

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 electrocatalyst for the oxygen reduction reaction (ORR) in acid medium as well as on its performance as cathode electrode in a single Proton Exchange Membrane Fuel Cell (PEMFC). The electrocatalyst is synthesized by chemical reduction of PdCl₂, CuCl₂ and H₂PtCl₆ with NaBH₄ in THF, and is characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Cyclic voltammetry (CV) and rotating disc electrode (RDE) are performed for electrochemical characterization in a 0.5 M H₂SO₄ at 25 °C. Results of thermal treatment at 200 and 300 °C in H₂ atmosphere show a growth of nanocrystallite particles and an enhancement of the crystallinity of the electrocatalyst. Shifts towards positive 2θ XRD values are associated to the incorporation of elements inside the crystalline structure of the sample. Electrochemical results show a decrease in the electrocatalytic activity as the temperature of the thermal treatment increases. The maximum power density, W_{max} of 350 mW cm⁻² is achieved using Pd₅Cu₄Pt without thermal treatment with 0.8 mg cm⁻² cathode electrocatalyst loading of the PEMFC. This result is attributed to the formation of new inactive-ORR phases on the electrocatalyst with the thermal treatment.

Keywords: Electrocatalyst synthesis, Pd₅Cu₄Pt, PEMFC, ORR.

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 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 PEMFCs [2]. However the elevated price and scarcity of Pt are the principal drawbacks that limit its use, so that research efforts are oriented to search novel electrocatalyst 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 electrocatalysts with improved catalytic activ-

ity for the ORR in comparison with Pd alone cathodes. Also some recent reports [5-7] indicate that bimetallic PdCu electrocatalysts present attractive catalytic activity towards the ORR in acid media and a good performance in a PEMFC. A recent study has demonstrated that low Pt content improve the performance and stability of PdSn electrocatalyst [8]. Moreover, some studies have showed the influence of the thermal treatment temperature on the stability of electrocatalysts [9-11].

The present research is aimed to study the thermal treatment effects in the Pd₅Cu₄Pt electrocatalyst and in its electrochemical activity for the ORR in acid medium as well as on its performance as a cathode electrode in a single PEMFC.

2. EXPERIMENTAL

2.1. Electrocatalyst Synthesis

The trimetallic Pd₅Cu₄Pt electrocatalyst was produced by a NaBH₄ reduction of PdCl₂, CuCl₂ and H₂PtCl₆·6H₂O in a THF solution as reported in the literature [3, 4, 8]. Briefly, a chemical reactor was charged with the metallic salts and THF, maintaining the solution under stirring. Then NaBH₄ as reducing agent was

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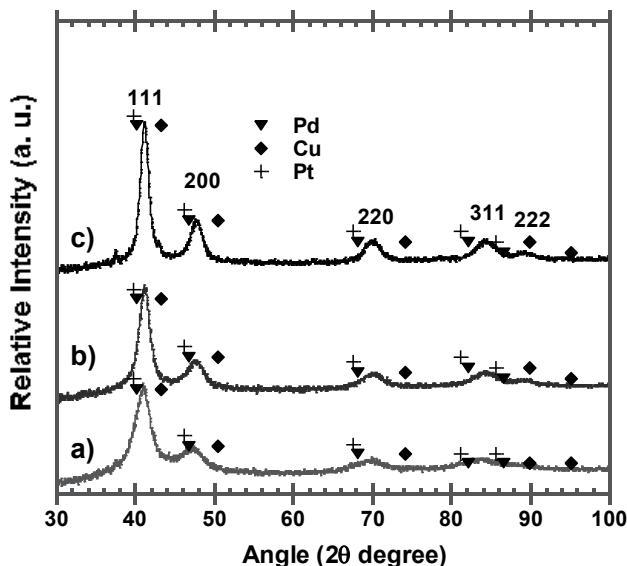


Figure 1. XRD spectra of $\text{Pd}_5\text{Cu}_4\text{Pt}$ electrocatalyst (a) as-synthesized, (b) treated at 200 °C, and (c) treated at 300 °C.

slowly added. After the reduction, the reaction products were washed, and then were dried at 60 °C. The obtained black powder was separated in three samples: the first sample was kept as-synthesized; the others were thermally treated 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 ° min⁻¹. The morphology of the materials was analyzed using a Carl Zeiss (GEMINI FESEM) microscope operated at 15 kV.

2.3. Electrochemical Characterization

The ORR was evaluated in a 0.5M H_2SO_4 electrolyte saturated with oxygen. The electrochemical measurements were performed in a potentiostat/galvanostat (PARSTAT model 2273). Electrochemical experiments were realized 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 vs NHE) as reference electrode. CV and RDE experiments were carried out on an electrocatalyst thin film deposited on a glassy carbon surface electrode mounted on an interchangeable RDE (Pine Instruments). The working electrode was prepared according to the methodology reported elsewhere [3-5]. $\text{Pd}_5\text{Cu}_4\text{Pt}$ thin film deposited on the glassy carbon electrode was prepared by the addition 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). Rotation rate of the working electrode was in the range between 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, electrocatalyst and monomer layers, was used to prepare the membrane electrode assembly (MEA). Each MEA was prepared by spraying the $\text{Pd}_5\text{Cu}_4\text{Pt}$ electrocatalyst 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 (Pt/C, Etek, 20 wt%, with a loading of 0.5 mg cm⁻²) at the anodic side of the Nafion® 117 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 (Compcell GT, Electrochem 890B) in a single cell rig of 5 cm² of geometrical area. The gas pressures at the anode and cathode side were kept at 30 psi. The fuel cell test station was operated with high purity H_2 and O_2 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

Figure 1 shows the XRD patterns of $\text{Pd}_5\text{Cu}_4\text{Pt}$ as-synthesized (1a), thermal treated at 200 °C (1b) and 300 °C (1c). The diffraction patterns are shifted from the (fcc) crystalline hexagonal phase of palladium (JCPD card 65-2867, inverted triangles in Fig. 1) 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 treated at 200 °C (Fig. 1b) and its intensity increases as a result of an increase of 100 °C in the heat treatment (Fig. 1c). This peak can be associated to the copper present in the surface layer (JCPD card 04-0836) i.e. the formation of new Cu phases on the electrocatalyst with the thermal treatment. Also crystallite size and crystallinity increase as effect of the annealing, estimated with the width of the peaks. The crystallite size and crystallinity were determined for each compound by fitting the diffraction patterns using the software Topas Academic. Results are shown in Table 1, where as expected, the lowest crystallite size and crystallinity correspond to the electrocatalyst as-synthesized.

Studies of $\text{Pd}_5\text{Cu}_4\text{Pt}$ by SEM (Figure 2-I), for the as-synthesized electrocatalyst (a) exhibited irregular agglomerates with less than 100 nm in an average size and hollows in the surface. In the case of the $\text{Pd}_5\text{Cu}_4\text{Pt}$ heated at 200 °C (b), the result is similar to the as-synthesized; there is an increase of the size of agglomerates and a decrease of the superficial hollows. In the Figure 2-Ic it is noticeable the formation of complex structures due to the thermal treatment at 300 °C like bridges linking the agglomerates. Mapping images are showed in Figure 2-II, the green color represents the copper in the electrocatalysts. It is distinguished that the Cu is becoming more superficial with the thermal treatment; this is indi-

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

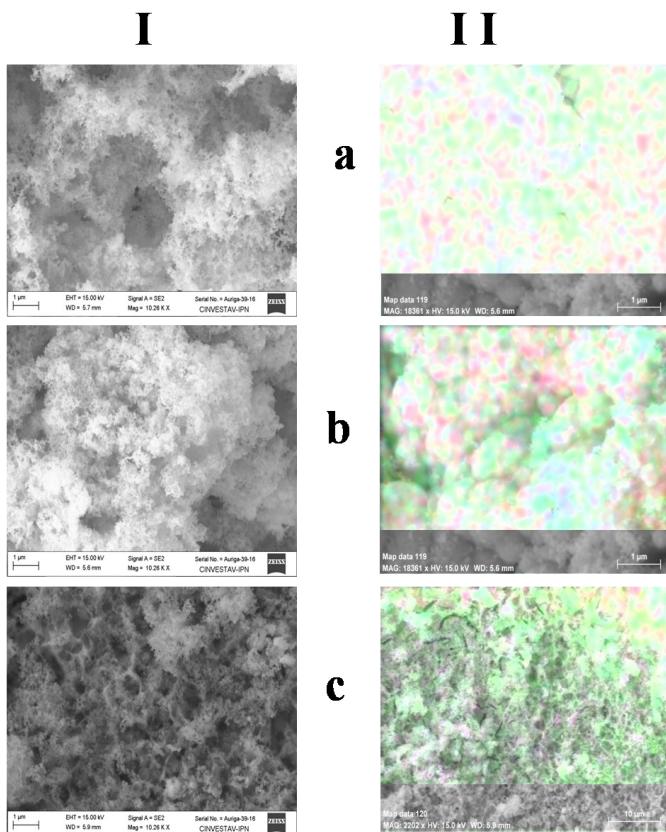


Figure 2. SEM (I) and Mapping (II) images of trimetallic electrocatalyst (a) as-synthesized, (b) treated at 200 °C, and (c) treated at 300 °C.

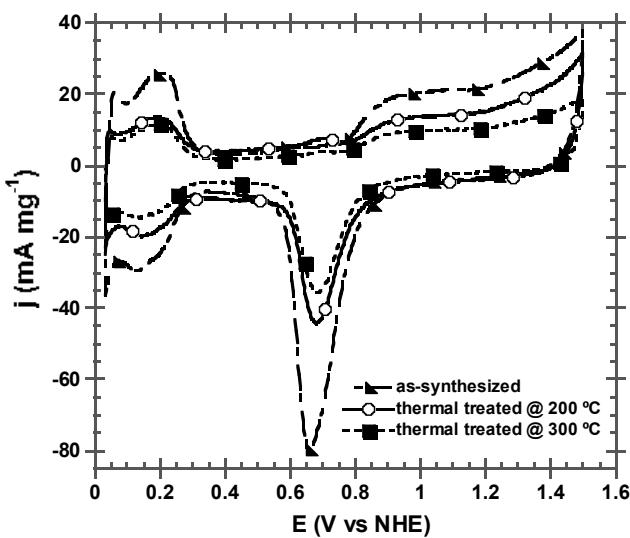


Figure 3. Cyclic voltammograms of Pd_5Cu_4Pt electrocatalysts in N_2 purged 0.5 M H_2SO_4 electrolyte at 25 °C

cated by the increase in the color intensity of the images as the temperature of the thermal treatment increases.

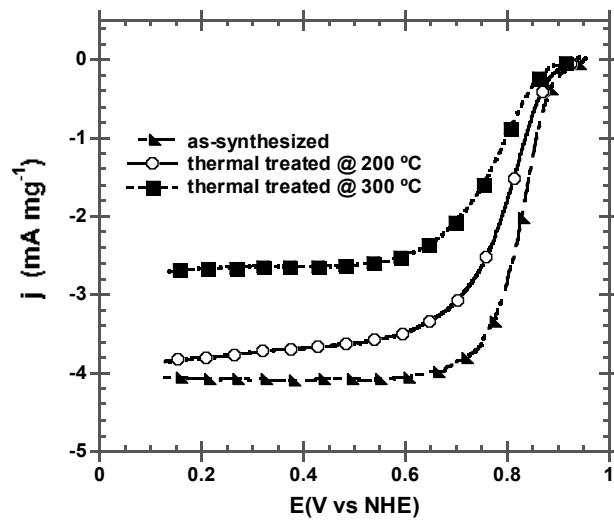


Figure 4. Polarization curves for the ORR on Pd_5Cu_4Pt in an O_2 -saturated 0.5 M H_2SO_4 at room temperature at 1600 rpm. Scan rate: 5 mV s⁻¹.

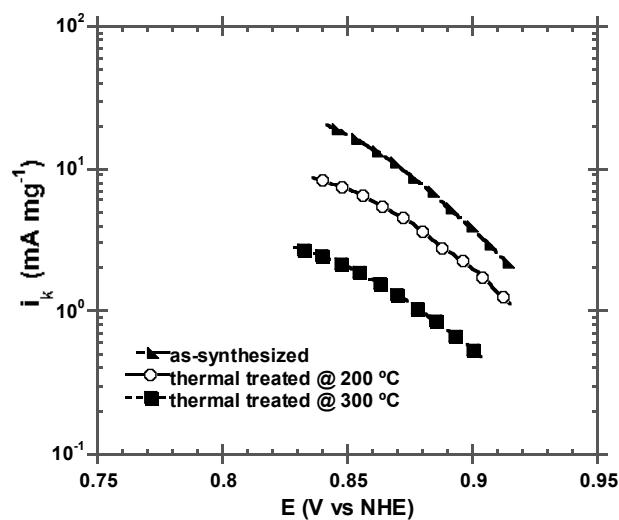


Figure 5. Mass-transfer corrected Tafel plots of the ORR on Pd_5Cu_4Pt electrocatalysts at 25 °C.

3.2. Electrochemical Characterization

Before CV experiments the working electrode was subjected to 30 cycles in the range of 0.0-1.5 V vs NHE, in order to remove oxides and impurities on the electrode surface and obtain reproducibility in the voltammograms. The CV 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 Pd_5Cu_4Pt thin film electrode, the current was normalized by the amount in mg of electrocatalyst. The proton adsorption-desorption peaks are in the potential range of 0.03-0.30 V vs 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 vs NHE appears a peak in the cathodic current, associ-

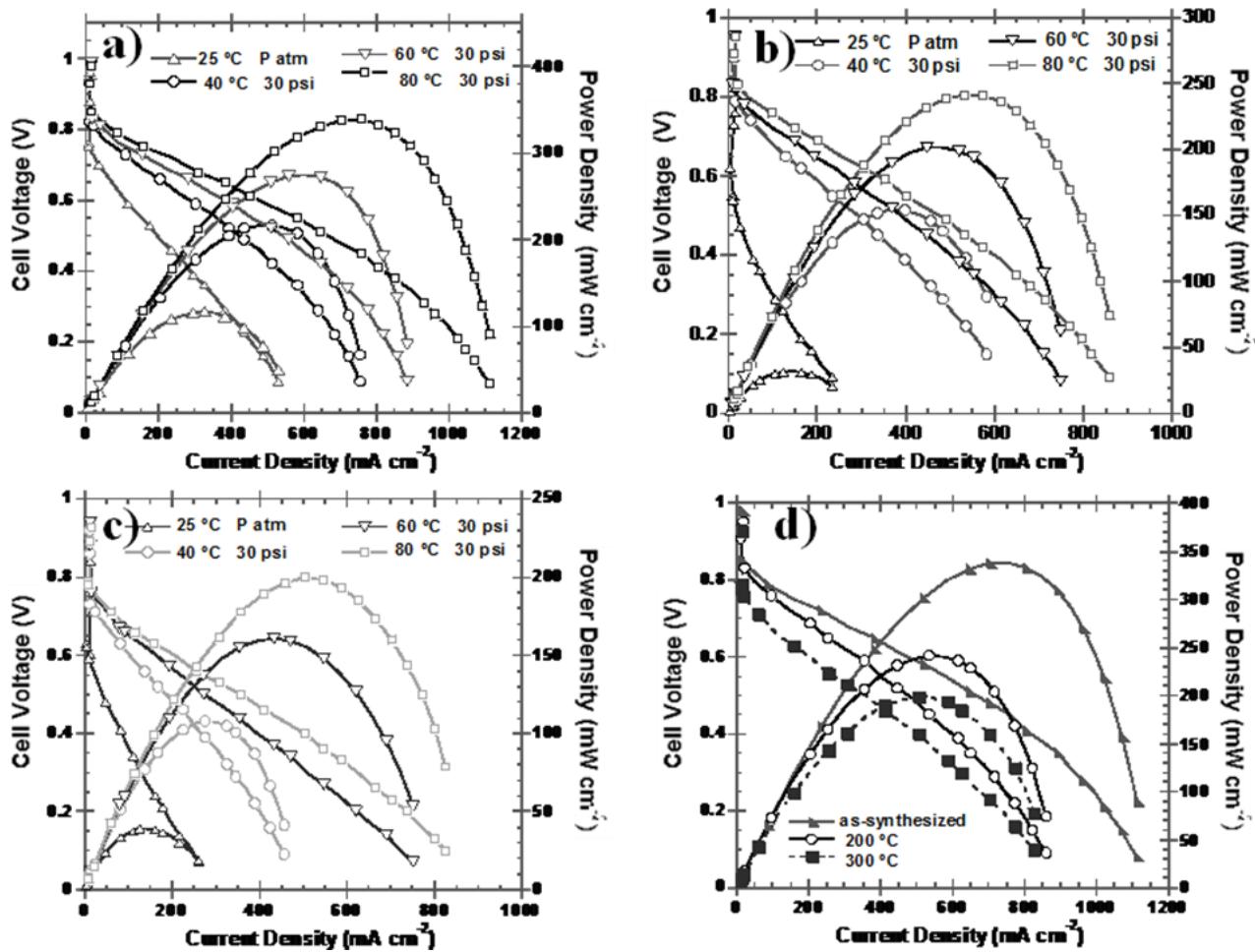


Figure 6. Single fuel cell performance of $\text{Pd}_5\text{Cu}_4\text{Pt}$ as cathode: (a) as-synthesized, (b) treated at 200 °C, and (c) treated at 300 °C. The fuel cell was operated with H_2/O_2 at different temperatures. (d) Comparison of performances at 80 °C and 30 psi.

ated to OH adsorption on the exposed Cu atoms from the surface layer. This peak increases as the temperature of thermal treatment increases. Otherwise the current density decreases as the temperature of the thermal treatment increases; similar result was observed and reported by E. Antolini for bimetallic Pt-based electrocatalysts [10]. This behavior could be associated to the formation of new phases with superficial Cu.

ORR polarization curves at 1600 rpm for the as-synthesized and thermally treated $\text{Pd}_5\text{Cu}_4\text{Pt}$ electrocatalyst are presented in Figure 4. 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 vs NHE) followed by the well defined diffusion limiting currents region are also distinguish. The $\text{Pd}_5\text{Cu}_4\text{Pt}$ electrocatalyst treated 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 and mapping image.

Figure 5 shows the mass transfer-corrected Tafel plots of $\text{Pd}_5\text{Cu}_4\text{Pt}$ electrocatalysts in an oxygen-saturated 0.5M H_2SO_4 solution obtained from RDE measurements at 25 °C (plots not in-

cluded). 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 overpotential from which kinetic parameters were deduced.

The kinetic parameters deduced from the Tafel plots are summarized in Table 2. Values of Tafel slope (-b), and charge transfer coefficient (α) are almost the same for the three electrocatalysts and are similar to those reported for the PdCu compound synthesized by the same method [5]. The exchange mass current value (i_0) of $2.98 \times 10^{-4} \text{ mA mg}^{-1}$ of the $\text{Pd}_5\text{Cu}_4\text{Pt}$ annealed at 300 °C shows the slowest catalytic activity for oxygen reduction, whereas $\text{Pd}_5\text{Cu}_4\text{Pt}$

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
$i_0 (\text{mA mg}^{-1})$	2.68×10^{-3}	1.01×10^{-3}	2.98×10^{-4}

without thermal treatment exhibits the highest i_0 , indicating higher catalytic activity than the thermally treated materials. The reduced activity can be attributed to the formation of a new phase that does not favor the ORR in acid media.

3.3. PEMFC Performance

In order to study the temperature effect on the MEA performance, polarization and power density curves were recorded at 25, 40, 60 and 80 °C. Figure 6 shows the fuel cell performance at different temperatures using Pd_5Cu_4Pt as cathode electrocatalyst: (a) as-synthesized, (b) treated at 200 °C, and (c) heated 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 Pd_5Cu_4Pt is activated by temperature. Figure 5d presents a comparison under the same experimental conditions (i.e. cell temperature 80°C, gas pressure 30 psi), of materials with and without thermal treatment as cathode. 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. It is appreciated that in the three cases open circuit voltages of around 1 V were obtained. The highest W_{max} and E_{OC} are presented by the Pd_5Cu_4Pt as-synthesized its W_{max} is about 100 and 140 mW cm⁻² higher than that presented by the thermally treated electrocatalysts at 200 and 300 °C, respectively. The increase in the temperature of the thermal treatment does not have a significant effect in the PEMFC performance, where the difference between the W_{max} values is about 20 %.

4. CONCLUSIONS

An easy and effective method for the synthesis of a trimetallic nanotrocatalyst (crystallite under 10 nm in sizes) is presented. It is notorious the thermal treatment effects over the catalytic activity for the ORR in acid medium and in a single PEMFC performance. The decrease in the catalytic activity with the increase in temperature of the thermal treatment is ascribed to the formation of a new phase, probably a copper phase that is not 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 indicate that a thermal treatment of Pd_5Cu_4Pt is not recommendable because it reduces the catalytic activity by the formation of a Cu phase on the electrocatalyst surface.

5. ACKNOWLEDGEMENTS

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Table 3. Values obtained from 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