

# Microwave Assisted Synthesis of Ru<sub>3</sub>Pd<sub>6</sub>Pt Cathode Catalyst in a PEM Fuel Cell

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Received: November 05, 2012, Accepted: January 30, 2013, Available online: July 08, 2013

**Abstract:** Nanoparticles of Ru<sub>3</sub>Pd<sub>6</sub>Pt have been previously produced by different synthesis routes that involve high temperatures and relative high pressures and long time. The usage of a conventional microwave assisted synthesis reduces environmental risk impact as well as the cost effective production in large scale with minimum set up modifications. These features are the motivations for the use of microwaves in the synthesis of the Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst for PEM fuel cell applications to reduce the Pt loading. In this communication a tri-metallic electrocatalyst was produced by the reduction of the corresponding metallic salts, RuCl<sub>3</sub>, PdCl<sub>2</sub>, and H<sub>2</sub>PtCl<sub>6</sub> in ethylene glycol using a modified conventional microwave device. Oxygen reduction reaction kinetic analysis results conducted to a Tafel slope, ( $-b = 41.2 \pm 1.7$  mV dec<sup>-1</sup>) at low overpotential, and exchange current density ( $i_0 = 3.01 \pm 0.39 \times 10^{-5}$  mA cm<sup>-2</sup>) in 0.5M H<sub>2</sub>SO<sub>4</sub>. This electrocatalyst exhibited good performance and stability in a single H<sub>2</sub>/O<sub>2</sub> PEM fuel cell.

**Keywords:** Microwave assisted synthesis, Ru<sub>3</sub>Pd<sub>6</sub>Pt, oxygen reduction reaction, PEM fuel cells.

## 1. INTRODUCTION

Platinum and its alloys remain as the most currently used catalysts in acid-based proton exchange membrane fuel cells (PEMFCs), because of their ability to function under such harsh conditions. In literature reports has been focused on minimizing the amount of Pt used especially for cathodes that employ a high loading of Pt or to replace it with less expensive materials [1-3]. For this reason, a great deal of research has focused on the development of novel electrode materials as a replacement of Pt. In this direction, Ru and Pd based catalysts have demonstrated an active and selective oxygen reduction reaction (ORR), comparable with state-of-the art carbon supported Pt electrocatalyst. Ru and Pd compounds are not only about five times cheaper than Pt, but also more electrochemically stable compared with other transition metals such as Co and Fe. The utilization of hydrogen and oxygen in PEMFCs with novel membranes and electrocatalysts represent an appealing solution to our growing need of clean and renewable energy source and to our desire for protecting the environment.

In the present investigation, the synthesis and characterization of Ru<sub>3</sub>Pd<sub>6</sub>Pt is proposed in order fabricate a stable electrocatalyst and to enhance the catalytic activity of this compound for the ORR in acid media and in a single PEM fuel cell, comparable to the behav-

ior observed in each of its own nano-metallic elements. Different routes of synthesis of catalysts have been developed in our group of research and the drift has been to decrease the energy consumption, decrease the use of solvents and precursors, and reduce the time of synthesis. Microwave assisted synthesis is an option and is usually employed for production of nanostructured materials because of their easier and faster implementation than other techniques [4-5]. The microwave energy can be transferred directly to the reactive species [6], since the reactions could be carried out in reduced times [7-9]. In this work a conventional microwave oven with a minimum setup modifications were used for the preparation of a three metallic nanocatalyst. Results of electrochemical characterization conducted to a nanostructured Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst which could be considered as a good candidate for cathode catalyst in H<sub>2</sub>/O<sub>2</sub> PEM fuel cells.

## 2. EXPERIMENTAL

### 2.1. Electrocatalyst preparation

The trimetallic electrocatalyst [10] was produced on a conventional microwave oven by the reduction of corresponding metallic salts. The RuCl<sub>3</sub> (Aldrich, 3.8 mM), PdCl<sub>2</sub> (Aldrich, 7.9 mM), H<sub>2</sub>PtCl<sub>6</sub> (Aldrich, 1.5 mM) was added in 100 ml of ethylene glycol (Aldrich), as reported in literature [9]. The microwave oven was a conventional one (LG Model MS1147G) with a nominal frequency of 1250 Hz and kept under nitrogen bubbling. The solution was

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subjected to 15 cycles of 10s on and 20s off after boiling the solution was clear and dark particles were visible in the sediment of the flask. The maximum temperature registered was 190°C with an infrared thermometer. Then it was cooled at room temperature. The reaction product was washed several times with deionized water and acetone. Afterwards, the powders were dried overnight at 60°C and kept in a closed vessel. The resulted dark-fine powder was used for electrochemical measurements and physical characterization.

## 2.2. Physical characterization

X-ray diffraction was performed using a D8 Advance Diffractometer (Bruker) with monochromatic Cu K $\alpha$  radiation ( $\lambda=1.54\text{ \AA}$ ) in a measuring range of 35° to 90° of 20 degree with a step width of 0.02° min $^{-1}$ . The average particle sizes and crystallinity degree were estimated using Topas Academic software. Transmission electron microscopy were used to observe the particle morphology (JEOL-2200FS) operated at 200 kV equipped with energy-dispersive X-ray (EDX) spectroscopy used to obtain an average chemical composition of the catalyst.

## 2.3. Electrochemical characterization

Diverse techniques were used to determine the kinetic parameters of the ORR on Ru<sub>3</sub>Pd<sub>6</sub>Pt. A common half cell was used and equipped with a three electrodes system having a glassy carbon disc electrode ( $\phi=0.4\text{ cm}$ ) as the working electrode, a platinized titanium mesh as counter electrode and an Hg<sub>2</sub>/Hg<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> 0.5 M (0.68 V/NHE) as reference electrode. A 3.5  $\mu\text{l}$  aliquot was deposited on the electrode surface from a solution previously prepared with a mixture of 40 ml of ethyl alcohol (Aldrich, spectroscopic grade) and 5  $\mu\text{l}$  containing Nafion (5 wt.%, Du Pont, 1000 EW) and 1 mg of supported catalyst at 26% on Vulcan carbon. The estimated amount of catalyst on the glassy carbon electrode surface was about 0.164 mg cm $^{-2}$ . The electrolyte was prepared from sulphuric acid (Merck, 97%) and ultra pure water (Millipore, 18 MΩ cm). The electrochemical active electrode surface was determined by the CO<sub>2</sub> stripping technique, at 0.1 V/NHE by the saturation with CO<sub>2</sub> followed by the saturation with N<sub>2</sub> [10]. The potential was scanned from the starting potential to 0.05 V and then goes to 1.2 V. The sweep rate was 20 mV s $^{-1}$ . A cyclic voltammetry was applied where the solution was saturated with nitrogen high purity (99.997%, Infra) for 25 minutes, and the potential scan from the open circuit potential to 0.05 V and then returned to 1.2 V for a 50 cycles at scan rate the 100 mV s $^{-1}$ . After the solution was saturated with high purity oxygen (99.99%, Infra), RDE experiments were performed at scan rate 5 mV s $^{-1}$ . The hydrodynamic experiments were recorded in the rotation rate ranged from 100–1600 rpm. All the experiments were performed at room temperature (24°C), and measurements referenced to NHE.

## 2.4. Preparation and characterization of a MEA

The catalyst performance was tested in a commercial fuel cell test system (Compucell GT, Electrochem 890B) in a single cell with a geometric area of 5 cm $^2$  operated with H<sub>2</sub> and O<sub>2</sub> (99.999%) at 100 cm $^3$  min $^{-1}$ . The performance was obtained from 25° to 80°C. The humidification was maintained 5°C above cell temperature. A carbon cloth was used as diffusion layer in the cathodic side and a commercially available electrode in the anodic side (Pt, 0.5 mg cm $^{-2}$ , 20 wt% Pt/C, E-TEK). The cathodic ink was prepared from a

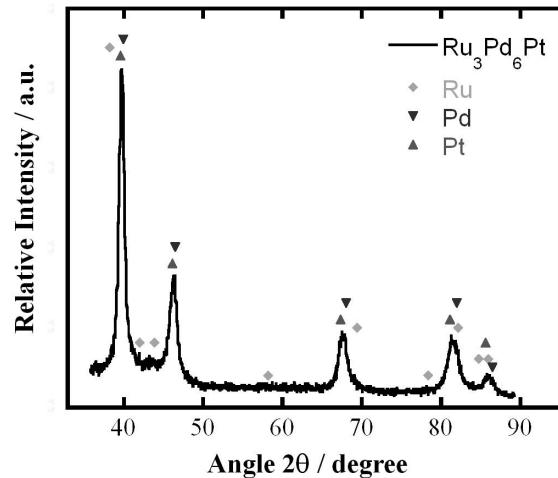


Figure 1. XRD pattern of the as synthesized Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst.

previously solution of 3750  $\mu\text{l}$  ethyl alcohol (Aldrich, spectroscopic grade) and 125  $\mu\text{l}$  Nafion (5 wt% solution, 1000 EW) and 10 mg of carbon dispersed catalyst at 40 wt%. The estimated amount of catalyst on the glassy carbon electrode surface was about 0.8 mg cm $^{-2}$ . The MEAs were prepared by spraying the corresponding ink onto cathodic side. Nafion® 115 (Du Pont®) was used as polymer electrolyte membrane, which was chemically pretreated according to the procedure described in references [13, 14]. The assembly was hot-pressed at 120°C and 11 kgf cm $^{-2}$  for 2 minutes.

## 3. RESULTS AND DISCUSSION

### 3.1. Physical characterization

The X-ray diffraction of the Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst is shown in Figure 1. The powder electrocatalyst showed five diffraction peaks at 20° of 40°, 47°, 67°, 81° and 87°, identified as single hexagonal fcc phase of palladium and in the same range for the single hexagonal fcc platinum. The experimental pattern matches well with the standard crystallographic tables JCPDS cards 01-065-2867 and JCPD 01-065-2868 for Pd and Pt, respectively. The peak on the 43° is attributed to Ru presence. Using Topas Academic Software a particle size was determined with 9 nm in average size.

A transmission electronic micrograph image is shown in Figure 2. It is observed a crystalline form immerse in an amorphous part. Analyzing the image in Digital Micrograph 5.0 an estimate of 7 nm of a particle size with spherical form was determinate. These results are in agreement with results from the XRD analysis. From EDX spectroscopy the average chemical composition estimated in atomic percent was 34.5 of Ru, 57.5 of Pd and 8 of Pt.

### 3.2. Electrochemical characterization

The cyclic voltammetry of the Ru<sub>3</sub>Pd<sub>6</sub>Pt electrode was characterized using the supporting electrolyte of H<sub>2</sub>SO<sub>4</sub> 0.5 M solution at 100 mVs $^{-1}$  scan rate under nitrogen purged conditions. In this experiment the electrode was submitted to 50 cycles in order to obtain a reproducible voltammogram.

Figure 3 shows corresponding voltammograms on Ru<sub>3</sub>Pd<sub>6</sub>Pt under nitrogen atmosphere before (gray line) and after (black line) the CO<sub>2</sub> stripping technique. Results show good-defined peaks

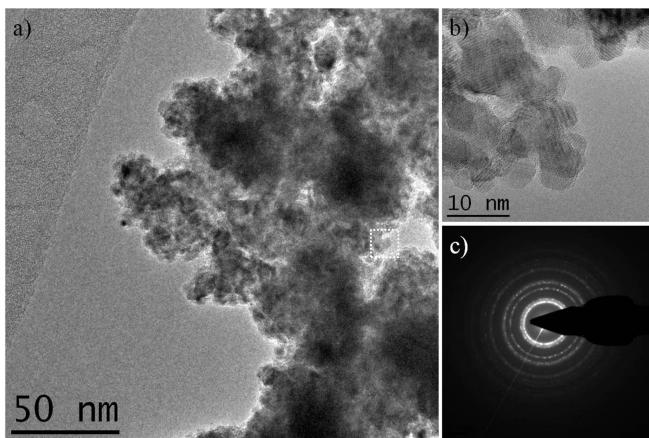


Figure 2. TEM images of: a) Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst, b) zoom from the dotted white box and c) diffraction electron pattern of the catalyst.

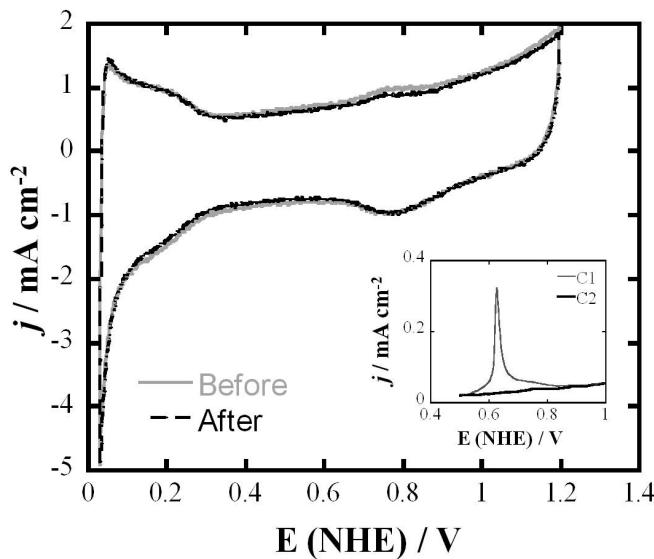


Figure 3. Cyclic voltammograms of Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst in 0.5 M H<sub>2</sub>SO<sub>4</sub> in O<sub>2</sub>-free atmosphere (gray line) before the CO stripping technique and after CO stripping (black line). Sweep rate 100 mV s<sup>-1</sup>. Inset: CO stripping after CO<sub>2</sub> adsorption on Ru<sub>3</sub>Pd<sub>6</sub>Pt at 0.15 V/NHE. Sweep rate 20 mV s<sup>-1</sup>.

associated with adsorption/desorption of hydrogen, characteristic on the polycrystalline noble metals. Also, observed characteristic peaks conclude us, the tri-metallic nano-electrocatalyst resistant towards the CO<sub>2</sub>. The CO<sub>2</sub> stripping technique was applied to know the electrochemically active surface area showed in an inset the figure 3 where a continuous line shows a base line. The EAS was used for the ongoing hydrodynamic experiments estimated by the equation (1).

$$EAS = \frac{Q}{m_c Q_{Ru_3Pd_6Pt}} \quad (1)$$

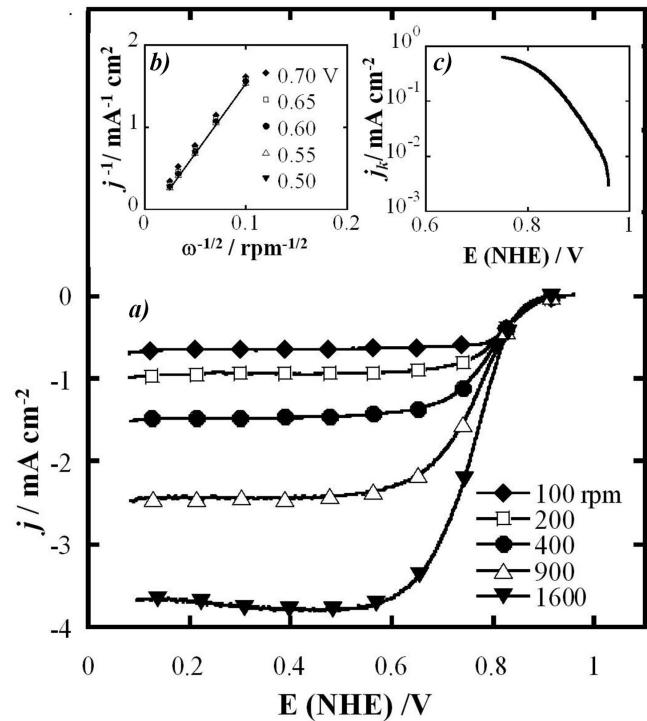


Figure 4. a) RDE plots for ORR on Ru<sub>3</sub>Pd<sub>6</sub>Pt in 0.5M H<sub>2</sub>SO<sub>4</sub> in O<sub>2</sub>-saturated atmosphere. b) Koutecky-Levich plot at different potentials and c) Mass transfer corrected Tafel plot.

Where  $Q$  is the integrated area under the CO<sub>2</sub> desorption peak,  $m_c$  is catalyst load and  $Q_{Ru_3Pd_6Pt} = 0.42 \text{ mC cm}^{-2}$  [12] is the charge associated with the CO<sub>2</sub> monolayer in the electrode surface. This value was taken into account considering that palladium is the major component of the catalyst. An EAS of 1.55 cm<sup>2</sup> where determined from the integrated curves and a roughness factor around 9.5 was estimated.

The hydrodynamic polarization curves of the Ru<sub>3</sub>Pd<sub>6</sub>Pt catalyst in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 4 a). A typical shape is observed with three different regions a kinetic control between the ocp to 0.8 V/NHE; a kinetic-diffusion controlled region between 0.8-0.7 V/ENH and finally a diffusion controlled region below 0.7 V/ENH. The Fig. 4 b) shows a Koutecky-Levich graph expressed by equation 2 [15-18] where a thin layer film is over the ink type electrode:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_D} \quad (2)$$

where  $J_k$  is a kinetic current density and  $J_D$  is a diffusion current density expressed by the term  $0.2 nFD^{2/3}C_{O_2} v^{-1/6} \omega^{1/2}$  where 0.2 is a constant used when the  $\omega$  is expressed in revolutions per minute,  $n$  is the number of exchanged electrons,  $F$  is a Faraday constant (96485 C mol<sup>-1</sup>),  $D$  is a diffusion coefficient of the molecular oxygen in H<sub>2</sub>SO<sub>4</sub> 0.5 M ( $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $v$  is the kinematic viscosity ( $1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ ) and  $C_{O_2}$  is the concentration of the molecular oxygen ( $1.1 \times 10^{-6} \text{ mol cm}^{-3}$ ) [19]. Mass-transfer corrected Tafel plot is show in a Fig. 4 c) determined by the equation 3 [15-16]:

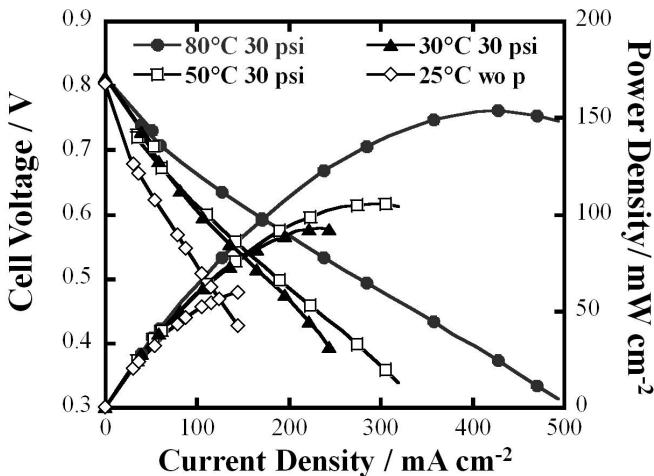


Figure 5. Single fuel cell performance of  $\text{Ru}_3\text{Pd}_6\text{Pt}$  cathode catalyst (40% wt)/C with catalyst loading of  $0.64 \text{ mg cm}^{-2}$  and anode of Pt (20 wt %)/C with catalyst loading of  $0.5 \text{ mg cm}^{-2}$ , operating with high purity  $\text{H}_2/\text{O}_2$  at temperatures from 25 to 80°C.

$$j_k = \frac{j - j_D}{j_D - j} \quad (3)$$

Kinetic parameters deduced from the straight line of the fig. 5 c), at low overpotential were Tafel slope of  $41.2 \pm 1.7 \text{ mV dec}^{-1}$ , transfer coefficient  $\alpha = 0.62 \pm 0.02$  and exchange current density  $j_0 = 3.01 \pm 0.39 \times 10^{-5} \text{ mA cm}^{-2}$ . From these results it is not possible to asseverate that a first electron transfer is the rate determining step for the ORR to water formation on  $\text{Ru}_3\text{Pd}_6\text{Pt}$  catalyst. Although kinetics pathway mechanism studies by the RRDE technique is now in progress.

### 3.3. Single fuel cell performance

Figure 5 shows the voltage-current density-power density performance curve of the  $\text{Ru}_3\text{Pd}_6\text{Pt}$  cathode catalyst dispersed in Vulcan Carbon and deposited by aspersion onto Nafion 115 using a commercial Pt ( $0.5 \text{ mg cm}^{-2}$  20wt%/C, E-TEK) as anode catalyst [20]. This figure exhibit a typically bell shaped response. The performance was obtained at different temperatures for the  $\text{Ru}_3\text{Pd}_6\text{Pt}$  cathode catalyst ( $0.64 \text{ mg cm}^{-2}$ , 40 wt%/C). The ocp registered were around a 0.8 V/NHE. The maximum performance obtained at 80°C and 30 psi with a flow rate  $100 \text{ cm}^3 \text{ min}^{-1}$  was  $153 \text{ mW cm}^{-2}$  which is lower in comparison to reported in literature. Efforts are now in route in order to improve the performance of the single fuel cell by modifying the technique of MEA preparation and the optimization of the catalysts loading.

## 4. CONCLUSIONS

The microwave assisted technique is a good method to synthesize nanosized catalysts where  $\text{Ru}_3\text{Pd}_6\text{Pt}$  catalyst with 7 nm in size was produced. Electrochemical results of the  $\text{Ru}_3\text{Pd}_6\text{Pt}$  catalyst for the ORR in 0.5M  $\text{H}_2\text{SO}_4$  can be considered as a promising low Pt content material which is required to overcome the challenges of

reduces the cost of the PEMFC. Cyclic voltammetry and RDE experiments conducted to determine an EAS of  $1.55 \pm 0.09 \text{ cm}^2$  from the  $\text{CO}_2$  stripping and kinetic parameters which promote the  $\text{Ru}_3\text{Pd}_6\text{Pt}$  catalyst as an outstanding candidate for PEM fuel cells applications.

## 5. ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the National Council of Science and Technology, CONACYT (grants FOINS-2250-6 and 101537) and Science and Technology Institute, ICYTDF (grant PICCO 10-3). FLN thanks CONACYT for the doctoral fellowship. Adolfo Tavira for XRD measurements and Vicente Paz del Angel for TEM micrographs.

## REFERENCES

- [1] N.A. Karim, S.K. Kamarudin, Appl. Energy, 103, 212 (2013).
- [2] G. Ramos-Sánchez, M.M. Bruno, Y.R.J. Thomas, H.R. Corti, O. Solorza-Feria, Int. J. Hydrogen Energy, 37, 31 (2012).
- [3] A.A. Gewirth, M.S. Thorum, Inorg. Chem., 49, 3557 (2010).
- [4] S. Song, Yi Wang, Pei Kang Shen, J. Power Sources, 170, 46 (2007).
- [5] S. Harish, S. Baranton, C. Coutanceau, J. Joseph, J. Power Sources, 214, 33 (2012).
- [6] B.L. Hayes, Aldrichimica Acta, 37, 66 (2004).
- [7] J.J. Salvador-Pascual, V. Collins-Martinez, A. López-Ortiz, O. Solorza-Feria, J. Power Sources, 195, 3374 (2010).
- [8] A. Sarkar, A. V. Murugan, A. Manthiram, Fuel Cells, 10, 375 (2010).
- [9] C. Grolleau, C. Coutanceau, F. Pierre, J.M. Leger, J. Power Sources, 195, 1569 (2010).
- [10] F. Leyva-Noyola, O. Solorza-Feria, Int. J. Electrochim. Sci., 7, 11389 (2012).
- [11] P. Nekooi, M. K. Amini, Electrochim. Acta, 55, 3286 (2010).
- [12] Ch. Yang, N.K. Van der Laak, K.-Yu Chan, X. Zhang, Electrochim. Acta, 75, 262 (2012).
- [13] K. Suárez-Alcántara, O. Solorza-Feria, Electrochim Acta, 53, 4981 (2008).
- [14] D.C. Martínez-Casillas, O. Solorza-Feria, ECS Transactions, 36, 565 (2011).
- [15] A. Cuesta, A. Couto, A. Rincón, M.C. Pérez, A. López, C. Gutiérrez, J. Electrochim. Chem., 586, 184 (2006).
- [16] A.J. Bard, L. Faulkner in Electrochemical methods: principles and applications. New York. Wiley, 2001, p. 341.
- [17] A. Velasco Martínez, M. Torres Rodríguez, M. Gutierrez Arzaluz, P. Angel Vicente, O. Solorza Feria, Int. J. Electrochim. Sci., 7, 7140 (2012).
- [18] A. Ezeta-Mejía, O. Solorza-Feria, H.J. Dorantes-Rosales, J.M. Hallen López, E.M. Arce Estrada, Int. J. Electrochim. Sci., 7, 8940 (2012).
- [19] C. Coutanceau, P. Crouigneau, J.M. Leger, C. Lamy, J. Electroanal. Chem., 379, 389 (1994).
- [20] D.C. Martínez-Casillas, G. Vázquez-Huerta, J.F. Pérez-Robles, O Solorza-Feria, J. Power Sources, 196, 4468 (2011).