



THERMAL TREATMENT EFFECTS ON Pd₅Cu₄Pt ELECTROCATALYST FOR THE OXYGEN REDUCTION REACTION IN A PEM FUEL CELL

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ABSTRACT

The research is aimed to study the thermal treatment effects in the electrochemical activity of Pd₅Cu₄Pt catalyst for the oxygen reduction reaction, ORR, as well as on its performance as cathode electrode in a single proton exchange membrane fuel cell, PEMFC. The electrocatalyst was synthesized by chemical reduction of PdCl₂, CuCl₂ and H₂Cl₆Pt•6H₂O with NaBH₄ in THF. Annealing in H₂ atmosphere was performed at 200 and 300 °C. The electrocatalysts were characterized by X-ray diffraction and scanning electron microscopy. Cyclic voltammetry (CV) and rotating disc electrode (RDE) were performed for electrochemical characterization in a 0.5 M H₂SO₄ at 25 °C. Results of thermal treatment showed the growth of nanocrystallite particles and an enhancement of the crystallinity of the electrocatalyst. Notorious shifts towards positive XRD 2θ values are associated to the incorporation of elements inside the crystalline structure of the sample. The electrochemical results showed a decrease in the electrocatalytic activity as the temperature of the annealing increase. The maximum power density, W_{max}, was 350 mW cm⁻² was achieved using Pd₅Cu₄Pt without thermal treatment with 0.8 mg cm⁻² catalyst loading as cathode in a PEMFC. These results are attributed to the formation of new inactive-ORR phases with the thermal treatment.

Key words: PEMFC, trimetallic catalyst, ORR, cathode.



1. INTRODUCTION

A polymer electrolyte membrane fuel cell (PEMFC) offers several advantages such as improved energy efficiency and environmentally friendly power source. The main areas of application include transportation, distribution of energy and portable power systems [1]. In a PEMFC using hydrogen as fuel, the kinetic of the cathodic oxygen reduction reaction (ORR) is slower by several orders of magnitude than the anodic reaction. Therefore the ORR is the rate determining step in the performance of the fuel cell, and to find a better cathodic electrocatalyst than Pt continues being the challenge worldwide of several research groups.

Up to now Pt and its alloys are the most active and widely used electrocatalysts for PEMFC [2]. However elevated price and scarcity of Pt are the principal drawbacks that limit its use, so that research efforts are oriented to search novel catalyst without platinum or with the least possible content of this metal.

In this sense, our research group has previously reported [3-5] bimetallic Pd-based catalysts with improved catalytic activity for the ORR in comparison with the Pd alone. Also some recent reports [5-7] indicate that bimetallic PdCu electrocatalysts present attractive catalytic activity towards the ORR in acid media and in a PEM fuel cell. A recent study has demonstrated that low Pt content improve the performance and the stability of PdSn electrocatalyst [8]. Moreover, some studies have showed the influence of the heat treatment temperature on the stability of electrocatalysts [9-11].

The present research is aimed to study the thermal treatment effects in the Pd₅Cu₄Pt catalyst and in their electrochemical activity for the ORR in acid medium, and as cathode electrode in a single PEMFC.

2. EXPERIMENTAL

2.1 Electrocatalyst preparation

The trimetallic catalyst was produced by a NaBH₄ reduction of PdCl₂, CuCl₂ and H₂PtCl₆•6H₂O in a THF solution as reported in literature [3,4, 8]. Briefly, a chemical reactor was

charged with the metallic salts and THF, maintaining the solution under stirring. Then NaBH_4 as reducing agent was slowly added. After the reduction, the reaction products were washed and dried at 60 °C. The obtained black powder was separated in three samples: the first sample was kept as-synthesized; the others were annealed at 200 and 300 °C respectively, in a hydrogen atmosphere for 1 hour each one. Finally all the samples were maintained in closed vessels prior to physical and electrochemical characterizations.

2.2 Physical characterization

The electrocatalysts were physically characterized by X-ray diffraction (XRD) using a X'Pert PRO PW3040 (PANalytical) with monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406$ Angstroms) in a 2θ range from 30 ° to 100° with a step width of $0.2^\circ \text{ min}^{-1}$. The morphology of the materials was observed using scanning electron microscopy (SEM), from a Carl Zeiss (GEMINI FESEM) operated at 15 kV.

2.3 Electrochemical characterization

The oxygen reduction reaction was evaluated in a 0.5M H_2SO_4 electrolyte saturated with oxygen for 30 min. Electrochemical experiments were performed in a conventional single-compartment three-electrode electrochemical cell. A platinum mesh was used as counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ / 0.5 M H_2SO_4 (MSE=0.680 V/NHE) as reference electrode. The electrochemical experiments were performed in a potentiostat/galvanostat (PARSTAT model 2273).

Cyclic voltammetry (CV) and rotating disk electrode (RDE) experiments were carried out on a catalyst thin film deposited on a glassy carbon surface electrode mounted on an interchangeable rotor RDE (Pine Instruments). The working electrode was prepared according to the methodology reported elsewhere. $\text{Pd}_5\text{Cu}_4\text{Pt}$ thin film deposited on the glassy carbon electrode was prepared by the addition of 3 μL of a suspension resulting from the mixture of 60 μL of ethanol and 8 μL of Nafion® (5 wt. %, Du Pont 1000EW) and 1 mg $\text{Pd}_5\text{Cu}_4\text{Pt}$ (40 wt.%/C). The

rotation rate of the working electrode was in the range of 100 and 1600 rpm, at a scan rate of 5 mV s⁻¹

2.4 Preparation and characterization of the membrane electrode assemblies

A three layered structure, diffusion, catalyst and monomer layers, was used to prepare the membrane electrode assembly (MEA) in order to test Pd₅Cu₄Pt catalyst as cathode electrode in a single PEMFC. Each MEA was prepared by spraying the catalyst ink on the cathodic side of the pre-treated Nafion[®] 117 (Dupont Fluoro Products) membrane. Then the gas diffusion layer (carbon cloth) at the cathodic side and the commercial electrode at the anodic side of the 117 Nafion membrane was placed, followed by hot-pressing of the assembly at 120 °C and 11 kg cm⁻² for 1.5 min.

The MEAs were tested with a commercial fuel cell system (Compucell GT, Electrochem 890B) in a single cell rig with 5 cm² of geometrical area. The gas pressures at the anode and cathode side were kept at 30 psi for H₂ and 30 psi for O₂, respectively. The fuel cell test station was operated with high purity H₂ and O₂ at 100 cm³ min⁻¹. Humidification of reactant gases was kept 5 °C above the temperature of the cell. The performance was measured under steady-state conditions from 25 to 80 °C.

3. RESULTS AND DISCUSSION

3.1 Physical characterization

X-ray diffraction patterns of Pd₅Cu₄Pt synthesized are shown in Figure 1. The diffraction patterns are shifted from the (fcc) crystalline hexagonal phase of palladium (JCPD card 65-2867) towards more positive 2θ values, this can be associated to the formation of the expected new phases as a result of the incorporation of elements inside a crystalline structure. This shift increases as the temperature of thermal treatment increases. A small peak at 89 2θ degree appears after the material is annealed at 200 °C and its intensity increases as a result of an increase of 100 °C in the heat treatment. This peak is associated to the copper present in the surface layer (JCPD

card 04-0836) i.e. the Cu is coming more superficial with the thermal treatment. Also crystallite size and crystallinity increase as effect of the annealing, estimated with the width of the peaks.

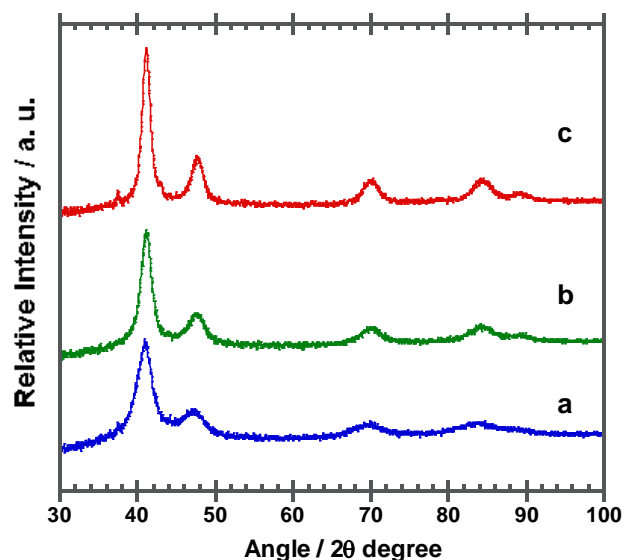


Figure 1. XRD spectra of Pd₅Cu₄Pt electrocatalyst (a) as-synthesized, (b) annealed at 200 °C, and (c) annealed at 300 °C. The black vertical lines are the phases reported for Palladium.

The crystallite size and crystallinity were determined for each compound by fitting the diffraction patterns using the software MDI jade 5.0. Results are shown in Table 1, where as expected, the lowest crystallite size and crystallinity correspond of the electrocatalyst as-synthesized (a). Previous studies [12] indicate that the decrease in the percentage of crystallinity of an electrocatalyst is related to an increase in its catalytic activity toward the ORR.

Table 1. Structural Properties deduced from the XRD patterns.

Parameter	as-synthesized	200 °C	300 °C
Crystallite size (nm)	4	6	8
Crystallinity (%)	30.93	43.89	55.98

Studies of $\text{Pd}_5\text{Cu}_4\text{Pt}$ by SEM, Figure 2, for the as-synthesized electrocatalyst (a) exhibited irregular agglomerates with less than 100 nm in an average size. In the case of the $\text{Pd}_5\text{Cu}_4\text{Pt}$ annealed at 200 °C (b), the result is similar to the as-synthesized; the only change is an increase of the size of agglomerates as expected. In the Figure 2 c it is noticeable the formation of complex structures due to the thermal treatment at 300 °C.

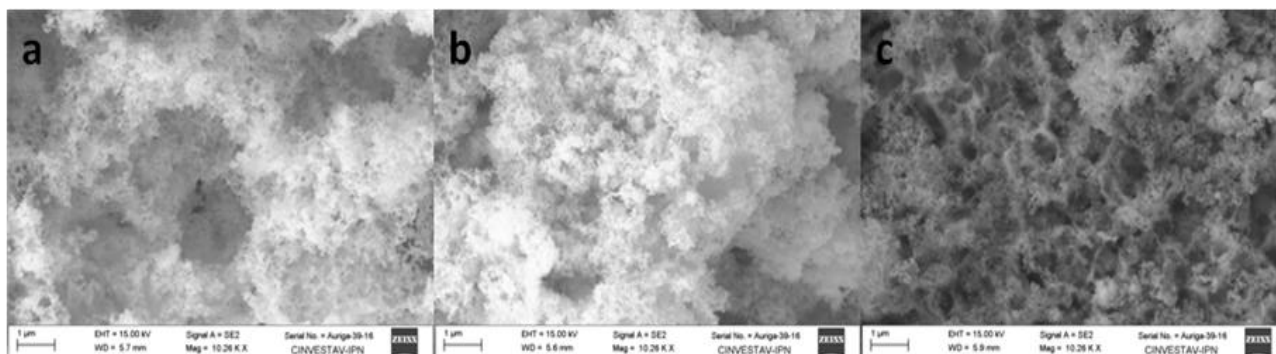


Figure 2. SEM images of trimetallic electrocatalyst (a) as-synthesized, (b) annealed at 200 °C, and (c) annealed at 300 °C.

3.2 Electrochemical characterization

Before to CV the working electrode was subjected to 30 cycles in the range of 0.0-1.5 V/NHE, in order to remove oxides and impurities on the electrode surface and obtain reproducibility in the voltammograms. The cyclic voltammetry characterization of the electrode was performed in a nitrogen purged 0.5M H_2SO_4 solution, scan rate = 100 mV s^{-1} . Figure 3 shows the voltammograms of $\text{Pd}_5\text{Cu}_4\text{Pt}$ thin film electrode. The proton adsorption-desorption peaks are in the potential range of 0.03-0.30 V/NHE. However, the hydroxide adsorption-desorption peak potentials are different from that reported for Pd and PdCu [5]. In the potential range of 0.6-0.8 V appears a peak in the cathodic current, associated to the leaching of exposed Cu atoms from the surface layer. The peak increases as the temperature of thermal treatment increases. Otherwise the current density decreases as the annealed temperature of the samples increases; similar result was observed and reported by E. Antolini for bimetallic Pt-based catalysts [10]. This behavior could be associated to the formation of new phases with superficial Cu.

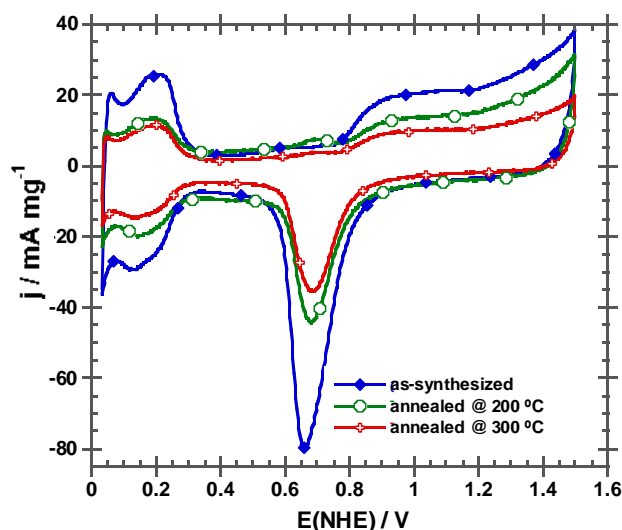


Figure 3. Cyclic voltammograms of Pd₅Cu₄Pt electrocatalysts in N₂ purged 0.5 M H₂SO₄ electrolyte at 25 °C.

Figure 4 shows the ORR polarization curves for the as-synthesized and annealed Pd₅Cu₄Pt electrocatalyst. In all the curves defined charge transfer control or activation regions are observed, and increases of currents in the mixed kinetic-diffusion control region (0.85 to 0.75 V/ NHE) followed by the well defined diffusion limiting currents region are also distinguish. The Pd₅Cu₄Pt electrocatalyst annealed at 300 °C presents the highest overpotential for the ORR and the lowest current density at the same experimental conditions, being this material which exhibits the highest copper phase in the XRD spectra.

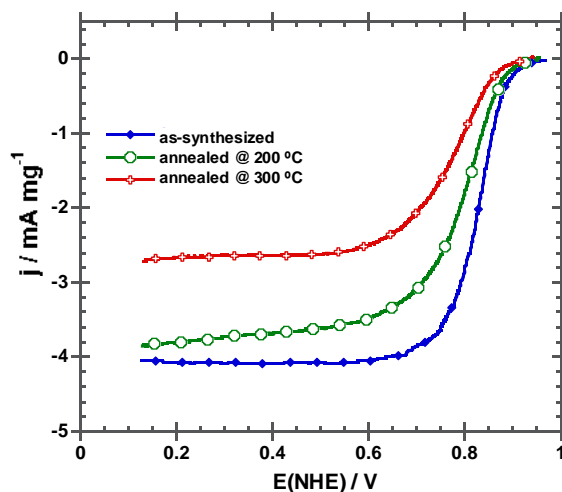


Figure 4. Polarization curves for the ORR on Pd₅Cu₄Pt in an O₂-saturated 0.5 M H₂SO₄ at room temperature at 1600 rpm. Scan rate: 5 mV s⁻¹.

Figure 5 shows the mass transfer-corrected Tafel plots of Pd₅Cu₄Pt electrocatalysts in an oxygen-saturated 0.5M H₂SO₄ solution obtained from RDE measurements at 25 °C (plots not included). This figure shows a decrease in the catalytic activity as the annealing temperature increases. The catalytic activity of these materials can be measured in terms of parameters deduced from mass transfer-corrected Tafel slope. The slopes of each electrocatalyst show a linear behavior at high current density from which kinetic parameters were deduced.

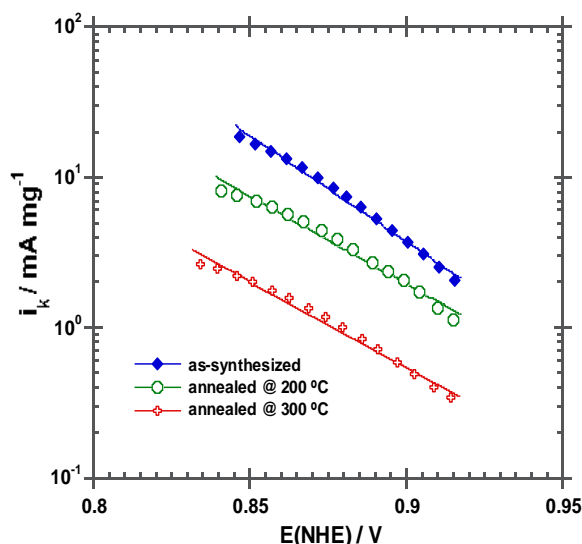


Figure 5. Mass-transfer corrected Tafel plots of the ORR on Pd₅Cu₄Pt electrocatalysts at 25 °C.

The kinetic parameters deduced from the Tafel plots are summarized in Table 2. Values of slope ($-b$), and transfer coefficient (α) are almost the same for the three electrocatalysts and are similar to those reported for the PdCu compound [5]. The exchange mass current value (i_0) of 2.98×10^{-4} mA mg⁻¹ of the Pd₅Cu₄Pt annealed at 300 °C shows the slowest catalytic activity for oxygen reduction, whereas Pd₅Cu₄Pt without thermal treatment exhibits the highest i_0 , indicating the higher catalytic activity than the annealed materials. The reduced activity can be attributed to the formation of a new phase that does not favor the ORR.

Table 2. Kinetic Parameters for ORR deduced from the Tafel plots.

Parameter	As-synthesized	200 °C	300 °C
-b (V dec⁻¹)	0.099	0.098	0.098
α	0.59	0.60	0.60
i_0 (mA mg⁻¹)	2.68×10^{-3}	1.01×10^{-3}	2.98×10^{-4}

3.3 Preparation and characterization of the membrane-electrode assemblies

In order to study the temperature effect on the MEA performance, curves of cell voltage and power density were recorded at 25, 40, 60 and 80 °C. The fuel cell was fed with H₂/O₂ gases under 30/30 psi pressure. Figure 6 shows the fuel cell performance at different temperatures using Pd₅Cu₄Pt as cathode catalyst: (a) as-synthesized, (b) annealed at 200 °C, and (c) annealed at 300 °C. An improvement of MEA performance with the increased temperature was observed in all the three cases. The maximum power density (W_{\max}) was achieved at 80 °C for all the materials, indicating that the oxygen reduction on Pd₅Cu₄Pt is activated by temperature. Figure 5d presents comparison under the same experimental conditions, of materials with and without thermal treatment. As in the electrochemical experiments the electrocatalyst untreated exhibits higher performance than the other two materials. Open circuit voltages (E_{OC}) and W_{\max} for each one are presented in Table 3.

Table 3. Values obtained in PEMFC Performances.

Parameter	as-synthesized	200 °C	300 °C
E_{OC} (V)	1	0.95	0.93
W_{\max} (mW cm⁻²)	340	240	200

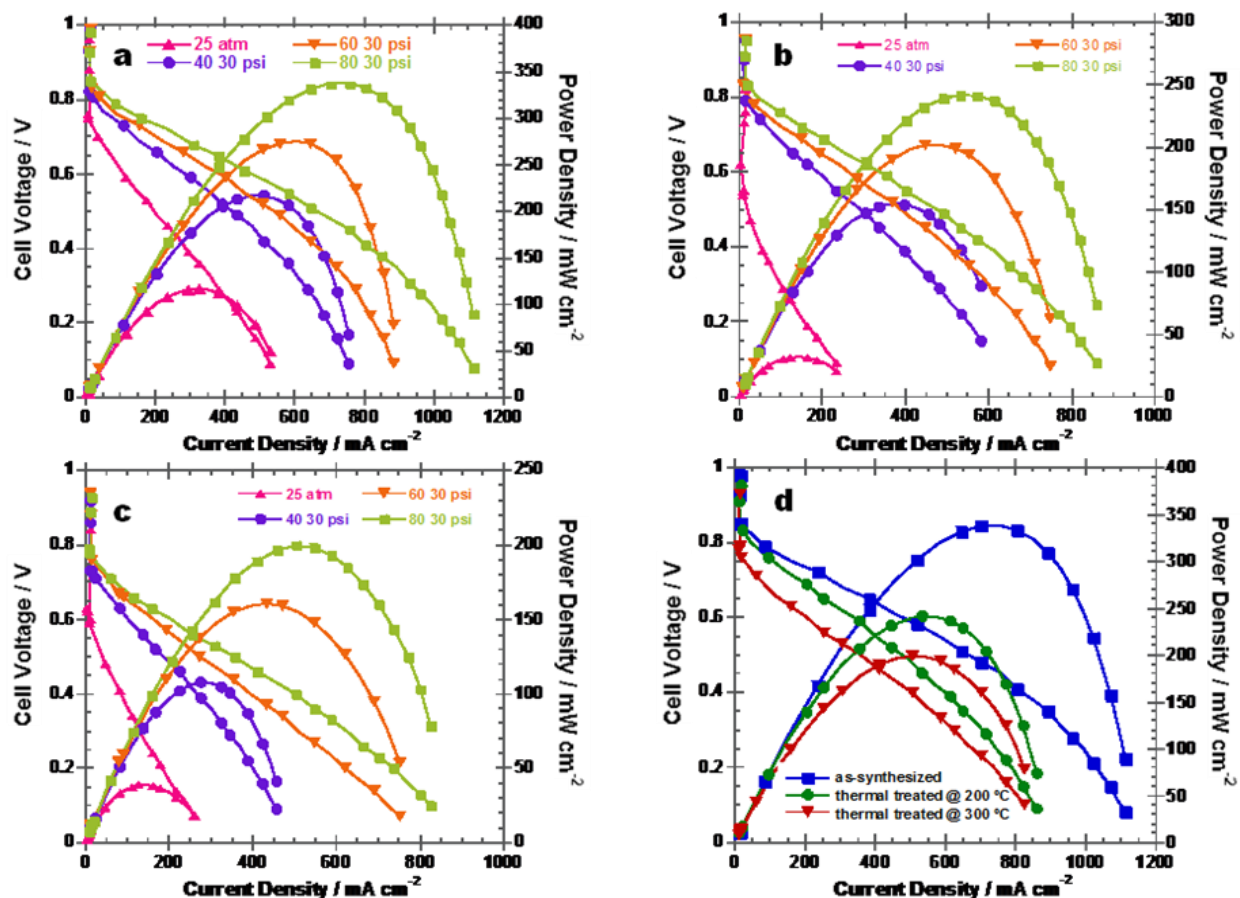


Figure 6. Single fuel cell performance of Pd₅Cu₄Pt as cathode: (a) as-synthesized, (b) annealed at 200 °C, and (c) annealed at 300 °C. The fuel cell was operated with H₂/O₂ at different temperatures. (d) Comparison of performances at 80 °C and 30 psi.

Nevertheless the open circuit voltages were around 1 V in all cases. The highest E_{OC} is presented by the Pd₅Cu₄Pt as-synthesized, with W_{max} of 100 mW cm⁻² and 140 mW cm⁻² above than that presented by the annealed electrocatalysts at 200 and 300 °C, respectively. The change in the annealing temperature does not have a significant effect in the PEMFC performance, where the difference between the W_{max} values is only 20 %.

4. CONCLUSIONS

An easy and effective method of synthesis for trimetallic nanocatalyst (crystallite under 10 nm in sizes) is presented. The present study shows the thermal treatment effects over the catalytic activity for the ORR in acid medium and in a single PEMFC. The decrease in the catalytic activity with the annealing, and the increase in temperature of the thermal treatment, is attributed to the formation of a new phase, probably a copper phase that is non active for the oxygen reduction. This effect is appreciated in a decrease in the maximum power density on the PEMFC performance of about 40 %. These results indicated that a thermal treatment of Pd₅Cu₄Pt is not recommendable as this reduces the catalytic activity and increases the particle size and.

5. ACKNOWLEDGEMENTS

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