

**SYNTHESIS AND EVALUATION OF Pt-ALLOYS SUPPORTED ON MWCNTs  
AS ETHYLENE GLYCOL-TOLERANT ORR CATHODES**

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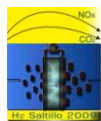
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**ABSTRACT**

In this work, a Pt-Co/MWCNT alloy (atomic ratio 70:30) was synthesized and evaluated as oxygen reduction reaction (ORR) cathode for Direct Ethylene Glycol Fuel Cells (DEGFC) applications. The alloy showed good performance for the ORR in acid medium, while in the presence of 0.125M EG (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) the MWCNTs-supported electrocatalyst showed a very high selectivity for the cathodic reaction and a high degree of tolerance to the organic fuel, i.e., a very small shift in the onset potential for the ORR,  $E_{onset}$ , and no peak current densities associated to the oxidation of EG, a detrimental effect of organic fuels normally observed in the case of Pt-alone electrocatalysts.

*Palabras clave: MWCNTs, Pt-alloys, ethylene glycol, Oxygen Reduction Reaction, Direct Ethylene Glycol Fuel Cells*



### 1.- Introduction

On the road to commercialization, highly performing and electrochemically stable Direct Alcohol Fuel Cells (DAFCs) must overcome several technical issues. One of the most important is the development and test of novel electrocatalysts as cathodes which must be highly active for the ORR, selective and tolerant to organic fuels. Pt-alloys have outperformed Pt-alone cathodes in this application due to their high degree of tolerance to organic molecules.<sup>1, 2, 3</sup> Such alloys show an electrochemical behavior where apparently no adsorption of liquid fuels on their surface takes place, thus preferentially adsorbing and promoting the reduction of O<sub>2</sub> at relatively low overpotentials.

Methanol is the most studied fuel in DAFCs, but this alcohol is toxic.<sup>4</sup> Hence, other liquid fuels are being proposed as an alternative to MeOH. Ethylene glycol is an interesting option due to its high theoretical capacity and because is markedly less dangerous than methanol.<sup>4, 5, 6</sup> However, it has been demonstrated that EG also permeates through commercially available membranes, leading to the same *crossover* predicament as seen in the case of ethanol and methanol.<sup>1, 5</sup> Related to this phenomena, recent studies show that Pt-Pd alloys or Pd-alone electrocatalysts uphold a superior performance for the ORR in EG-containing solutions related to Pt-alone materials, confirming the degree of tolerance of such cathode materials to the alcohol. This catalytic characteristics make them candidate materials for DEGFCs cathode applications.<sup>7, 8</sup>

The aim of this exploratory work is to study the behavior of a MWCNTs-supported Pt-Co alloy (atomic ratio 70:30) for the ORR in the presence of C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> in acid medium. Even though this may not be the optimized chemical composition of this alloy for the ORR, its electrochemical performance is presented and compared to that of a commercial Pt/C electrocatalyst.

### 2.- Experimental Section

#### 2.1 Synthesis of Pt-Co/MWCNT

The synthesis procedure by the impregnation-reduction method using NaBH<sub>4</sub> (Sigma Aldrich) has been described previously.<sup>9</sup>

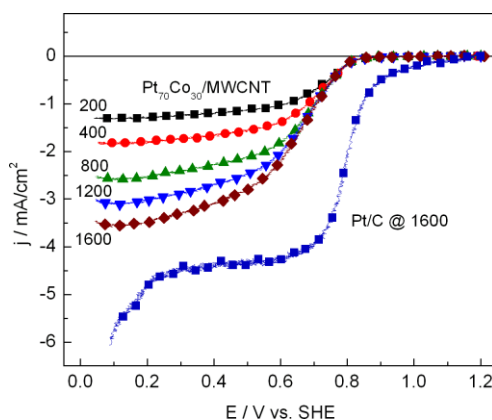
#### 2.4 Catalytic ink and electrochemical set-up

Experimental details regarding the preparation of the catalytic ink have been described elsewhere.<sup>10</sup> 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  $\mu$ L 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 °C were performed in  $O_2$ -saturated 0.5M  $H_2SO_4$  or 0.5M  $H_2SO_4 + 0.125M C_2H_6O_2$  solutions. The scan rate was 5 mV/s.

### 3.- Results and Discussion

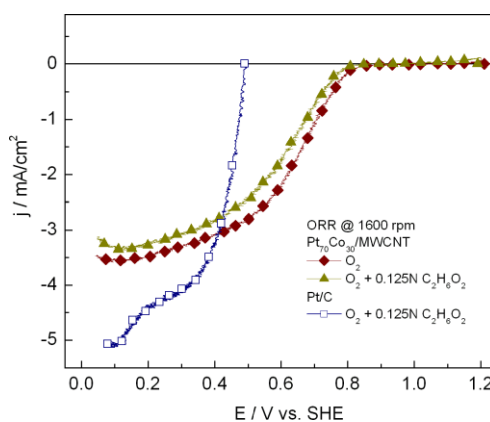
Figure 1 depicts the polarization curves of the ORR at Pt-Co/MWCNT at different rotating rates ( $\omega$ , in rpm). The expected increase in current densities at higher values of  $\omega$  can be clearly seen in the Figure. The curves can be divided in the three regions (kinetic, mixed and diffusional) normally observed for Pt-based electrocatalysts. For the sake of comparison, the LSV of the ORR at commercial Pt/C with  $\omega=1600$  rpm is also shown in Figure 1. The ORR current density at the Pt electrocatalyst is higher than that of Pt-Co/MWCNT with the same rotating rate. Moreover,  $E_{onset}$  is evidently higher on Pt/C than the value of  $E_{onset}$  on Pt-Co/MWCNT. Therefore, it is clear that the catalytic activity of Pt<sub>70</sub>-Co<sub>30</sub>/MWCNT for the ORR is lower than the activity of the Pt/C electrocatalyst.



**Figure 1.** ORR at home-prepared Pt-Co/MWCNT and commercial Pt/C.

Figure 2 shows the LSVs of the ORR ( $\omega=1600$  rpm) at Pt-Co/MWCNT in the absence and presence of 0.125M EG. It can be clearly observed that the presence of  $C_2H_6O_2$  do not change the shape of the polarization curve, an indication that the catalytic activity of the Pt-Co/MWCNT alloy for the ORR remains

unaffected in the solution containing the fuel. The LSV of the ORR in the presence of the same concentration of EG with Pt/C as the cathode is also shown in this Figure. Evidently,  $E_{onset}$  shifted to more negative values. Also, a high peak current density emerged with EG (not shown), a typical behavior of Pt/C when organic substances are present.<sup>1, Error! Bookmark not defined.</sup> Such poor behavior of the Pt/C electrocatalyst significantly increases the cathode overpotential, diminishing the efficiency of the fuel cell.



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

Electrolyte: 0.5M H<sub>2</sub>SO<sub>4</sub>. Temperature: 25°C. Scan rate: 5 mV/s.

#### 4.- Conclusions

The electrocatalyst showed a high activity toward the ORR, although its chemical composition is not optimized, as demonstrated by the fact that the performance this alloy was lower than Pt/C for this reaction. The tolerance characteristics to EG of the Pt-Co/MWCNT, however, are very important, sustaining a high performance in acid solution containing the organic molecule.

#### 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



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- <sup>1</sup> F.J. Rodríguez Varela and O. Savadogo, *Asia-Pac. J. Chem. Eng.* 4 (2009) 17.
  - <sup>2</sup> T. Lopes, E. Antolini, F. Colmati and E.R. Gonzalez, *J. Power Sources* 164 (2007) 111.
  - <sup>3</sup> 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.
  - <sup>4</sup> U.B. Demirci, *Environ. Int.* 35 (2009) 626.
  - <sup>5</sup> E. Peled, V. Livshits, T. Duvdevani, *J. Power Sources* 106 (2002) 245.
  - <sup>6</sup> V. Livshits, A. Philosoph and E. Peled, *J. Power Sources* 178 (2008) 687.
  - <sup>7</sup> F. J. Rodríguez Varela, S. Fraire Luna, R. Dabek Klapco, *J. New Mat. Electrochem. Systems* (2009) in press.
  - <sup>8</sup> F. J. Rodríguez Varela, S. Fraire Luna and O. Savadogo, *Energies* (2009) submitted.
  - <sup>9</sup> D. Morales-Acosta, L.G. Arriaga, L. Alvarez-Contreras, S. Fraire Luna and F.J. Rodríguez Varela, *Electrochem. Commun.* 11 (2009) 1414.
  - <sup>10</sup> F.J. Rodríguez Varela and O. Savadogo, *J. Electrochem. Soc.* 155 (2008) B618.