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High Performance Carbon Supported Palladium Catalyst in Anodes of Proton Exchange Membrane Fuel Cell.

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Carbon support palladium catalyst (Pd/C) were prepared by borohydride method and characterized by XRD, TEM and EDX and then used to prepare anodes and cathodes for performance evaluation in single cell. For comparison were also used anodes and cathodes prepared with the commercial platinum catalyst (Pt/C), which allowed verifying the efficiency of using Pd/C in cathodes, anodes or both electrodes. It was found similar performance at room temperature, even at the cathode; however, the temperature rise was kinetically favorable to oxygen reduction reaction of cathodes with Pt/C which was not observed for Pd/C cathodes. Moreover, Pd/C anodes showed maximum performance of 83 % related to Pt/C at 85 °C, a behavior that was virtually constant at all temperatures studied and that justifies the application of palladium on fuel cell anodes to platinum replacement on the cost and nature reserves perspectives. The characterization confirmed the palladium FCC crystal structure, a mean particle size of 4.4 nm, presence of some agglomerates and the synthesis method efficiency that resulted in metallic loading of 19.88 % for a nominal load of 20.0 %. The performance achieved by the standards used in MEAs preparation at IPEN and the standards evaluation adopted resulted in a performance higher than reported in the literature motivating this publication.

Keywords: Membrane Electrode Assembly (MEA), Catalytic Layer, Palladium catalyst, Cost reduction, Proton Exchange Membrane Fuel Cell (PEMFC).

1. INTRODUCTION

Fuel cell are devices that convert chemical energy off a fuel into electricity with high efficiency [1-3] and are seen as a great opportunity to reduce pollutants emission [4] for their efficiency to convert alcohols into energy beyond the possibility of direct supply with pure hydrogen, which results in water formation as waste of energy generation process [1,5,6]. The use of platinum an expensive and scarce metal to catalyze fuel cell reactions is the state of the art [7-10], but has been impeditive to its large-scale application leading to growing interest in the use of alternative catalysts [7,11], palladium is a metal that have characteristics very similar to platinum [12], showing catalytic activity for oxygen reduction reaction (ORR) and to hydrogen oxidation reaction [12,13] hence has been widely studied today [8,14,15] due to the higher nature reserves and relatively low cost [4,13], currently between 3 and 5 times lower than that of platinum. Some experiments with palladium catalysts reported in the literature [8,9,13,16,17,18,19] has shown efficiency often lower of the platinum, reaching values between 12 and 32 % of the platinum (Pt/C) using pure H_2 and O_2, precluding palladium catalyst application despite its lower cost, the best result was reported by ALCAIDE et. all. [20] achieve 71 % of platinum performance, so we decided to study palladium catalyst application in accordance with the membrane electrode assemblies preparation procedures used at IPEN. Until now no article presented a performance for hydrogen oxidation reaction with palladium catalyst without alloys really close to platinum performance.

2. EXPERIMENTAL PART

Pd/C catalyst with 20 wt.% metal was prepared by borohydride method [21] and characterized by X-ray diffraction (XRD) in the RigaKu Miniflex II diffractometrer using Cu Kα radiation source (*l* = 0.15406 nm), where the diffractogram was recorded from 2θ = 20° to 90° with a step size of 0.05° and a scan time of 2s per step. The morphology, distribution, and mean particle size were determined by counting more than 460 particles from different regions of sample obtained from transmission electron microscopy (TEM) using a JEOL JEM-2100 electron microscope operated at 200 kV, and metal / carbon relationship was verified by energy dispersive X-ray (EDX).

In the prepared of catalyst layer was used weight ratio 65/35 between catalyst and dry Nafion, following the pattern that has been used at IPEN [6]. The suitable catalyst were mixed with Nafion D520 solution by ultrasonic and then applied to GDL by hand painting. In membrane electrode assemblies (MEAs) preparation was used Nafion 115 membrane and gas diffusion layer (GDL) called MF15 (IPEN Patent PI 1106530-3). Additionally electrodes and MEAs with the same structure described were prepared using Pt/C BASF catalyst to compare results. Thus MEAs were prepared with anode and cathode of palladium (Pd/Pd), anode and cathode of platinum (Pt/Pt), and both combinations anode of palladium and cathode of platinum (Pd/Pt) and the opposite (Pt/Pd). Such MEAs were evaluated in single cells with H_2 and O_2 analytical and atmospheric pressure and temperatures between 25 and 100 ° C.

3. RESULTS AND DISCUSSION

X-ray diffraction analysis (**XRD)** confirmed the palladium metallic particles formation by means of peaks shown in Figure 1.

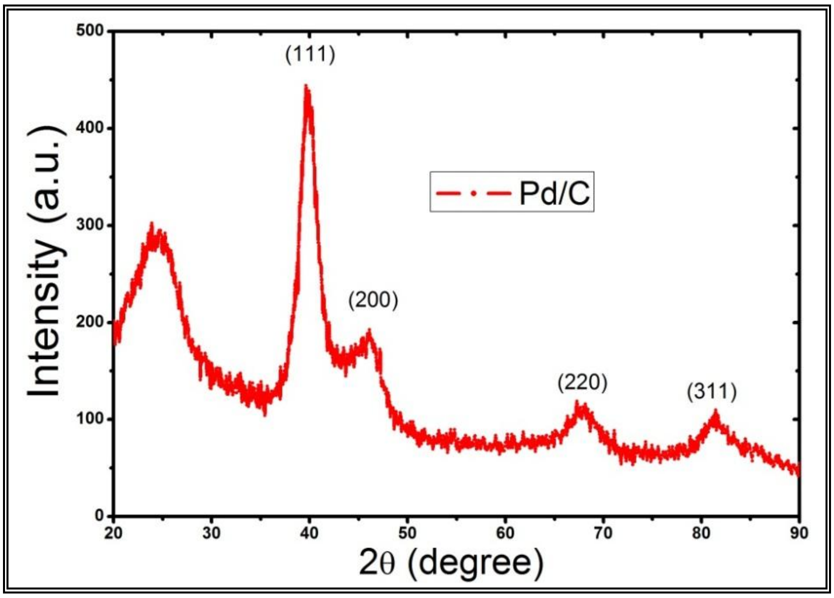

Figure 1. **X-ray diffractogram of Pd/C catalyst.**

By means of Figure 1 can be seen the characteristic broad peak at about 25º in 2θ associated with the Vulcan XC72R support. For Pd/C catalyst it was observed four peaks at approximately 2θ = 40,10º, 46,40º, 68,1º and 82,0º, which are associated with the (111), (200), (220) and (311) planes, respectively, of the face-centered cubic (fcc) structure characteristic of palladium**.** Figure 2 shows a transmission electron micrograph of Pd/C catalyst and its particle size distribution.

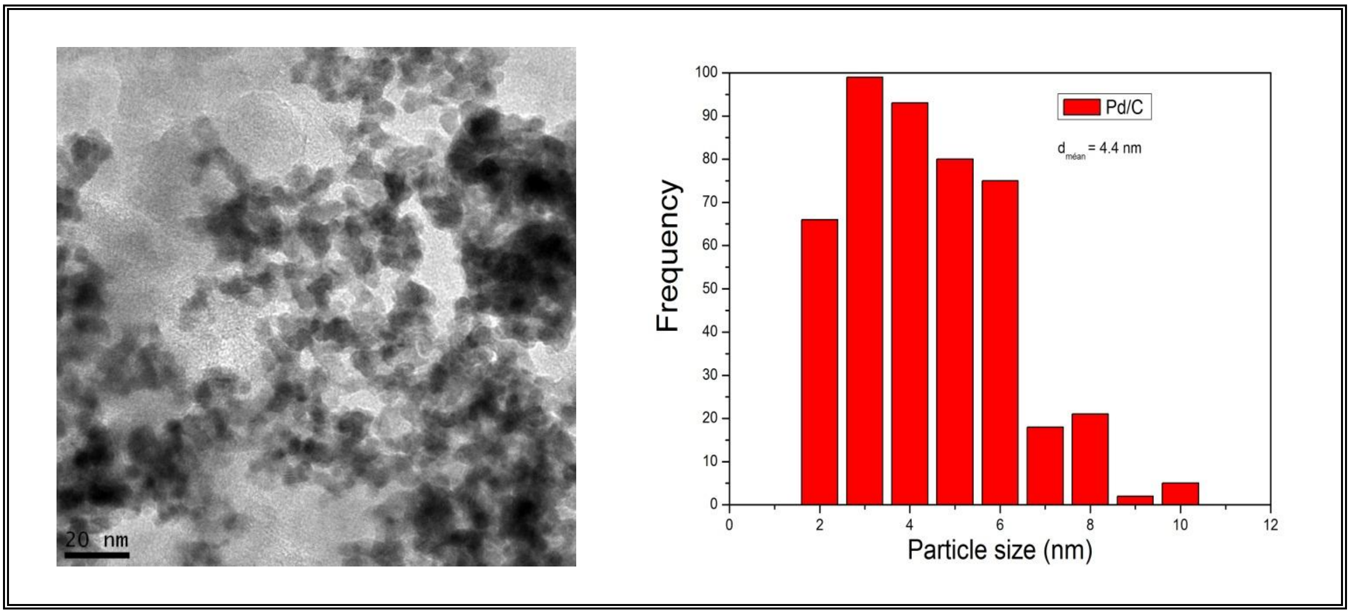

Figure 2.Transmission electron microscopy and particle size distribution of Pd/C catalyst.

The transmission electron microscopy shown in Figure 2 allows to visualize the metal distribution on carbon support, being visible the presence of agglomerated particles as reported on literature [4,12,15], so improvements in synthesis method are desirable to achieving higher activity favoring Pd/C. By means of the images obtained was made the particle size estimation, resulting in an average value of 4.4 nm. The Energy Dispersive X-Ray Analysis (EDX) showed 19.88 % by mass of palladium on carbon support confirming the effectiveness of synthesis performed.

After characterized the catalyst was used on MEA preparation and evaluated in single cell. Figure 3 shows the performance of MEA with Pd/Pd and Pt/Pt and at 25 °C.

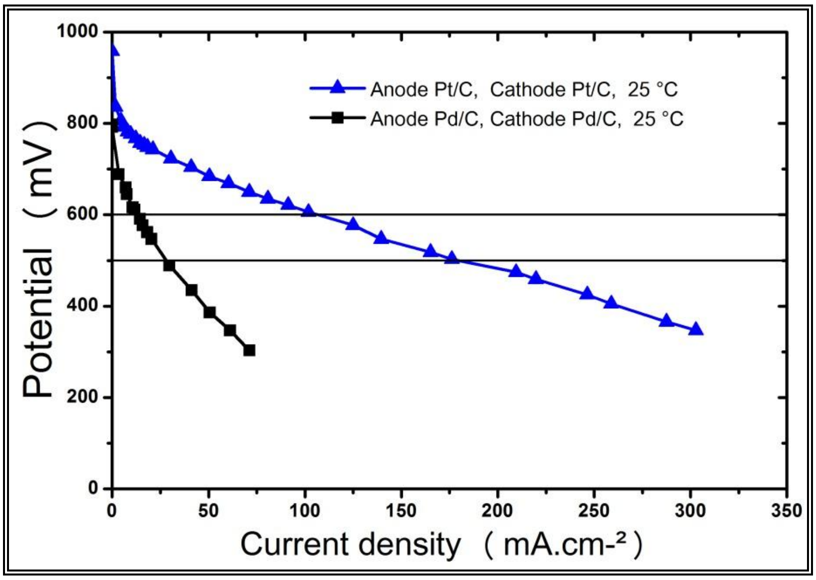

Figure 3. Polarization curves of MEAs with catalysts Pt/Pt and Pd/Pd (anode/cathode)**.** Active area of 5 cm². Anode 0.4 mg metal per cm ² supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm ² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water.

On the Figure 3 it can be seen that the performance of Pd/Pd is about 17 % of that obtained for Pt/Pt, what is similar to reported in the literature [9,10,11,15], Thereafter, to check the influence of the kinetics of the reactions with the Pd/C catalyst, it was evaluated in anodes and cathodes individually, thereby MEAs were evaluated with anodes and cathodes of palladium or platinum alternately. Figure 4 shows resulting performance.

Through the polarization curve shown in Figure 4 can be seen that use of platinum at any electrode with palladium on the other make better the overall cell performance at 25 °C, reaching 80 % of the observed for MEAs with Pt/C on both electrodes. A comparison between the maximum performances of each kind of MEA was performed by studying the temperatures of H_2, O_2 and single cell, seeking maximum performance conditions for each one. Thus such performances are related to kinetic reactions fostering by heating but also with the membrane humidification conditions and reactants flow. The best performances obtained are shown in Figure 5.

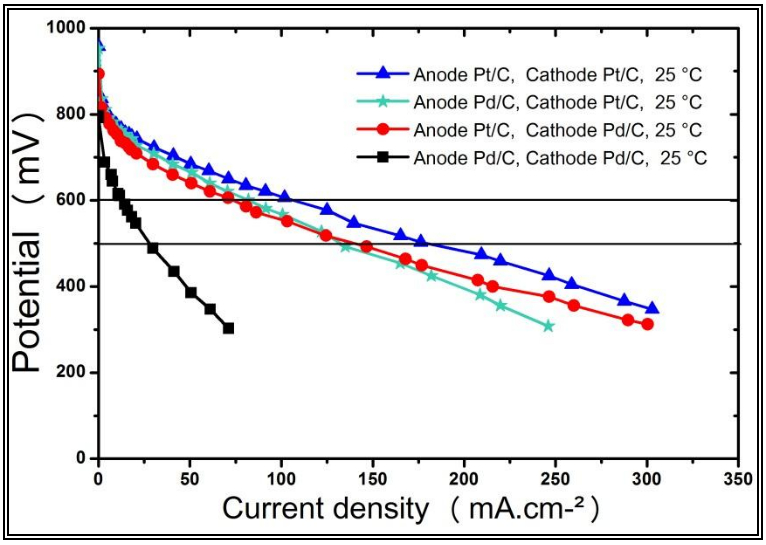

Figure 4. Polarization curves of MEAs with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) electrodes. Active area of 5 cm². Anode 0.4 mg metal per cm ² supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm ² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water.

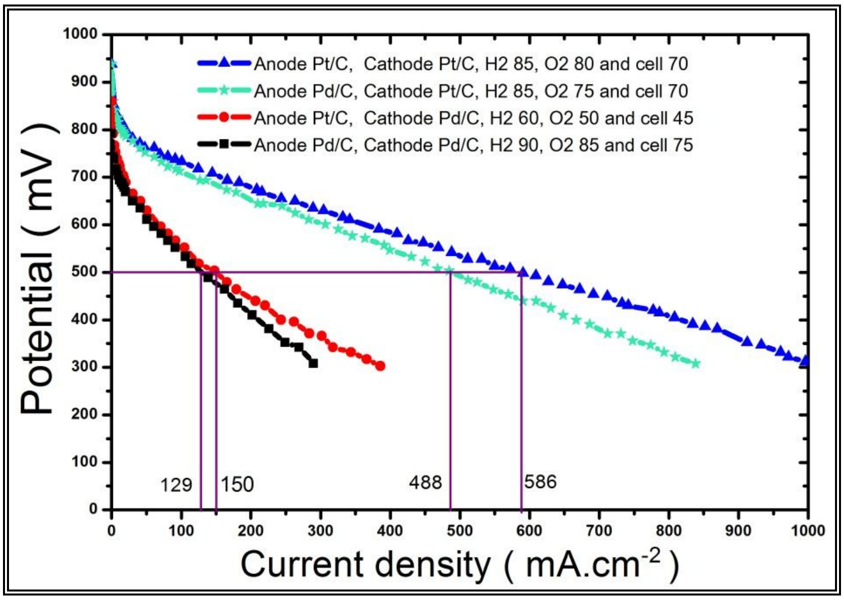

Figure 5. Polarization curves of MEAs with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) **e**lectrodes. Active area of 5 cm². Anode 0.4 mg metal per cm² supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm ² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water. Temperatures of H_2, O_2 and cell that resulted in better performances are presented in the legend of the curves.

Throughout the best operation condition study it was found that changes in temperature affect differently the performance of each kind of MEA, so a study was made between 25 and 100 °C to all of them. Since to present polarization curves for each temperature hinder a global analysis was prepared a diagram showing only the current densities obtained at 500 mV. Figure 6 shows a diagram of MEAs prepared with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd electrodes combinations.

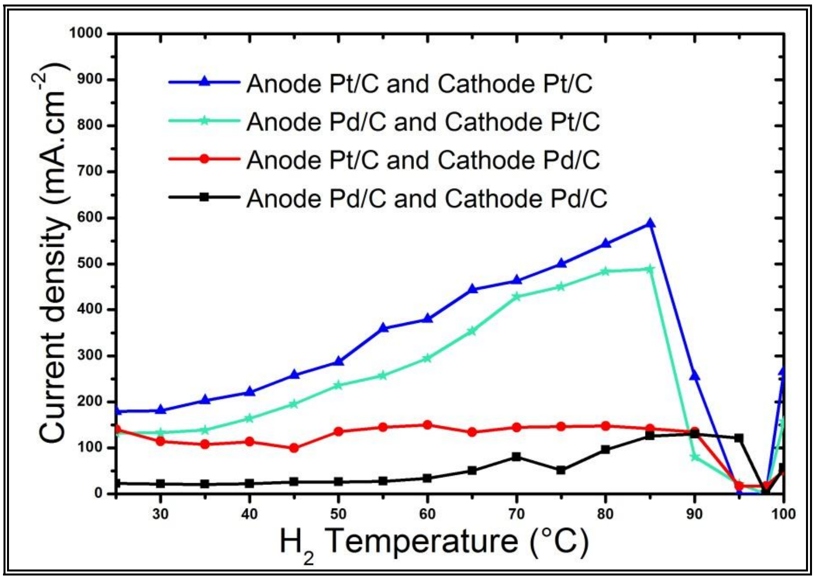

Figure 6. Diagram of current density versus temperatures at 500 mV of MEAs prepared with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) electrodes. Active area of 5 cm². Anode 0.4 mg metal per cm ² supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm ² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water.

From the demonstrated in Figure 6, MEAs with Pt/Pt electrodes perform better than other at 500 mV under the same conditions (except for the drop in performance that occurred at 95 °C and was attributed to the cell flooding). By means of Figure 6 also can be seen that MEAs with Pd/Pt electrodes exhibit performance peak at 85 °C only 17 % lower than that of MEA with Pt/Pt, which is a result favorable to palladium anodes application due to its cost far lower than platinum [4,8,9,13].

Once the assessment of catalyst activity by electrochemical techniques is often not effective on cell experience [7], the question that arose was whether the performances observed in Figure 6 means a similar activity between platinum and palladium in the anodic reaction of PEMFC or if there was a great influence of the operating conditions in the performances obtained. Thus, once the open circuit potential (OCP) of MEAs is the starting point for the charges transfer and for the overpotentials occurrence which reduce the cell performance [2], and that the activation is the major overpotential at the polarization curve beginning [2], the evaluation of OCP variation as function of operating conditions seemed a good parameter to compare the catalysts activities. Figure 7 presents this study for MEAs with all electrodes combinations that have been studied. As can be seen by Figure 7 MEAs with Pt/Pt and Pd/Pt exhibit similar OCP independent of the anode catalyst used, the value remained close to 950 mV with a slight reduction above 85 °C, MEAs with palladium electrodes presented OCP near of 800 mV, but without decrease as a function of operating conditions while MEAs with Pt/Pd showed OCP ranging between 900 and 800 mV as a function of temperature.

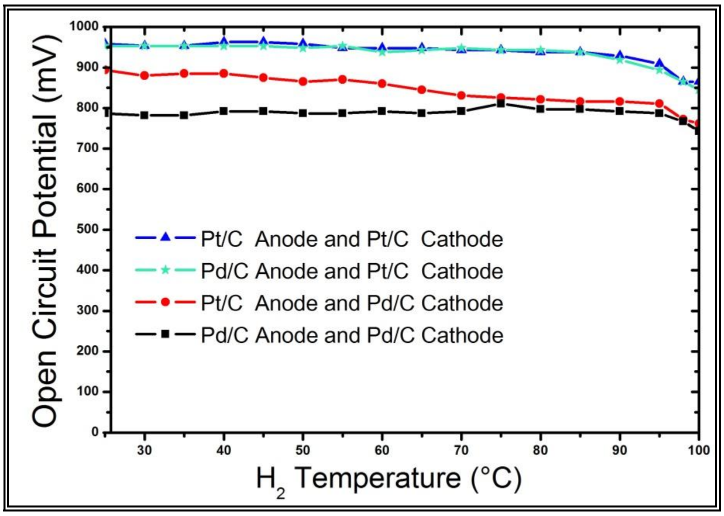

Figure 7. Open circuit potential evaluation of MEAs prepared with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) electrodes. Active area of 5 cm². Anode 0.4 mg metal per cm² supplied with 160 mL.min-1 H_2 at 1 atm. Cathodes 0.4 mg metal per cm² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water.

Once the OCP data is directly related to the catalyst activity and with the electrode/electrolyte interface, thus the analysis of Figure 7 confirms the activity of palladium as a catalyst for the anodic reaction, leaving doubts about the possibility of obtaining better results by optimizing the MEA triple phase reaction for this catalyst. To better visualization of the presented data Figure 8 shows polarization and power densities curves of MEA with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd in the better conditions.

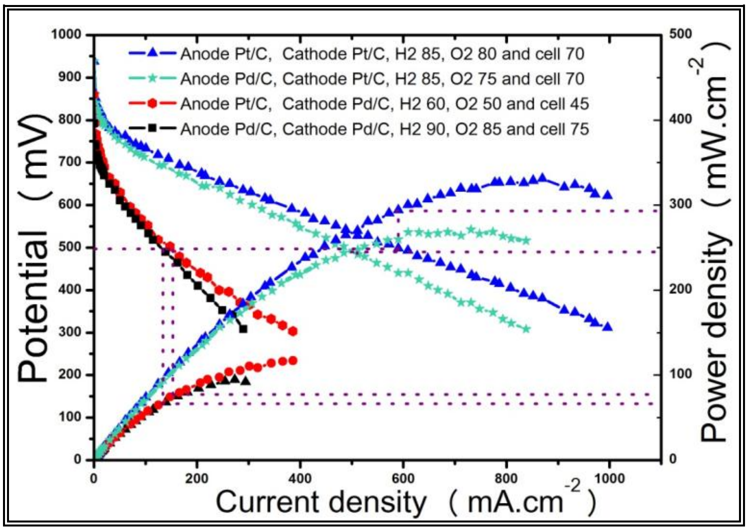

Figure 8. Polarization and power densities curves of MEA with catalysts Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) electrodes. Active area of 5 cm². Anode 0.4 mg metal per cm² supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm² supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water. Temperatures of H_2, O_2 and cell that resulted in better performances are presented in the legend of the curves.

Evidently power densities shown in Figure 8 confirm that observed in previous polarization curves, the values of power density and the performance comparison related to platinum catalyst are shown in Table 1.

Table 1. Power density of MEAs prepared with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) at 500mV and performance comparison related to platinum catalyst.

Electrode		Power densities at 500 mV ($mW.cm^{-2}$)	Performance related to Pt/C (%)
Anode	Cathode		
Pt/C	Pt/C	293	-
Pd/C	Pt/C	244	83,3
Pt/C	Pd/C	75	25,6
Pd/C	Pd/C	65	22,2

From the data of Table 1 it can be seen that the application of palladium on anodes represents a small loss of performance with respect to power density at 500 mV, however, the power module of a fuel cell system would have to compensate this difference increasing the active area, which represent more expenses in bipolar plates and other components, so despite the cost and reserves perspectives the feasibility of palladium application, even in anodes, must be further evaluated.

4. CONCLUSIONS

The borohydride method was suitable to prepare the palladium on carbon supported catalyst (Pd/C) and resulted in catalysts with average particle size of 4.4 nm which was considered adequate, although improvements in the process can lead to a better metal distribution, absence of agglomerates and smaller particle size are desirable.

The Pd/C catalyst synthesized has low activity in the oxygen reduction reaction and activity only 17 % lower than Pt/C in the hydrogen oxidation in MEAs using Nafion 115 membrane. This fact already indicates feasibility of applying palladium in platinum anodes replacement, but more studies on the influence of alloying on the performance of palladium catalyst, especially regarding oxygen reduction reaction and durability tests of palladium-based electrocatalysts are indispensable to confirm the efficacy of this metal in the platinum replacement. Only after verifying the best composition of cathodes and anodes the palladium based catalyst will be possible perform a cost estimation including the number of bipolar plates, every systems and controllers to then be truly confirmed the economic viability of this innovation.

Study the variations of current densities and of open circuit potentials in function of temperature in the cell conditions showed procedures useful to improve understanding of behavior and activity of the catalyst in the cell, although such evaluation may have been influenced by the water management or by triple phase reaction formed in the MEAs in the cell, what also need be evaluated in future studies.

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