

High catalytic activity for Glycerol electrooxidation by binary Pd-based nanoparticles in Alkaline Media

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Introduction

Glycerol is a non flammable and volatile compound obtained from biodiesel production. Presentin a good theoretical energy density (5.0 kWh kg^{-1}), this fuel seems to be a very interesting possibility for Direct Alcohol Fuel Cell (DAFC) technology to reach high current density from its electrooxidation. Pd-based catalysts have been as claimed as a stable material to oxidize alcohols such as propanol, ethanol, ethylene glycol, and glycerol in alkaline media [1]. Besides, the addition of a second metal or metal oxides on Pd have showed good results for the oxidation of glycerol [2].

In this work, we aimed to investigate glycerol oxidation in alkaline medium employing PdM (M= Sn, Ru, Ni, Fe, and Mn) catalysts supported on Carbon Vulcan prepared by the microwave-assisted heating.

Experimental

Electrocatalysts with nominal composition PdM (50:50), M = Sn, Ru, Ni, Fe, and Mn, supported in carbon Vulcan XC-72 were prepared by the microwave-assisted heating (MW) in order to obtain catalysts with 40 % wt metal loading.

The electrocatalysts were characterized by X-ray diffraction (DRX), Energy dispersive X-ray (EDX), electrochemical techniques such as: cyclic voltammetry (potential range - 1.00 to 0.40 V vs Hg/HgO) and chronoamperometry at (- 0.2 V vs Hg/HgO for 30, 60 and 90 min) in the presence of NaOH 1.0 mol L^{-1} and glycerol 0.5 mol L^{-1} .

Results and Discussion

The experimental composition obtained for the prepared catalysts with Mn, Ni and Fe are close to the nominal one and showed a XRD pattern characteristic of the face-centered cubic (FCC) crystalline structure of Pd (Table 1). The catalysts containing Sn and Ru showed a different composition from the nominal one, that is much justified by the formation of Pd₂Sn orthorhombic phase [3] and a mixture of PdRu (fcc) + Ru (hcp) in the case of Sn and Ru, respectively. This behavior for Sn and Ru is in agreement with their respective phase diagram. The crystallite size for all the catalysts lies in the range 4.2 to 6.9 nm.

Table 1: Physical and electrochemical results for glycerol electro-oxidation on Pd-based/C catalysts

Composition Experimental	D (nm)	E _{onset} / V vs. Hg/HgO	Real surface area / m ² g _{Pd} ⁻¹
Pd/C	6.87	- 0.490	13.49
Pd ₆₃ Sn ₃₇ /C	4.32	- 0.454	67.47
Pd ₅₄ Fe ₄₆ /C	3.12	- 0.491	25.08
Pd ₅₃ Mn ₄₇ /C	4.90	- 0.494	47.32
Pd ₅₇ Ni ₄₃ /C	3.11	- 0.387	17.95
Pd ₇₁ Ru ₂₉ /C	3.95	- 0.471	35.74

Electrochemical characterization by cyclic voltammetry in the absence of glycerol showed that all of the catalysts display characteristic peaks of OH-

adsorption and PdO formation as described in [4]. The effect of adding a second metal on Pd-catalyst was noticed by the increase in the real surface area calculated through the peak of PdO reduction. The onset potential of glycerol oxidation was obtained by the cyclic voltammograms was ~ - 0.49 V vs Hg/HgO for all of the compositions, figure 1.

The inset in figure 1 shows the voltammetric and chronoamperometric experiments, where the presence of the second metal seems to contribute in the increase of the catalytic activity compared to pure Pd catalyst. The catalytic activity for these materials presented the following order: PdRu > PdMn = PdFe > PdSn > PdNi > Pd. Chronoamperometry experiments were performed in triplicate to evaluate the catalysts stability. For 90 minutes, Pd₇₁Ru₂₉/C, Pd₅₄Fe₄₆/C, Pd₅₃Mn₄₇/C maintained the same values of current density. However, the Pd₆₃Sn₃₇/C catalyst presented a decrease in the catalytic activity with an oscillating current. We did not observe a clear correlation between real surface area and catalytic activity. In fact, the most efficient catalyst, Pd₇₁Ru₂₉/C, had the highest amount of Pd but the smallest real surface area, suggesting that the formation of an isolated mettalic Ru has a significant contribution on glycerol oxidation.

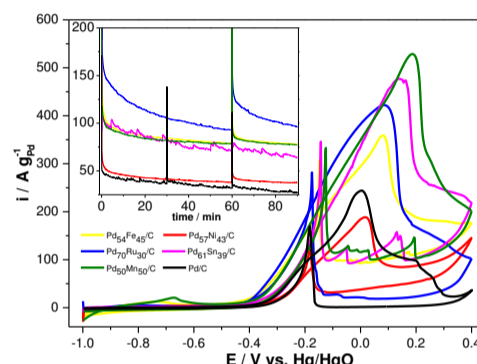


Figure 1: Cyclic voltammograms on Pd-based/C catalysts at 10 mV s^{-1} in the presence of glycerol (0.5 mol L^{-1} + 1.0 mol L^{-1} NaOH), **Inset:** Current vs time plot for the glycerol electro-oxidation (0.5 mol L^{-1} + 1.0 mol L^{-1} NaOH) at - 0.2 V vs Hg/HgO on Pd-based/C catalysts. Current values normalized by the Pd loading.

Conclusion

All the prepared catalysts showed the crystalline structure of face-centered cubic Pd, except Pd₆₃Sn₃₇/C that also presented orthorhombic geometry, and Pd₂Sn and Pd₇₁Ru₂₉/C that presented hexagonal Ru. The microwave-assisted heating procedure formed well distributed nanoparticles, with size lower than 6.9 nm. The Pd₇₁Ru₂₉/C catalyst showed the best results for glycerol electrooxidation probably due to the formation of isolated metallic Ru.

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