained above the electrolyte surface during the RRDE tests. Hydrodynamic experiments were recorded in the range of rotation rate from 100 to 900 rpm at 5 mVs^{-1} . Between RRDE measurements, the acid electrolyte was saturated with pure oxygen for 5 minutes to attain the stable open circuit potential. Kinetic parameters were estimated using the geometric surface area of the working electrode.

3. RESULTS AND DISCUSSION

3.1 The cyclic voltammetry

Cyclic voltammetry (CV) has become a very popular technique for initial electrochemical studies of new system, and has proved be very useful for electrode surface activation and obtaining information about stability and distribution of the actives sites on the catalytic electrode surface. The cyclic voltammetry characterization of the electrodes was performed in a nitrogen-saturated $0.5 \text{ M H}_2\text{SO}_4$ solution, at 50 mV s^{-1} . In this experiment, each electrode was submitted to 40 cycles in order to obtain electrochemical information mentioned above. Figure 1 show voltamperometric responses of samples described in table 1 and designed as M1 and M2.

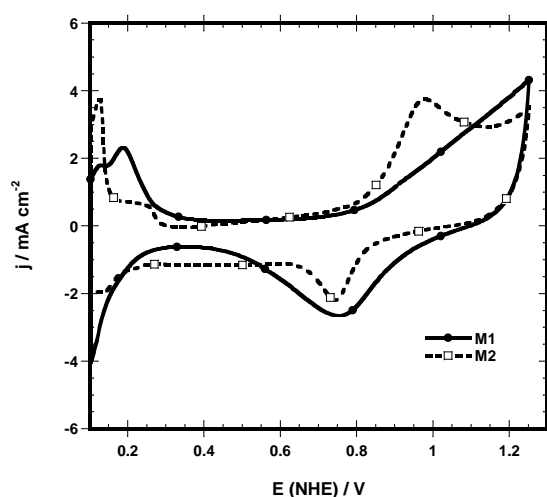


Figure 1. Voltammograms of M1 (Pd/C) and M2 (Pt/C-photo) samples, in N_2 saturated $0.5 \text{ M H}_2\text{SO}_4$ at 25°C

Both catalysts showed peaks associated with hydrogen adsorption/desorption around of 0.1 and 0.25 V (NHE), before to the hydrogen evolution. Between 0.25 and 0.45 V (NHE), the observed currents are associated to the charge of the electrolytic double layer. Above 0.45 V (NHE), oxygen chemisorptions begins and above 1.20 V (NHE), oxygen evolution takes place. As the potential is reversed to cathodic direction, the chemisorbed oxide layer is reduced between 1.0 and 0.5 V (NHE). The reduction peaks of M1 show a slight difference in the current magnitude. As well known, the peaks intensity is due to the distribution of the electrocatalytic sites on the electrode surfaces.

3.2 Rotating disk electrode, RDE.

Figure 2 shows RDE experiments, where the polarization curves were performed after activation at different rotation rates in oxygen-saturated 0.5M H_2SO_4 solution at 25°C.

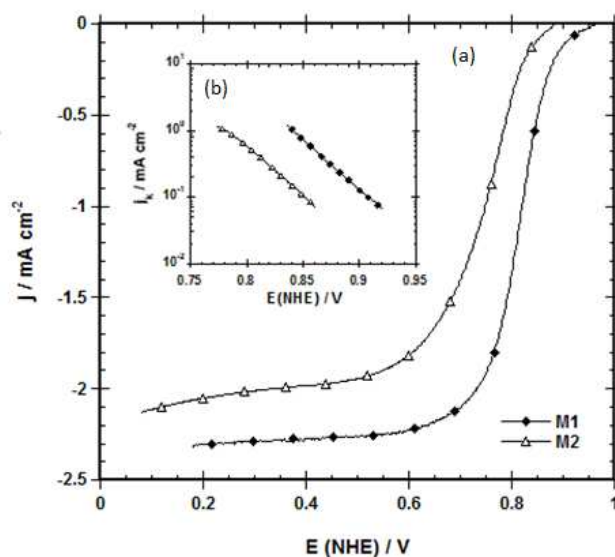


Figure 2. The polarization curves of RDE: a) Curves at 1600 rpm; Inset b) Mass transfer corrected Tafel plots of oxygen saturated 0.5 M H_2SO_4 solution.

The polarization curves show three well defined potential zones: charge transfer, mixed and mass transport. The variation of the polarization curves measured at 1600 rpm is shown in figure 2 (a). The disk currents reached a plateau of the diffusion limited currents. These curves indicate

that the M1 (Pd/C-400°C) is more active than the M2 (Pt/C-Photo) for the ORR. Inset of figure 2, the mass transfer corrected Tafel plot, deduced from analysis of polarization curves is observed, corrected by using the following equation [12]:

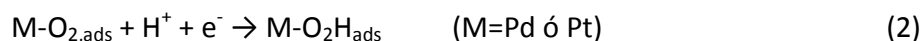
$$j_K = \frac{j^* j_L}{j_L - j} \quad (1)$$

where j is the measured current density, j_k the kinetic current density and j_L the limited current density. In all cases the Tafel plots show a linear behavior in the mixed activation–diffusion region. It is also observed from the Tafel plots that the overpotential decreases in the M1 sample. A Tafel slope of 70 mV dec^{-1} was deduced for M1 and 73 mV dec^{-1} for M2. At 0.1 mA cm^{-2} there are about 50 mV at which the cathode overpotential decreases for the ORR reaction on M1 in comparison to that observed on M2. Values of the kinetic parameters determined from figure 2, are summarized in Table 2.

Table 2. Kinetic parameters from carbon supported Pd and Pt electro-catalysts for the ORR in 0.5M H_2SO_4

Samples	E_{ca} V/NHE	$-b$ mV dec^{-1}	α	j_o mA cm^{-2}	Potential / V $j = 0.1 \text{ mA cm}^{-2}$	% H_2O_2	V
M1	0.95	70	0.83	2.28×10^{-5}	0.90	4.8	0.55
M2	0.9	73	0.80	7.31×10^{-5}	0.85	3.8	0.40

It has been reported that Tafel slope at low current density corresponds to the first electron transfer to the adsorbed oxygen and represents the rate-determining step [13-14]:



3.3 Rotating ring- disk electrode, RRDE.

The ORR is a complex reaction that proceeds via several consecutive and parallel elementary steps. It has been accepted that this occurs along two principal pathways: the first is

the direct O_2 reduction to water formation with $4e^-$ transfer; the second is the so-called “peroxide pathway”, which involves the transfer of $2e^-$ to H_2O_2 formation as intermediate. In this study, the RRDE technique was used to determine the amount of hydrogen peroxide produced. The collection efficiency (N) was obtained experimentally from the slope of an i_R versus i_D plot at different rotation speeds, using 5×10^{-3} M $K_3Fe(CN)_6$ solution in 0.1 M K_2SO_4 . A value of $N = 0.16$ was deduced from the thin film deposited on the glassy carbon electrode. The ring potential was kept at +1.48V (NHE) during all of the electrochemical experiments, where oxidation of the H_2O_2 formed by O_2 reduction on the disk electrode is detected in the ring. Steady-state polarization curves under hydrodynamic conditions obtained for the ORR in the disk, and the currents of the hydrogen peroxide oxidation in the ring on M1 and M2 electrodes are shown in Figure 3 (a) y (b). In the oxygen saturated solution, in both cases currents in the disk and ring are observed as a function of rotation speed.

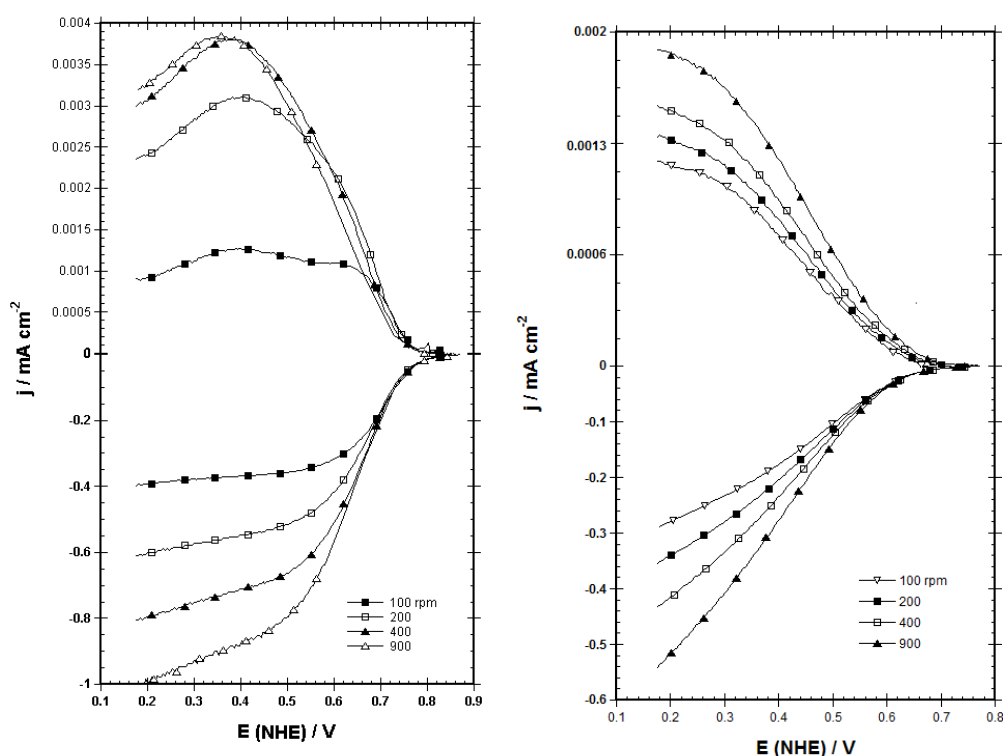


Figure 3. Steady state polarization curves at different rotation speed as a function of disk potential for ORR in 0.5 M H_2SO_4 at 25 °C, Pt ring held at 1.45 V/NHE a) M1 (Pd/C-400°C) disk and b) M2 (Pt/C-Photo) disk.

The disk currents did not reach a perfect plateau of the diffusion limited currents, and this is due to the small amount of catalyst (0.20 mg cm^{-2}) of the thin film formed on the glassy carbon electrode with the catalytic ink, but it is clearly defined its dependency with the rotating speed. The peroxide percentages were evaluated from the following equation [15]:

$$\%H_2O_2 = \frac{200 I_R/N}{I_D + I_R/N} \quad (3)$$

The amount of H_2O_2 produced with the electrode potential in the electrochemical process of the ORR reaches a value of 4.8 % at 0.55 V/NHE on M1 (Pd/C-400°C) electrode, while on M2 (Pt/C-Photo) electrode a value of 3.8% at 0.40 V/NHE is attained. These results indicate that M2 has a yield near 96.5 % of H_2O ($\%H_2O = 100 - \%H_2O_2$), following preferentially the four-electron transfer mechanisms to water formation (*i.e.*, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$), being as shown in Figure 4, M2 (Pt/C-Photo) the best electro-catalyst for the ORR in sulfuric acid media.

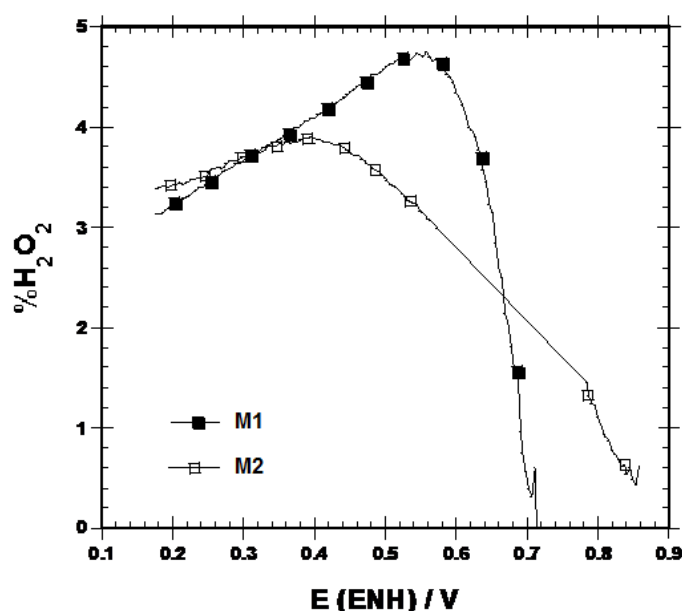


Figure 4. The potential dependence on the hydrogen peroxide formation in acid media.

4. CONCLUSIONS

For the ORR on samples M1 (Pd/C-400°C) and M2 (Pt/C-Photo), at potentials lower than 0.7 V, there is strong potential dependence on the hydrogen peroxide formation. The amount of H₂O₂ produced reached a maximum of 3.8% on M2 (Pt/C-Photo) catalyst at 0.40 V/NHE, while the H₂O₂ produced on M1 (Pd/C-400°C) catalyst was 4.8 % at 0.55 V/NHE. The amount of intermediate produced in both cases suggests that the molecular oxygen was predominantly reduced to H₂O. The best electro-catalyst for the cathodic reaction in sulfuric acid media is M2 (Pt/C-Photo).

5. ACKNOWLEDGEMENTS

This work has been supported by the IPN under project SIP-20113593, SIP-20111338 and CONACYT project 130254.

REFERENCES

- [1] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Appl. Catal. B, **56**, 9 (2005).
- [2] J. Oiao, B. Li and J. Ma, J. Electrochem. Soc. B, **436**, 156 (2009).
- [3] A. Liu, Z. Brady, B. Carter, R. Litteer, B. Budinski, M. Hyun and J. Muller, J. Electrochem. Soc, **155**, 979 (2008).
- [4] D. Santa Rosa, D. Pinto, V. Silva, R. Silva and C. Rangel, Int. J. Hydrogen Energy, **32**, 4350 (2007).
- [5] C. Acharya, W. Li, Z. Liu, G. Kwon, C. Turner, A. Lane, D. Nikles, T. Klein, M. Weaver, J. Power Sources, **192**, 324 (2009).
- [6] Monica Lizbeth Luna Martínez, “Síntesis y caracterización electroquímica de compuestos de paladio soportados en carbón tratado térmicamente para la reacción de de reducción de oxígeno”, Tesis de Licenciatura ESIQIE, 13 de agosto del 2010.
- [7] R.G. González-Huerta, M. L. Luna-Martínez, O. Solorza-Feria, ECS Transactions, **20**, 267 (2009).

- [8] R. González Huerta, P. González Puente, O. Solorza Feria, J. New Mat. Electrochemical System, **14**, 69 (2011).
- [9] José Adrián Pérez Galindo, “Síntesis y caracterización electroquímica de catalizadores de Pt/C para la reacción de reducción de oxígeno en medio ácido utilizando diferentes precursores de Pt”, Tesis de Licenciatura ESIQIE, 21 de Octubre del 2010.
- [10] B. Ruiz-Camacho, M. A. Valenzuela, J. A. Pérez-Galindo, F. Pola, M. Miki-Yoshida, N. Alonso-Vante, R. G. González-Huerta, J. New Mat. Electrochemical System, **13**, 183 (2010).
- [11] B. Ruiz Camacho, R. G. González Huerta, M. A. Valenzuela, Topics in Catalysis, **54**, 512 (2011).
- [12] M. en C. Beatriz Ruiz Camacho “Síntesis, caracterización y evaluación de catalizadores de Pt/semiconductor/C para la reacción de reducción de oxígeno”, examen de doctorado, ESIQIE-IPN, 24 Junio 2011.
- [13] K. Suárez Alcántara, A. Rodríguez Castellanos, S. Durón Torres, O. Solorza-Feria, Journal of Power Sources, **171**, 381, (2007).
- [14] G. Ramos-Sánchez a, A.R. Pierna b, O. Solorza-Feria, Journal of Non-Crystalline Solids, **354**, 5165 (2008).
- [15] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, J. Electroanal. Chem., 495 (2001) 134-145.