

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

**Fast Synthesis of M@Pt (M=Ru, Pd, Fe₃O₄) Core-shell Nanostructures and their Evaluation as Anodes for the
Oxidation of Ethanol**

N.M. Sánchez-Padilla¹, S.M. Montemayor¹, F.J. Rodríguez Varela^{2,*}

¹Depto. Materiales Cerámicos, Facultad de Ciencias Químicas de la Universidad Autónoma de Coahuila,
V. Carranza s/n, Saltillo, Coahuila, México, CP 25280

²Grupo de Recursos Naturales y Energéticos, CINVESTAV Unidad Saltillo,
Carr. Saltillo-Monterrey km. 13.5, Ramos Arizpe, Coahuila, CP 25900

*E-mail: javier.varela@cinvestav.edu.mx

ABSTRACT

We report the fast synthesis and electrochemical evaluation of M@Pt core-shell nanostructures (where M=Ru, Pd, Fe₃O₄) for the ethanol oxidation reaction (EOR). Separately, the chemical precursor of each core material was synthesized in NaBH₄ in a reduction time of 60 s. The Pt shell was deposited afterwards on the cores also in 60 s using the same reducing agent. Pt-alone nanoparticles were synthesized in one minute as well for comparison purposes. The XRD results indicate that crystalline materials can be obtained with this rapid process. The average particle sizes of the core-shell nanostructures, determined with the Scherrer equation, were in the 6-8 nm range for the nanomaterials. The electrochemical evaluation revealed that the catalytic activity of the novel Fe₃O₄@Pt anode for the EOR is as high as that of the Ru@Pt material. The Pt-alone and Pd@Pt anodes showed a lower activity for such reaction. Durability tests performed on the Fe₃O₄@Pt and Ru@Pt anodes indicated a high stability of these catalysts in acid medium.

1. Introduction

In a society where oil is the major energy source, higher demand and lower supply makes its price fluctuate. Moreover, its use contributes to the global warming. For these reasons, everyday there are more research groups dedicated to find new energy sources or innovating already existing. Hydrogen is one of the fuels that are a promising alternative and it can be used in fuel cells. However, some of the problems related to the use of H_2 are its handling, transportation, storage, and in general, the logistic of its use [1-3]. The use of liquid fuels in fuel cells without reforming (Direct Liquid Fuel cells) is a good energetic option [4-6]. Ethanol is a renewable fuel commonly mentioned as a potential candidate for this application in Direct Ethanol Fuel Cells (DEFC). It offers several advantages over other liquids fuels, including facile transportation, non-toxicity, high energy density and it can be obtained from simple industrial processes [7-10].

One of the biggest challenges for the use of ethanol in fuel cells with proton exchange membranes is the catalyst performance to execute the oxidation at the anode. Pt is widely used on these cells, however, the presence of CO as intermediate from alcohol oxidation decrease significantly its performance. Therefore, there is a growing interest to develop catalyst that can oxidize organic molecules at low potentials and are not affected by the reaction intermediates. Pt-based alloys and nanostructures have proved to be the best option to oxidize alcohols, specifically methanol and ethanol. These nanomaterials have been synthesized by various methods. Although nanocatalysts with good physicochemical and electrochemical properties have been obtained, most processes require long time of synthesis under stirring and/or reflux [2, 6, 11-14].

In this work, we report the fast (one minute reaction times) and efficient synthesis of Pt-alone nanoparticles and M@Pt core-shell nanostructures (where M = Fe_3O_4 , Pd and Ru), using the mechanical agitation method (UT) and $NaBH_4$ as the reducing agent. We evaluate the catalytic activity of such nanocatalysts for the EOR in acid medium.

2. Experimental

For this study $Fe(NO_3)_3 \cdot 9H_2O$, $PdCl_2$, $RuCl_3$ and $H_2PtCl_6 \cdot 6H_2O$ as metallic precursors, and $NaBH_4$ as reducing agent were used. All chemicals were purchased from Aldrich and used without further purification. To obtain the *cores*, solutions of $NaBH_4$ (0.001 M) and the metallic sources (0.002 M) were prepared. The metallic salt solution was added dropwise into the solution containing the reducing agent at room temperature and mechanically stirred (UT method). The obtained products were washed and separated by centrifugation at 3000 rpm. The powders were characterized by XRD to determinate the crystallite size and the structural parameters.

To obtain the core-shell nanostructures, the *cores* were suspended on a fresh reducing solution (0.001 M $NaBH_4$) and a $H_2PtCl_6 \cdot 6H_2O$ solution (0.002 M) was slowly added at room temperature under UT stirring. M@Pt materials in a



1:1 (w/o) Me:Pt ratio were obtained. The powders were washed and centrifuged at 3000 rpm. The catalysts were characterized by XRD.

The catalytic activity of the nanocatalysts for the EOR was evaluated with a potentiostat (Voltalab). CVs were obtained in N_2 -saturated solution. Studies of ethanol oxidation were carried out immediately after the activation with the addition of 10 mL of 0.5 M ethanol into the N_2 -saturated solution. The electrolyte was 0.5 M H_2SO_4 . All electrochemical measurements were taken at 20 mV/s and room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the cores. The diffractogram of Fe_3O_4 shows the formation of ferric-ferrous oxide with a spinel-type phase ($FeO \cdot Fe_2O_3$ PDF 89-0691). Meanwhile, the Pd pattern shows the formation of a polycrystalline material (PDF 46-1043). On the other hand, the diffractogram of Ru indicates the formation of a quasi-amorphous core.

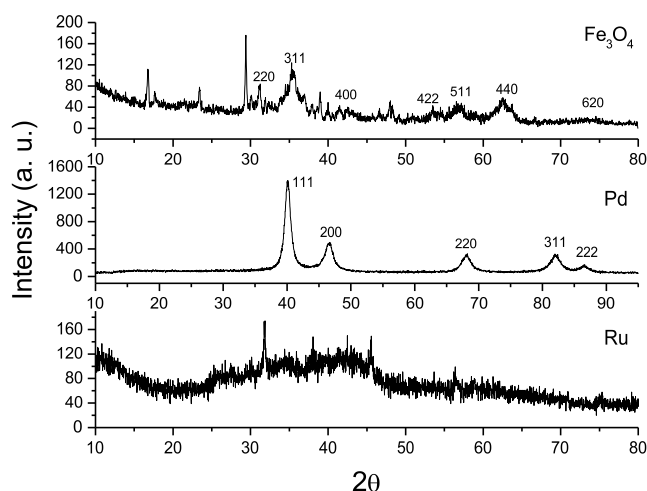


Figure 1. XRD patterns of the cores: Fe_3O_4 , Pd and Ru.

Figure 2 shows the XRD patterns of Pt-alone and the nanostructures (after deposition of Pt on the *cores*). In all cases the main peaks related to Pt (PDF 4-0802), with cubic structure and cell parameter $a = 3.9120 \text{ \AA}$, can be observed. The $Fe_3O_4@Pt$ material also shows the peaks related to magnetite. Because the sets of Pt and Pd are almost the same (both Pd and Pt have cubic structures and cell parameters likely 3.8930 vs 3.9120 \AA respectively), the diffractogram of the $Pd@Pt$ nanostructure indicates the planes related to Pt. Since the Ru material turned out to be quasi-

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

amorphous, only the peaks of Pt are present in the Ru@Pt diffractogram. The pattern of Pt-alone is also shown in Figure 2.

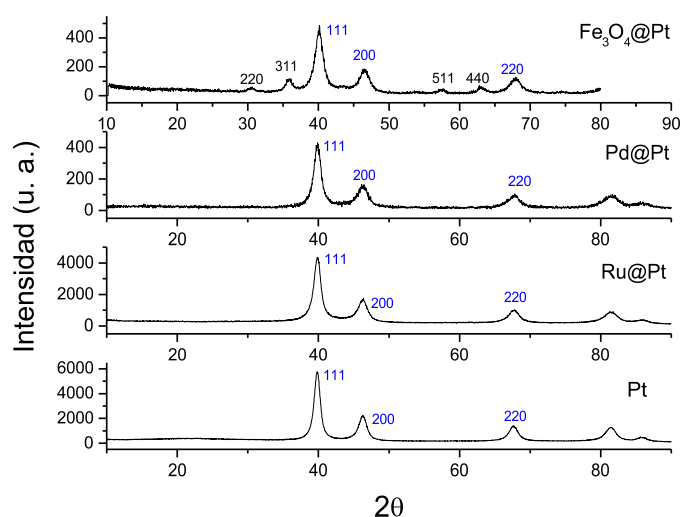


Figure 2. XRD patterns of the nanomaterials: $\text{Fe}_3\text{O}_4@\text{Pt}$, $\text{Pd}@\text{Pt}$, $\text{Ru}@\text{Pt}$ and Pt-alone.

Figure 3 shows the CVs of the EOR at the four nanomaterials. The catalytic activity for the anodic reaction decreases in the order $\text{Ru}@\text{Pt} > \text{Fe}_3\text{O}_4@\text{Pt} > \text{Pt} > \text{Pd}@\text{Pt}$. In the positive potential scan, maximum peak current densities of 3.2 mA/cm^2 and 2.9 mA/cm^2 are obtained from $\text{Ru}@\text{Pt}$ and $\text{Fe}_3\text{O}_4@\text{Pt}$, respectively. This means that the catalytic activity of $\text{Fe}_3\text{O}_4@\text{Pt}$ is close to that of the Ru-based anode. The activity of the $\text{Fe}_3\text{O}_4@\text{Pt}$ core-shell material is surprisingly high. To the best of our knowledge, this is the first time such nanostructure is evaluated as anode for the oxidation of organic molecules.

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

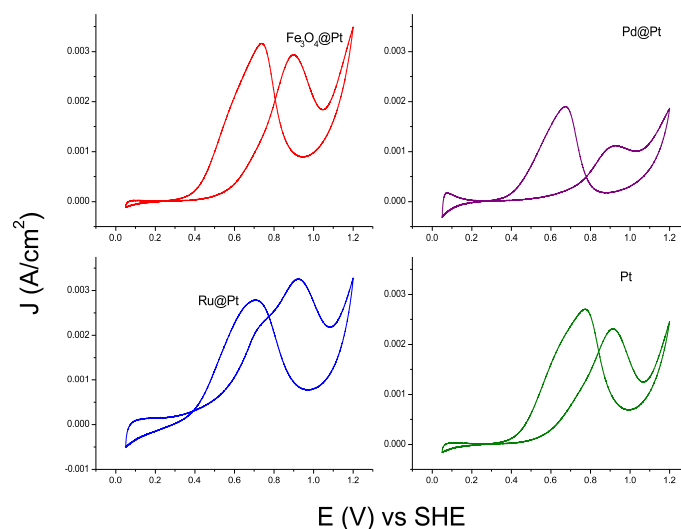


Figure 3. CVs of the EOR for $\text{Fe}_3\text{O}_4@\text{Pt}$, $\text{Pd}@\text{Pt}$, $\text{Ru}@\text{Pt}$ and Pt-alone in N_2 -saturated 0.5 M H_2SO_4 + 0.5 M $\text{C}_2\text{H}_5\text{OH}$ solution. Scan rate: 20 mV/s.

Figure 4 shows the chronoamperometric measurements, recorded at 895 mV vs SHE during 600 s. Clearly, the $\text{Ru}@\text{Pt}$ and $\text{Fe}_3\text{O}_4@\text{Pt}$ catalysts show a more stable performance than the other two catalysts for the EOR. The behavior of those two materials is quite similar. After 600 s, the current density at $\text{Ru}@\text{Pt}$ and $\text{Fe}_3\text{O}_4@\text{Pt}$ is 1 mA/cm^2 . Meanwhile, after such elapsed time, the current density is 0.8 and 0.4 mA/cm^2 for Pt-alone and $\text{Pd}@\text{Pt}$, respectively.

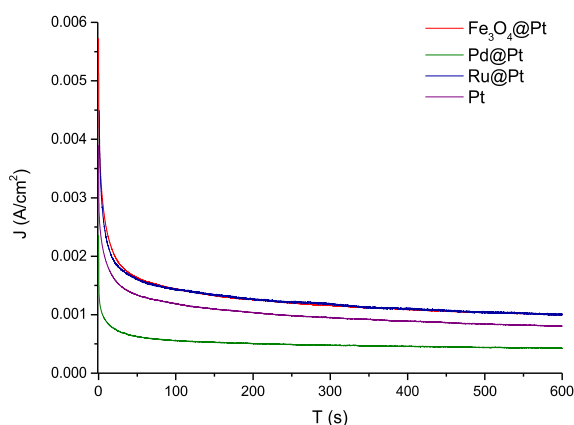


Figure 4. Chronoamperometric curves of the EOR at $\text{Fe}_3\text{O}_4@\text{Pt}$, $\text{Pd}@\text{Pt}$, $\text{Ru}@\text{Pt}$ and Pt-alone, measured at 895 mV vs SHE and room temperature.

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

4. Conclusions

In this work we present a facile synthesis process to obtain M@Pt (with M = Fe₃O₄, Pd and Ru) core-shell nanostructures. The XRD patterns show the formation of the core materials and metallic Pt after one minute synthesis under UT stirring. The Ru@Pt and Fe₃O₄@Pt nanomaterials show the higher catalytic activity for the EOR. To the best of our knowledge, this is the first time that Fe₃O₄@Pt nanostructures are evaluated as anodes for the oxidation of organic molecules.

5. Acknowledgements

The authors thank the Mexican National Council for Science and Technology (CONACYT) for financial support through grant 79870 and the Programa de Redes Temáticas.

6. References

- [1] F. Vigier, C. Contanceau, A. Perrard, E. Belgsir, C. Lamy, J. Appl. Electrochem., 34, 439-446 (2004).
- [2] C. Wan, C. Chen, Int. J. Hydrogen energy, 34, 9515-9522 (2009).
- [3] R. Wang, H. Wang, B. Wei, W. Wang, Z. Lei, Int. J. Hydrogen Energy, 35, 10081-10086 (2010).
- [4] C. Lamy, E. Belgsir, J.M. Leger, J. Appl. Electrochem., 31, 799-809 (2001).
- [5] X. Yuan, H. Wang, PEM Fuel Cell Electrocatalysts and Catalyst Layers, Springer, Canada (2008).
- [6] F. Kadirgan, S. Bayhan, T. Atilan, Int. J. Hydrogen Energy, 34, 4312-4320 (2009).
- [7] Fuel Cells Catalysis: A surface Science Approach, Edited by Marc T. M. Koper, Wiley & Sons, New Jersey 2009.
- [8] S. Heysiattalab, M. Shakeri, M. Safari, M. Keikha, J. Ind. Engineering Chemistry, 17, 727-729 (2011).
- [9] T. Lopes, E. Antolini, E. Gonzalez, Int. J. Hydrogen Energy, 33, 5563-5570 (2008).
- [10] J. Tayal, B. Rawat, S. Basu, Int. J. Hydrogen Energy, 37, 4597-4605 (2012).
- [11] D. Kaplan, M. Alon, L. Burstein, E. Peled, J. Power Sources, 196, 1078-1083 (2011).
- [12] H. Wang, R. Hang, H. Li, Q. Wang, J. Kang, Z. Lei, Int. J. Hydrogen Energy, 36, 839-848 (2011).
- [13] L. Lai, G. Huang, X. Wang, J. Weng, Carbon, 49, 1581-1587 (2011).
- [14] P. Ochal, J. Gomez, M. Tsyppkin, F. Seland, S. Sunde, N. Muthuswamy, M. Rønning, D. Chen, S. Garcia, S. Alayoglu, B. Eichhorn, J. Electrochem. Soc., 655, 140-146 (2011).