Design and Manufacture of a PEMFC Stack Using Pd_5Cu_4Pt/C as Cathodic Electrocatalyst

D.C. Martínez-Casillas[1], O.A. Gil-Esquivel[1], J.L. Díaz-Bernabé[1], A. Rodríguez-Castellanos[1], O. Solorza-Feria[1,*]

[1]Depto. Química, Centro de Investigación y de Estudios Avanzados del IPN,
A. Postal 14-740, 07360 México D.F., México.
[*]Tel: 57473715, fax 57473389, mail: osolorza@cinvestav.mx

ABSTRACT

This work presents the design, manufacture and performance evaluation of a PEMFC stack. The Pd_5Cu_4Pt/C cathodic electrocatalyst was synthesized by chemical reduction of $PdCl_2$, $CuCl_2$ and H_2Cl_6Pt with $NaBH_4$ in THF and supported on Vulcan Carbon by ultrasound assistance. The electrocatalyst was physically characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The design of the fuel cell stack was done using AutoCad software. Manufacture of the fuel cell was carried out by CNC router and CNC laser cutter. 8 membrane-electrode assemblies (MEAs) were prepared by spraying the Pd_5Cu_4Pt/C ink on the cathodic side of Nafion® NR 212 membranes. Then gas diffusion layer (carbon cloth) at the cathodic side and commercial electrode (Pt/C E-tek) at the anodic side of the Nafion membrane were placed, followed by hot-pressing of the assembly at 120ºC and 11 kg cm^{-2} for 1.5 min. The PEMFC stack characterization was performed by potenciostatic polarization test. The operation conditions of the stack were: feeding the fuel (H_2) and oxidant (O_2) at room temperature and a pressure of 1 atm, operation temperature varied from 25 to 42 ºC. Open circuit voltage (E_{OCV}) of the stack was around 7 V, obtaining a maximum power density of W_{max}=527 mW cm^{-2}.

1. Introduction

Decreasing of oil reserves as source of energy generation has caused the investigation of alternative energy sources, mainly those from renewable origin. 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 hydrogen-fuelled PEM fuel cell the cathodic oxygen reduction reaction (ORR) is several orders slower than the anodic reaction. Therefore, the ORR dominates the overall performance of such fuel cells. The ORR has been extensively studied and discussed. However this reaction continues being of great interest. Thus, finding a good ORR catalyst is a subject in PEMFC electrocatalysis.

Up to now, Pt and its alloys are the most active and stable electrocatalysts used for the ORR [2]. However, the high price of platinum and its availability on the planet show us the direction that we should follow, i.e. search new catalyst without Pt or with the least possible content of this metal. A recent study shows that Pd_5Cu_4Pt presents a good electrochemical activity towards ORR as well as performance as cathode in a PEMFC [3].

The aim of this work is the design and manufactures a PEMFC stack using Pd_5Cu_4Pt/C as cathodic electrocatalyst and coupling it to a MP4 multimedia player.

2. Experimental

2.1 Electrocatalyst synthesis

The trimetallic electrocatalyst was produced by a $NaBH_4$ reduction of $PdCl_2$, $CuCl_2$ and H_2PtCl_6 in a THF solution as reported in literature [3]. Briefly, a chemical reactor was charged with the metals precursors and THF, maintaining the solution was under stirring. Then, the reducing agent $NaBH_4$ was slowly added. Afterwards, reaction products were washed and then dried at 60 ºC. An ultrasonic probe was used to support the electrocatalyst on Vulcan carbon XRC-72 at 40 wt%. The Pd_5Cu_4Pt, Vulcan carbon and a water-ethylene solution was charged on a reactor where the solution was bubbled during 15 min with N_2. Then, it was sonicated with high intensity ultrasound for 1 hour. Finally, the obtained black powder was washed, dried and kept in a closed vessel prior to physical characterization.

2.2 Physical Characterization

The Pd_5Cu_4Pt/C was physically characterized by X-ray diffraction (XRD) using an X'Pert PRO PW3040 (PANalytical) with monochromatic Cu $K\alpha_1$ radiation (λ = 1.5406 Angstroms) in a 2θ range from 30º to 90º with a step width of 0.2° min^{-1}. Diffraction pattern was analyzed with MDI Jade 5.0 software to determine the average crystallite size. The electron transmission microscopy (TEM) was used to determine the morphology and particle size. The TEM images were obtained using a Philips CM-200 microscope, operated at 200 kV, equipped with energy-dispersive X-ray (EDX) spectroscopy used to obtain an average local chemical compositions of the sample.

2.3 Design, manufacture and evaluation of the PEMFC stack

The PEMFC stack consists of 8 cells plus an electronic converter to coupling it to the MP4 multimedia player. The design of the stack was executed by AutoCAD software, considering designs previously used in our research group [4-5]. Construction of monopolar, bipolar and end plates were carried out by milling machine through CNC controller. Gaskets, membranes and acrylic pieces were cut by a CNC laser cutter.

Fuel cells are constituted by plates of high density carbon with a thickness of 5 mm, 50 mm wide and 50 mm long. The flow field design of gas to the cathode and anode is shaped cross straight channels. Copper sheets were used as current collector and acrylic plates act as input and output channels for fuel and oxidant. Aluminum end plates, silicone gaskets and stainless steel studs were used. Between each carbon plate there is a membrane-electrode assembly (MEA), a three layered structure, diffusion, catalyst and monomer layers, was used to prepare the MEAs. Figure 1 shows an outline of the stack elements mentioned above from a side view.

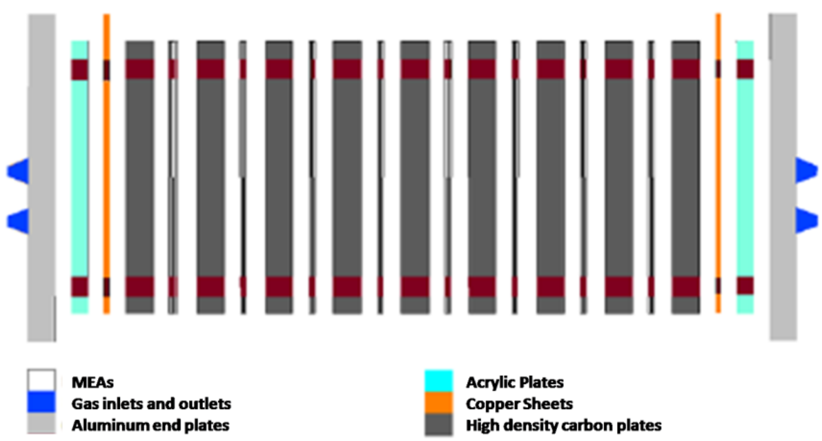

Figure 1. Side view of the PEMFC stack.

Each MEA was prepared by spraying the catalyst ink (Pd_5Cu_4Pt/C 40 wt%) on the cathodic side of the Nafion® NRE-212 (Dupont Fluoro Products) membrane, geometrical electrocatalyst area of 9 cm^2. Then, the gas diffusion layer (porous carbon cloth) at the cathodic side and the commercial platinum carbon cloth (Pt/C, E-TEK, 20 wt% with a loading of 0.5 mg cm^{-2}) at the anodic side of the membrane were placed, followed by hot-pressing of the assembly at 120 ºC and 11 kg cm^{-2} for 1.5 min. MEAs were inserted into the stack for testing. The performances of fuel cells were determined by potentiostatic polarization in a commercial fuel cell system (Compucell GT, Electrochem 890B). The gas pressures at the anode and cathode side were kept at 1 atm for H_2 and O_2. The fuel cell test station was operated with high purity H_2 and O_2 at 50 cm^3 min^{-1}. Humidification of reactant gases was kept at 25 ºC. Operation temperature varied in the range of 25-42ºC.

2.4 Electronic converter

An electronic DC/DC converter was designed and built in order to regulate the electrical energy generated in the PEMFC stack by a low-drop regulator. The lineal buck converter can operates with input voltages from 5 to 8 V and produce an output voltage of 3.8 V with a variation of ± 0.5 V. Figure 2 shows the power electronics, DC/DC converter.

Figure 2. Power electronics DC/DC converter.

3. Results and discussion

3.1 Physical characterization

The X-ray diffraction of the electrocatalyst synthesized is shown in Figure 3 also the crystalline planes of each metal are indicated. Is observable that the diffraction pattern is shifted from the fcc crystalline phase of palladium (JCPDC card 00-065-2867). A peak at 25 2θ degree indicates the carbon present in the compound. The crystallite size was determined by fitting the diffraction pattern using the software MDI jade 5.0. Estimated average crystallite size of about 9.5 nm.

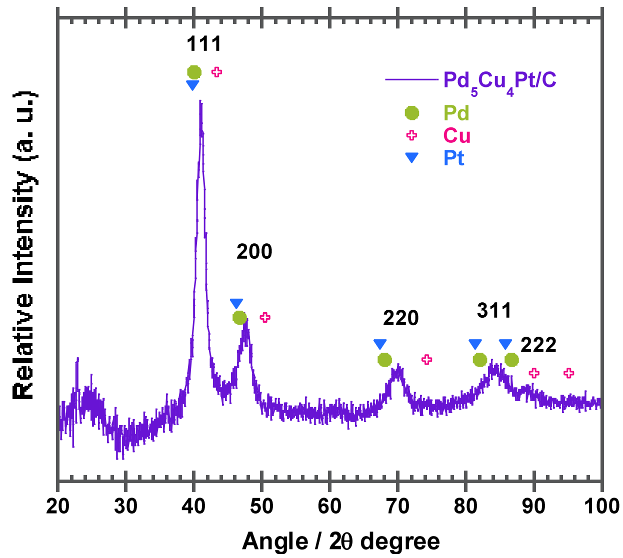

Figure 3. XRD spectra of Pd_5Cu_4Pt/C electrocatalyst.

Figure 4 shows a TEM image of agglomerated particles in nanometric size. It is appreciated that the particles are below 10 nm in size which is in agreement with results obtained from XRD data of Fig. 3. The inset in Fig. 4 shows the corresponding selected area of diffraction patterns. The average composition of the as-synthesized powders, as determined by EDS, was approximately 58 wt% C, 24 wt% Pd, 14wt% Cu and 4wt% Pt, this is in agreement with the expected 40 wt% for the Pd_5Cu_4Pt/C during the supporting technique. Focus on the electrocatalyst average composition was 57 at% Pd, 34 at% Cu and 9 at% Pt, in concordance with the started estimated composition of synthesis.

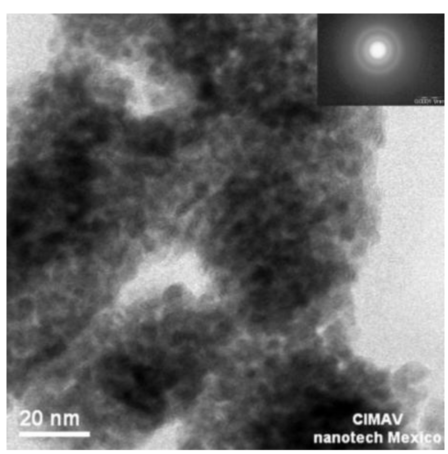

Figure 4. TEM image of the synthesized electrocatalyst. Inset electron diffraction pattern.

TEM mapping images for the Pd_5Cu_4Pt/C electrocatalyst, Fig. 5, shows a uniform elemental Pd, Cu, Pt and C distribution in the particles of the mapped area. Therefore these results agree with those reported for typical electrocatalyst analysis, and suggest that that the Pd_5Cu_4Pt/C nanocrystallite synthesis method is suitable for a cathode catalyst material. The next step was prepared the MEAs as previously reported [3], then assemble the PEMFC stack and characterize its performance.

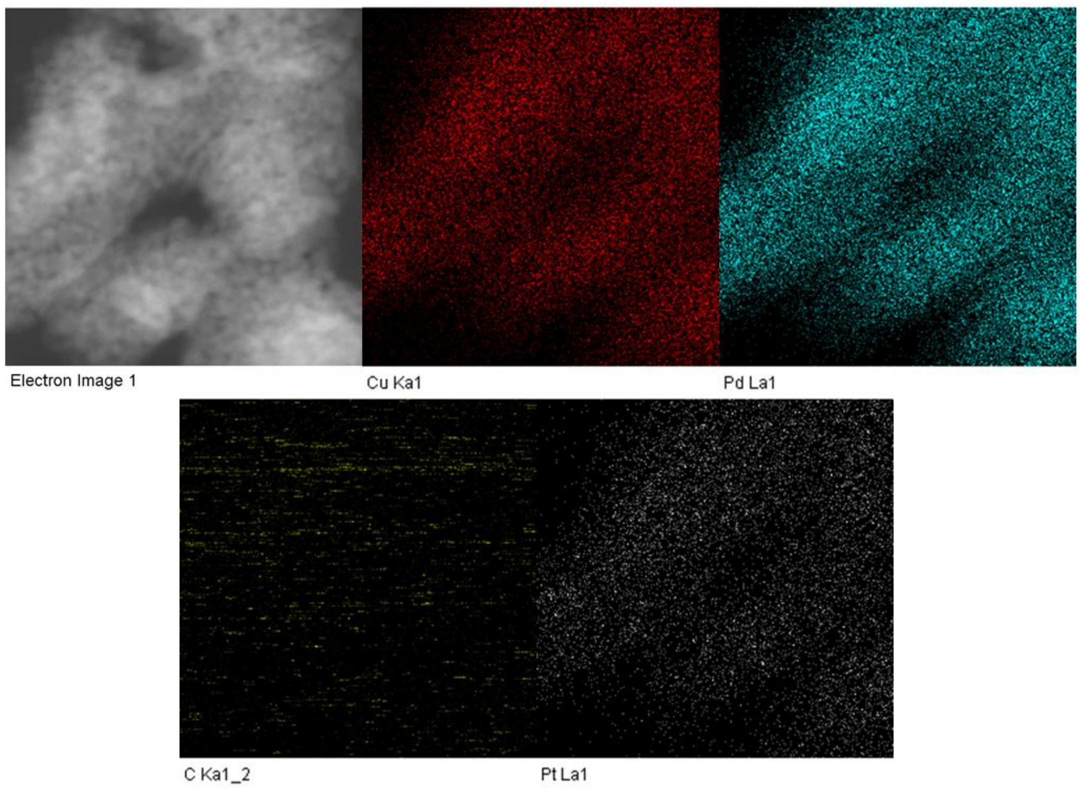

Figure 5. Mapping images of the components of the Pd_5Cu_4Pt/C electrocatalyst.

3.2 Performance of the PEMFC stack

Figure 6 shows the voltage-current response of the fuel cell stack, obtained as described in the experimental section. Can be appreciated an open circuit voltage (E_{OCV}) of the stack was 6.9 V, obtaining a maximum power density of W_{max}=527 mW cm^{-2}. The stack is able to provide the necessary energy to a MP4 multimedia player. In order to test current variations in the stack a curve of current versus time was recorded fixing the voltage at 5 V (maximum voltage required by the MP4). Figure 7 shows a stable response to that voltage for about 1200 min. These results indicate that the stack can be coupled to the electronic converter and finally connected to MP4 multimedia player.

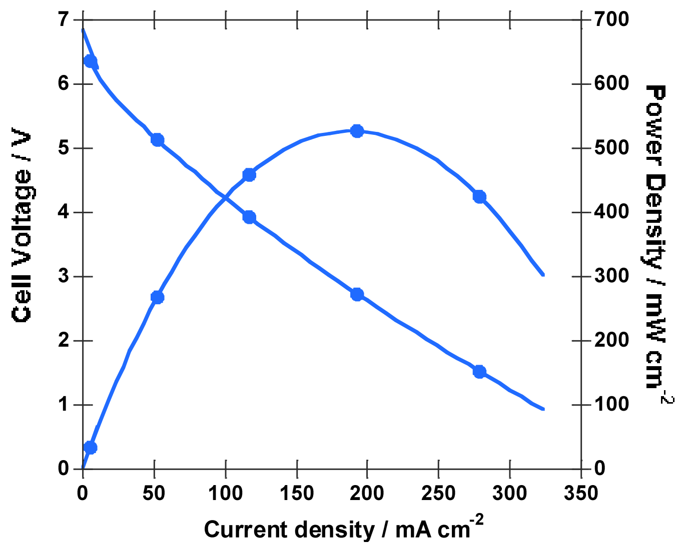

Figure 6. PEMFC stack performance.

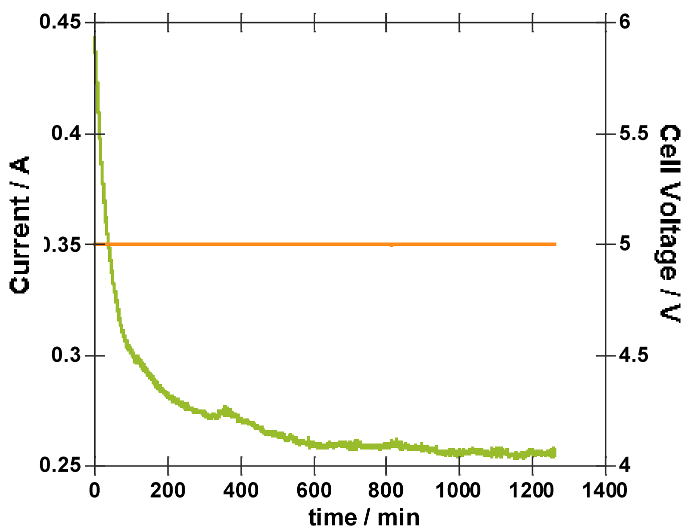

Figure 7. PEMFC stack stability.

3.3 Implementation of the prototype

Figure 8 shows a block diagram of the prototype coupled to the MP4 media player. For the implementation of the prototype two small gas containers were coupled to the cell for H_2 and O_2 storage. Then the gases are feed to the stack by two pumps working at 3V (that voltage can be obtained from the cell) the flows are 200 cc per minute. The stack is connected to the DC/DC converter in order to regulate the electrical energy obtained. Finally from the converter the MP4 multimedia player is connected to be charged. The final working prototype is shown in Figure 9.

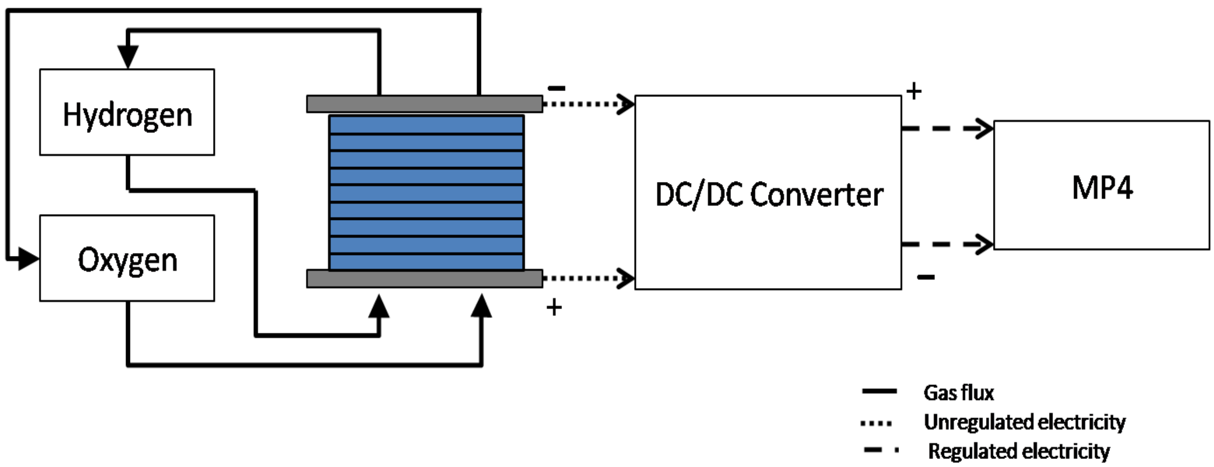

Figure 8. Block diagram of prototype.

Figure 9. Final prototype of PEMFC stack to charge a MP4 media player.

4. Conclusions

The present work shows an easy and effective method of synthesis employed for the preparation of nanometric trimetallic electrocatalyst. Physical characterization indicates the formation of particles with average crystallites around 10 nm in size.

Using the Pd_5Cu_4Pt/C as cathodic electrocatalyst a PEMFC stack was designed constructed. Feeding the stack with high purity hydrogen and oxygen a voltage of 6.9V and a maximum power density of W_{max}=527 mW cm^{-2} were achieved.

The stack was adapted in order to provide the necessary energy to a MP4 multimedia player. This demonstrative prototype is portable and shows that a new electrocatalyst can be used as cathodic electrocatalyst in a real device.

5. Akcnowledgements

We gratefully acknowledge the support of the Mexico’s National Council of Science and Technology, CONACyT, under grants 83247 and 101537. DCMC thanks CONACyT for the doctoral fellowship and OAGE for the bachelor fellowship. The authors acknowledge Dra. Virginia Collins Martínez from CIMAV for the TEM measurements.

6. References

[1] A.A. Gewirth and M.S. Thorum, Inorg. Chem., 49, 3557 (2011).
[2] M. Shao, J. Power Sources, 196, 2433 (2011).
[3] D.C. Martínez-Casillas, O.A. Gil-Esquivel and O. Solorza-Feria, J. New Mat. Electrochem. Systems, in press (2012).
[4] A. Rodríguez Castellanos, E. López Torres and O. Solorza Feria, J. Mex. Chem. Soc., 50, 97 (2007).
[5] E. Fuentes Quezada, A. Rodríguez Castellanos and O. Solorza Feria, Proceedings of X Congreso Internacional de la Sociedad Mexicana del Hidrógeno: “Energías Renovables”, XSMNH056, ISBN: 978-607-95325-1-2, Toluca México (2010).