

SYNTHESIS AND ELECTROCHEMICAL CHARACTERIZATION OF HIGHLY TOLERANT Pd ELECTROCATALYSTS AS CATHODES IN DIRECT ETHYLENE GLYCOL FUEL CELLS (DEGFC)

F.J. Rodríguez Varela^{1,*}, S. Fraire Luna¹ and O. Savadogo²

¹Grupo de Recursos Naturales y Energéticos, Cinvestav Unidad Saltillo, Carr. Saltillo-Monterrey Km. 13.5, Ramos Arizpe, Coahuila, C.P. 25900, México.

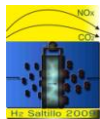
²Laboratoire d'Électrochimie et de Matériaux Énergétiques, École Polytechnique de Montréal, C.P. 6079, succ. Centre-Ville, Montréal, QC, H3C 3A7, Canada

*Tel (844) 438-9612, e-mail: javier.varela@cinvestav.edu.mx

ABSTRACT

Highly selective Pd electrocatalysts were synthesized by the formic acid method and evaluated as cathodes for DEGFC applications. In rotating disc measurements in acid medium, the Pd/C cathode showed important catalytic activity for the Oxygen Reduction Reaction (ORR). In the presence of ethylene glycol (EG, $C_2H_6O_2$), Pd/C exhibited an excellent electrochemical behavior and full tolerance to the organic molecule. No current density peaks associated to the EG oxidation reaction emerged and the shift in onset potential for the ORR (E_{onset}) toward more negative potentials was negligible on this cathode. Moreover, the evaluation of Pd/C in a DEGFC operating at 80°C demonstrated its high performance as cathode. As a comparison, commercial Pt/C was tested under the same conditions showing a limited selectivity for the ORR. The detrimental effect of EG on the Pt electrocatalysts resulted in high intensity current density peaks due to the oxidation of EG and a significant shift in E_{onset} . Given these results, it is expected that highly efficient Pd-based cathodes can find application in DEGFCs.

Keywords: Pd-based cathodes; Oxygen Reduction Reaction; tolerance to organic molecules; ethylene glycol as fuel; Direct Ethylene Glycol Fuel Cells

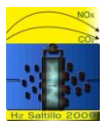


1.- Introduction

Direct Oxidation Fuel Cells (DOFCs) are an excellent alternative to H_2/O_2 PEMFCs in applications such as low-power electronic devices (lap-tops, PDAs, etc.) or stand-alone back up power systems. Nowadays, Direct Methanol and Ethanol Fuel Cells (DMFCs and DEFCs, respectively) are the most common fuel cells fueled with organic molecules, delivering high power densities at temperatures around 80 °C.^{1, 2, 3, 4} In recent years, very important technological constraints of the DOFCs have been overcome, one of the most important being the depolarization of anodes and cathodes based on Pt-alone electrocatalysts. The loss of catalytic activity of Pt during the electro-oxidation of small organic molecules results in significantly high anode overpotentials and lower fuel cell performances. Moreover, the crossover of small amounts of liquid fuel and/or reaction intermediates to the cathode side of the MEA causes a significant increase in cathode overpotentials and a considerably lower onset potential for the ORR when Pt-alone cathodes are used.^{1, 2, 3, 4, 5, 6, 7, 8, 9} Recently, the development of alcohol-tolerant cathode electrocatalysts allowed for a reduction in power density losses due to the presence of liquid substances in the cathode chamber of DOFCs.

Meanwhile, besides methanol and ethanol, ethylene glycol (EG, $C_2H_6O_2$) has been tested as organic fuel in DEGFCs. EG has a high solubility in aqueous solutions^{10, 11} and is safer to handle and as a fuel for fuel cell applications than methanol.¹² Moreover, $C_2H_6O_2$ is a non-toxic substance and has a high availability and low price compared to other fuels, which is a very important issue in the development of low-cost fuel cells. Furthermore, the complete oxidation of $C_2H_6O_2$ delivers 10 e⁻, i.e., more than CH_3OH (6e⁻) and it has been reported by Peled's group that the theoretical capacity of EG is higher than that of methanol (4.8 vs. 4 Ah/ml, respectively).¹² The same group has successfully worked on the development of high power density DEGFCs.^{13, 14, 15, 16}

However, the same problem related to poorly tolerant Pt-alone cathode electrocatalysts stands for DEGFCs, i.e., the detrimental effect of the crossover through the polymer membrane. In a recent communication, we have shown that the non-optimized $Pt_{40}Pd_{60}/MWCNT$ system has a high tolerance to EG.¹⁷ Moreover, the high degree of tolerance of commercial Pd/C electrocatalysts to such organic molecule was also demonstrated in our labs, although the catalytic activity of the Pd-alone cathode for the ORR in pure O_2 -saturated solution was lower than the activity of Pt/C.¹⁸ Under the experimental conditions, the performance of the Pt-alone electrocatalyst for the ORR was significantly reduced by the presence of EG in acid solution and the value of E_{onset} at this cathode was displaced nearly 450 mV towards more negative potentials in the presence of 0.125M EG.¹⁸



Thus, the development of highly selective and tolerant ORR cathodes is a key issue for the engineering of high performance DEFCs. The aim of this work is to study the performance of Pd electrocatalyst prepared by the formic acid method for the ORR without and with EG, and in DEFCs applications. Therefore, the electrocatalytic activity and selectivity of Pd/C for the ORR in the presence of EG are presented. Its performance as cathode material in a DEFC is evaluated and compared to that of a commercial Pt/C cathode. Further work currently being carried out at our labs is indicated.

2.- Experimental Section

2.1 Reagents

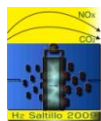
Palladium chloride (PdCl_2) and analytical grade $\text{C}_2\text{H}_6\text{O}_2$ and H_2SO_4 solutions were purchased from Aldrich. Pt/C powders were from E-Tek. Ultrapure 18.3 M Ω deionized water and high-purity N_2 and O_2 (AOC) were used during the experiments.

2.2 Synthesis of carbon supported Pd-based electrocatalyst

The investigated Pd/C electrocatalysts were prepared by the formic acid method.¹⁹ To prepare 2 g of the metallic electrocatalysts, Vulcan XC-72 (1600 mg) was sonicated and stirred in 240 ml of deionized water for 30 min to form slurry. The slurry was heated to 80°C and this temperature was kept throughout the synthesis process. Then, the required amount of the palladium precursor was added drop by drop under stirring and the solution was continuously agitated for 30 min. Afterwards, a volume in excess of 0.5M formic acid was slowly added to the solution containing the precursors, which was left at the preparation temperature overnight under stirring. Subsequently, the resulting suspension was left to cool to room temperature, filtered and thoroughly washed with deionized water. The nominal metallic loading of the electrocatalysts was 20 wt.% Pd/C.

2.3 Physicochemical characterization

The electrocatalysts were analyzed in a Philips X'Pert diffractometer (Cu K α radiation source, $\lambda_{\text{K}\alpha 1} = 1.54060$ Å). Diffractograms were taken over 10-80 degrees with 0.025 steps. Average particle sizes were obtained from the XRD measurements.



2.4 Catalytic ink and electrochemical set-up

Experimental details regarding the preparation of the catalytic ink have been described elsewhere.² A brief description of the procedure is as follows: separately, each of the electrocatalysts was sonicated in deionized water and Nafion solution (DuPont). Then, 10 μL of the solution was dispersed onto a polished glassy carbon disc (5 mm diameter). A bipotentiostat AFCBP1 from Pine Inst. was used to characterize the electrodes with a platinum mesh and a silver chloride (Ag/AgCl) as the counter electrode and the reference electrode, respectively. In this study, all potentials are reported vs. the standard hydrogen electrode (SHE). After activation of the electrocatalysts in deaerated electrolytes (with N_2), linear scan voltammetry (LSV) measurements taken under rotating conditions at 25 $^\circ\text{C}$ were performed in O_2 -saturated 0.5M H_2SO_4 or 0.5M $\text{H}_2\text{SO}_4 + (0.125, 0.25, 0.5 \text{ or } 1)\text{M C}_2\text{H}_6\text{O}_2$ solutions. The scan rate was 5 mV/s.

2.5 DOFC fixture

Cathodes containing Pd/C or Pt/C powders were fabricated in our laboratory by a catalytic ink method described previously.^{3, 20, 21} In order to complete the MEAs tested in the DEGFC setup, anodes containing commercial 20% PtSn/C (ETek) were prepared by the same procedure. In all cases, the catalyst loading was 1 mg/cm^2 . The polymer electrolytes were Nafion® 117. MEAs were fabricated by the hot-press method.^{20, 21} Galvanic polarization curves were obtained from a 2.25 cm^2 geometrical area fuel cell in a test station (FuelCon Evaluator). Throughout the tests, non-preheated ethylene glycol was pumped to the anode side without backpressure at a flow rate of 2 mL/min. The concentration of EG was 1 M. High purity O_2 at a flow rate of 0.5 L/min without backpressure was sent to the cathode chamber. The operating temperature of the cell was 80 $^\circ\text{C}$.

3.- Results and Discussion

3.1. Physicochemical characterization

The composition of Pd/C and Pt/C was evaluated by EDX. It was found that the composition in different microareas was lower than the nominal one. The results are shown in Table I. It should be kept in mind that these results correspond to an average composition and some of them were three times tested in order to verify their reproducibility. Figure 1 shows the XRD patterns of home-prepared Pd/C and commercial Pt/C. Both diffractograms display the characteristics of fcc Pt and Pd with peaks corresponding to the (111), (200) and (220) planes. The average particle sizes (d) calculated from the features of peak (220) using the Scherrer

equation^{2,3} and from TEM analysis (images not shown in this work) are presented in Table I. It can be seen that d corresponding to Pd/C is significantly larger than that of Pt/C. It can be concluded that one of the parameters that must be evaluated in order to synthesize Pd electrocatalysts with smaller average particle size and adequate metal/carbon weight ratio is the reducing agent, which should be strong enough to design electrocatalysts with small homogeneous particle size.

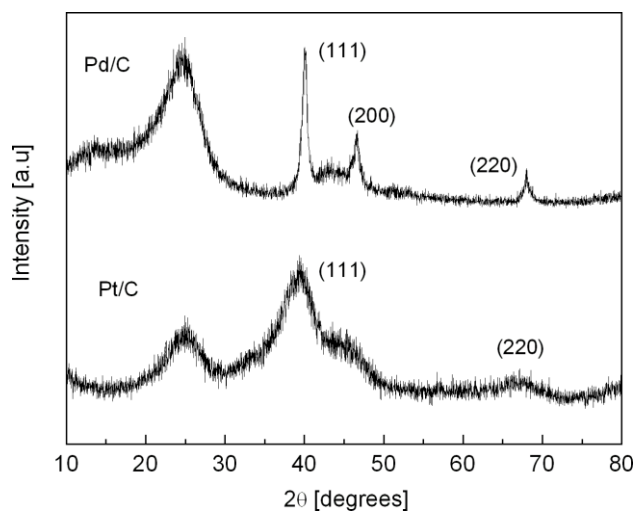


Figure 1. X-ray patterns of home-prepared Pd/C and commercial Pt/C.

Table I. Chemical composition and characteristics of supported Pd and Pt electrocatalysts.

Electrocatalyst	EDX (wt. %)	Particle size (nm)	
		XRD	TEM
Pd/C	13.5	10.1	9.7
Pt/C	14.1	2.2	2.4

3.2. Evaluation of ORR activity and tolerance to $C_2H_6O_2$

Figure 2 shows the linear scan voltammograms (LSVs) of the ORR without EG at Pd/C. The polarization curves show the increase in current densities at higher rotation rates. The LSVs show that the ORR on the

Pd/C electrocatalyst seems to be mostly under kinetic and mixed control in the potential region cycled, although an apparent plateau is reached at lower potentials.

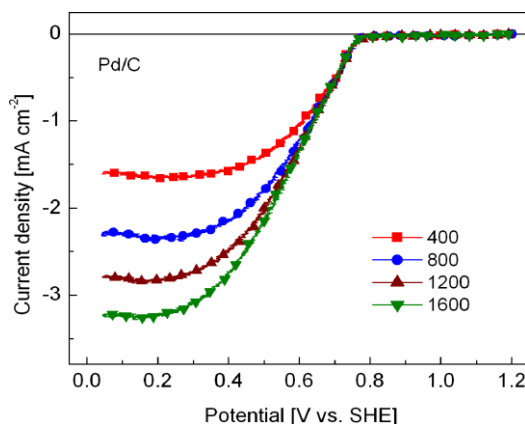


Figure 2. Polarization curves of the ORR at home-prepared Pd/C.

Electrolyte: 0.5M H₂SO₄. Temperature: 25°C. Scan rate: 5 mV/s.

The ORR disc current densities (j) can be related to the kinetic (j_k) and diffusional (j_d) current densities by using the well-known equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$1/j$ vs. $1/\omega^{1/2}$ plots at different potentials corresponding to the experimental values of Pd/C in Figure 2 are shown in Figure 3. As can be seen, the plots show linearity and parallelism, indicating first-order kinetics with respect to O₂.²² Also depicted in Figure 3 are the fitting of theoretical 4 and 2 e⁻ transfer reactions, calculated with the relationship:

$$B = 0.2nFD^{2/3}\nu^{-1/6}c_{O_2} \quad (2)$$

where 0.2 applies when ω is expressed in rpm, D is the diffusion coefficient of oxygen in sulfuric acid (1.4×10^{-5} cm²/s), c is the bulk concentration of oxygen (1.1×10^{-6} mol/cm³), ν is the kinematic viscosity of

the sulfuric acid (1.0×10^{-2} cm/s), F is the Faraday constant (96,500 C) and n is the number of electrons transferred.^{22, 23} Clearly in Figure 3, the slopes of the experimental data fit well with the $4 e^-$ theoretical slope, indicating that the ORR proceeds via an overall 4 electron transfer mechanism on the home-prepared Pd/C electrocatalyst.

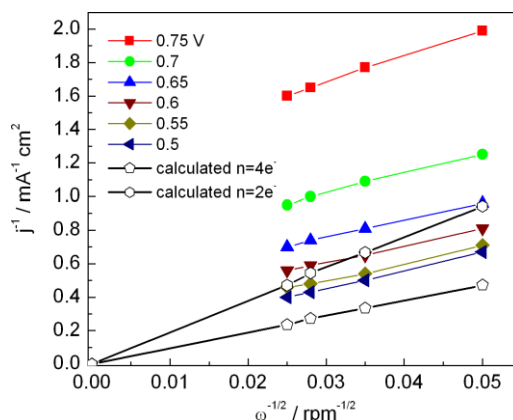


Figure 3. Levich-Koutecky plots corresponding to measured data of Pd/C (from Figure 2) and theoretical slopes for 4 and 2 e^- transfer reactions.

Figure 4 shows the LSVs of the ORR at Pt/C with $\omega=1600$ rpm without and with 0.125M EG. The detrimental effect of relatively small amounts of $C_2H_6O_2$ on the catalytic activity of Pt/C is important, with the curve in the presence of the organic molecule displaying a high peak current density due to the EG oxidation reaction at ca. 0.63 V vs. SHE. Moreover, the value of E_{onset} shifts nearly 0.65 V toward more negative potentials in the EG-containing solution related to its value without EG. Thus, the cathode overpotential at the Pt-alone material becomes appreciably higher in the presence of EG. Such low selectivity and poor electrochemical behavior of Pt/C in the fuel-containing solution is comparable to the loss in performance with ethanol² or methanol^{8, 24} shown by the same material and indicates the need for novel cathodes tolerant to EG in order to engineer high performance DEGFCs.

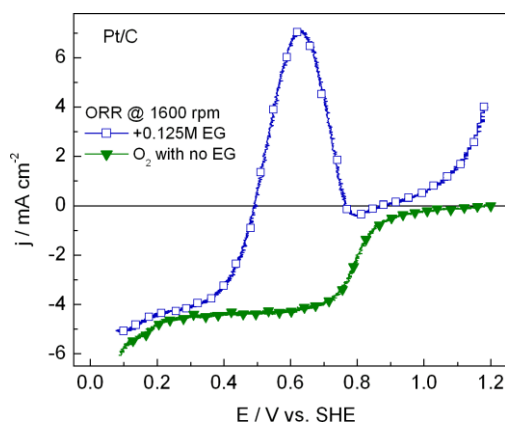


Figure 4. LSVs of the ORR in the absence and presence of 0.125M $C_2H_6O_2$ at Pt/C. Rotation rate: 1600 rpm. Electrolyte: 0.5M H_2SO_4 . Temperature: 25°C. Scan rate: 5 mV/s.

Figure 5 shows the LSVs of the ORR at Pd/C in acid solution containing increasing concentrations of EG (0.125, 0.25, 0.5 and 1M). The selectivity and full tolerance of the Pd electrocatalyst is demonstrated by a negligible shift in potential when EG is added to the electrolyte. For example, with 0.125M $C_2H_6O_2$ the potential shifts less than 10 mV at 0.2 mA/cm² related to the potential in EG-free solution, a very small value compared to a variation of nearly 530 mV at Pt/C at the same current density with the same amount of $C_2H_6O_2$ (Figure 4). Moreover, no peak current densities associated to the EG oxidation reaction emerged at Pd/C, indicating a low electrocatalytic activity of the cathode material for this anodic reaction.

This behavior suggests a zero or extremely low degree of adsorption of this organic fuel on the Pd catalytic sites. Similar results were reported elsewhere regarding the behavior of Pd and Pd-alloys in the presence of ethanol.²⁵ Such tolerance capacity gives important advantages to the family of Pd-based electrocatalysts as cathodes for DOFCs applications, i.e., highly tolerant Pd-cathodes may reduce the cathode overpotentials due to the crossover of liquid fuels and/or reaction intermediates through the polymer electrolyte, increasing the long term stability and allowing the fuel cell to deliver higher power densities.

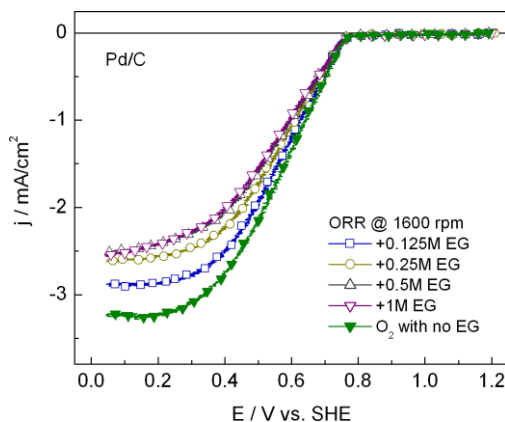


Figure 5. LSVs of the ORR in the presence of increasing concentrations of $C_2H_6O_2$ at Pd/C. Rotation rate: 1600 rpm. Electrolyte: 0.5M H_2SO_4 . Temperature: 25°C. Scan rate: 5 mV/s. The polarization curve without EG is also shown.

3.3 DEGFC performance

Figure 6 shows a comparison of the *current density vs. cell voltage* performance obtained from a DEGFC equipped with Pd/C or Pt/C cathodes operating at 80 °C. In both cases, PtSn/C anodes were used. All electrodes had a catalyst loading of 1 mg/cm² and were prepared as described in the experimental section. The fuel cell open circuit voltage with the Pd/C cathode is ca. 0.55 V, which is nearly 90 mV lower than that obtained with the Pt/C cathode. Also, at any given cell voltage, higher current densities are reached by the cell based on Pt/C. The lower performance of the Pd-alone cathode compared to the Pt electrocatalyst can in part be attributed to the large average particle size shown for this material in Table I. Long term experiments will be performed in order to evaluate the effect of EG crossover on the Pt/C and Pd/C cathodes. According to the behaviors seen in Figures 4 and 5, it is expected that the performance of Pt/C will decrease as the crossing of EG and/or intermediates increases. On the other hand, no negative effect of the crossover it is anticipated in the case of Pd/C.

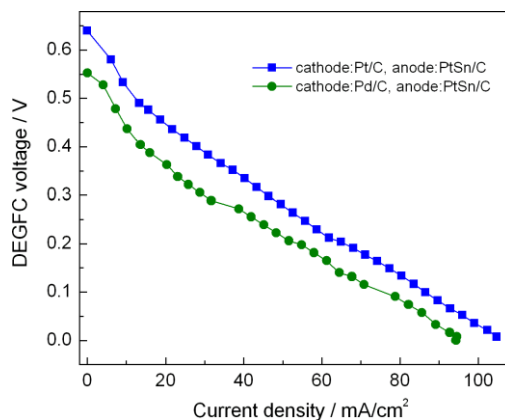
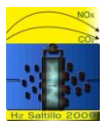


Figure 6. Polarization curves of the DEGFC equipped with Pd/C or Pt/C cathodes at 80 °C. Anodes: PtSn/C. Catalyst loading: 1 mg/cm². Membrane: Nafion® 117. EG concentration and flow rate: 1M and 2 mL/min. Oxygen flow rate: 0.5 L/min without backpressure.

4.- Conclusions

In this work we explored the use of Pd-based electrocatalysts as ethylene glycol-tolerant cathodes in half cell and complete fuel cell. The average particle size of Pd/C synthesized by the formic acid method determined by XRD and TEM analyses was considerably larger than that of commercial Pt/C. Stronger reducing agents such as sodium borohydride are currently being tested in our labs in order to control this parameter and obtain Pd powders within 2-5 nm particle size range. The Pd/C electrocatalysts showed a full tolerance to the organic molecule in acid medium, demonstrated by the fact that the onset potential of the ORR shifted insignificantly in the presence of EG, related to the value in the absence of the molecule. Moreover, no peak current density due to the catalytic oxidation of C₂H₆O₂ appeared at Pd/C during the scan, a behavior attributed to an extremely slow rate of adsorption of the molecule at the available Pd catalytic sites. The absence of oxidation peaks remained even at higher EG concentrations (i.e., 1M). In DEGFC tests, the cell based on a Pd/C cathode showed lower performance than the cell with Pt/C cathode. This difference can in part be attributed to the large particle size of Pd/C. However, important power densities were delivered when Pd/C was used. The electrochemical behavior of Pd-based electrocatalysts in the presence of ethylene glycol and ethanol in previous works suggests a multi-fuel capability of this family of materials, i.e., they can have high performances as cathodes in direct fuel cells fueled with a variety of liquid substances without being affected by the crossover effect.



5.- Acknowledgements

The authors wish to thank the National Council for Science and Technology (Conacyt-México) for financial support through Grant No. 52024.

6.- References

- ¹ A.S. Aricò, S. Srinivasan and V. Antonucci, *Fuel Cells* 1 (2001) 133.
- ² F.J. Rodríguez Varela and O. Savadogo, *J. Electrochem. Soc.* 155 (2008) B618.
- ³ F.J. Rodríguez Varela and O. Savadogo, *Asia-Pac. J. Chem. Eng.* 4 (2009) 17.
- ⁴ W.J. Zhou, W.Z. Li, S.Q. Song, Z.H. Zhou, L.H. Jiang, G.Q. Sun, Q. Xin, K. Pouliaitis, S. Kontou, P. Tsiakaras, *J. Power Sources* 131 (2004) 217.
- ⁵ O. Savadogo and F.J. Rodríguez Varela, *ECS Trans.* 1 (2006) 331.
- ⁶ T. Lopes, E. Antolini, F. Colmati and E.R. Gonzalez, *J. Power Sources* 164 (2007) 111.
- ⁷ E. Antolini, J.R.C. Salgado, L.G.R.A. Santos, G. Garcia, E.A. Ticianelli, E. Pastor, and E.R. Gonzalez, *J. Appl. Electrochem.* 36 (2006) 355.
- ⁸ H. Yang, C. Coutanceau, J.M. Léger, N. Alonso-Vante and C. Lamy, *J. Electroanal. Chem.* 576 (2005) 305.
- ⁹ J. Ling, G. Longtin and O. Savadogo, *Asia-Pac. J. Chem. Eng.* 4 (2009) 25.
- ¹⁰ R.B de Lima, V. Paganin, T. Iwasita and W. Vielstich, *Electrochim. Acta* 49 (2003) 85.
- ¹¹ V. Selvaraj, M. Vinoba and M. Alagar, *J. Colloid Interface Sci.* 322 (2008) 537.
- ¹² V. Livshits, A. Philosoph and E. Peled, *J. Power Sources* 178 (2008) 687.
- ¹³ V. Livshits and E. Peled, *J. Power Sources* 161 (2006) 1187.
- ¹⁴ S. Suarez, S.H. Chung, S. Greenbaum, S. Bajue, E. Peled and T. Duvdevani, *Electrochim. Acta* 48 (2003) 2187.
- ¹⁵ E. Peled, V. Livshits and T. Duvdevani, *J. Power Sources* 106 (2002) 245.
- ¹⁶ E. Peled, T. Duvdevani, A. Aharon and A. Melman, *Electrochem. Solid-State Lett.* 4 (2001) A38.
- ¹⁷ D. Morales-Acosta, L.G. Arriaga, L. Alvarez-Contreras, S. Fraire Luna and F.J. Rodríguez Varela, *Electrochem. Commun.* (2009), doi:10.1016/j.elecom.2009.05.019
- ¹⁸ F.J. Rodríguez Varela, S. Fraire Luna and R. Dabek Klapco, *J. New Mat. Electrochem. Systems* (2009), In press.
- ¹⁹ J.R.C. Salgado, E. Antolini and E.R. Gonzalez, *J. Power Sources* 141 (2005) 13.
- ²⁰ F.J. Rodríguez Varela and O. Savadogo, *J. New Mat. Electrochem. Systems* 9 (2006) 127.
- ²¹ F.J. Rodríguez Varela and O. Savadogo, *J. Electrochem. Soc.* 152 (2005) A1755.
- ²² G. Ramos-Sanchez, H. Yee-Madeira and O. Solorza-Feria, *Int. J. Hydrogen Energy* 33 (2008) 3596.
- ²³ K. Suárez-Alcántara and O. Solorza-Feria, *Electrochim. Acta* 53 (2008) 4981.
- ²⁴ V. Baglio, A. Di Blasi, C. D'Urso, V. Antonucci, A.S. Aricò, R. Ornelas, D. Morales-Acosta, J. Ledesma-Garcia, L.A. Godinez, L.G. Arriaga and L. Alvarez-Contreras, *J. Electrochem. Soc.* 155 (2008) B829.
- ²⁵ O. Savadogo and F.J. Rodríguez Varela, *J. New Mat. Electrochem. Systems* 11 (2008) 69.