

Analysis in situ of Pt colloidal nanoparticles deposited onto nafion 117 membrane for PEMFC applications

B. Escobar Morales¹, X. Mathew^{1*}, S.A. Gamboa¹ and U. Pal².

¹ Centro de investigaciones en energía. Universidad Nacional Autónoma de México. Temixco, Morelos 62580, México.

² Instituto de Física, Universidad Autónoma de Puebla, Puebla.

Pt colloidal nanoparticles were deposited by impregnating process onto the anode and cathode sides of a Nafion 117 membrane. Pt nanoparticles were prepared by chemical reduction of salts and colloidal dispersion. The impregnating time of Pt nanoparticles onto the membrane was optimized by analyzing the ionic conductivity of the modified membrane. It was possible to establish a direct performance in the protonic conduction through the membrane as a function of the particle size distribution of the catalyst deposited onto the surface of the membrane. The dispersion of impregnated nanoparticles was investigated by Atomic Force Microscopy. The electrochemical characterization was carried out to evaluate the electrocatalytic properties of the Pt impregnated onto the membrane. It was possible to establish that a change in impregnating time produces a change in the electrochemical behavior of the MEA. The results obtained from the analysis of the MEA by using modified Nafion 117 membrane with catalytic Pt colloidal nanoparticles allows to consider the possibility of using lower Pt loadings in MEAs for obtaining similar performances in experimental PEM Fuel Cell.

Keywords: Nanoparticles, Fuel cells, Electrocatalytic

1.- INTRODUCTION.

The nanoestructurade materials have traced an interdisciplinary effort, their physical and chemical properties have been opposing plentiful. The particles preparation of colloidal size has always been of great interest for the scientific community because many properties of the materials they not only depend on the chemical composition, if not also in the size and the shape of the particle [1-5]. The metallic nanoparticles have been obtained using several methods: thermal [8], photochemical [9], and electrochemical [10] to mention some examples. The chemical methods involve the nanometrics particles

growth that have been synthesized starting from the reduction of the corresponding metallic ions in different solvents and organic materials as ligantes, surfactantes or polymers. Nevertheless, the nanoparticles synthesis with good dispersion is a first step, the following thing it is to support these colloidal dispersions on carbon and to obtain Pt nanoparticles very dispersed on support materials. One of the main applications of the Pt nanoparticles supported on carbon is in combustible cells PEM type. In this work a study of the optic properties of the impregnated Pt membrane is presented as well as its analysis of optical absorption. For the analytic chemistry, the importance of solution

color is based on the fact that the absorbed radiation is material characteristic that is being absorbed [11] and they are related with the particles size.

2. SYNTHESIS OF THE NANOPARTICLES MONOMETALLIC OF PT.

For the colloidal dispersions of nanoparticles monometallic of Pt they got ready solutions of platinum tetrachloride (98% Aldrich, 0.71 mM in 25 methanol ml), the corresponding crystalline material was dissolved in methanol room temperature. Later it was added poly (N-vinil-2-pirrolidone) (99.9% Aldrich, PVP, K-30, 75 mg. MW 10,000) as protective polymer. Finally, a solution of NaBH_4 (1ml of 0.044 M) was added to the resulting solution. A stable, homogeneous colloidal dispersion and of dark brown coloration was the result of the addition of the NaBH_4 . The same procedure was used for the preparation of the other two colloidal dispersions; the molaridades was of 2.61 mM and 1.3 mM.

2.1 IMPREGNATION OF THE Pt NANOPARTICLES ONTO NAFION.

For the impregnations of the colloidal dispersions of Pt membranes onto Nafion 117 were manufactured by Dupont. Before used it the membrane should be washed in several solutions to remove rakes of organic and inorganic pollutants. The activation process is in the following way: 1) Laundry in H_2O_2 to 3% during 30 minutes to temperature among the 70-80 °C. 2) Rinse H_2O in boil during 15 min. (twice). 3) Immersion in H_2SO_4 1M during 1 hour to 85° C. 4) I rest in H_2SO_4 1M during 48 hours. 5) rinse H_2O in boil during 15 min. (twice).

3. CHARACTERIZATION.

A Shimadzu UV-3101PC double beam spectrophotometer with 2 nm wavelength and 1 cm light path length was used to record the spectra absorption in the 300–800 nm wavelength range of the colloids.

3.1 RESULTS AND DISCUSSION UV-VIS SPECTRA ABSORPTION.

Figure 1 shows the spectra absorption for three kinds of samples; membranes impregnated with colloidal dispersion to 2.61 mM of Pt monometallic nanoparticles dissolved in methanol in PVP presence. The figure 1 shows the absorption spectra of the metallic platinum nanopartículas impregnated on Nafion number 117 membranes to different immersion times. The absorption increment with the impregnation time establishes the incorporation of the platinum metallic particles in the Nafion number 117. When the graphics are no showing any pick indicate that a considerable mass of the platinum nanoparticles doesn't exist.

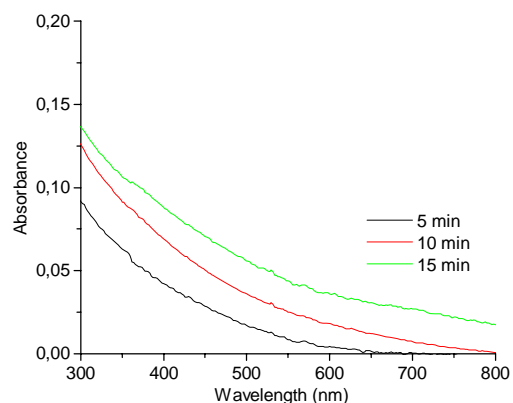


Figure 1 Spectra absorption for impregnated membranes to different times.

3.2 RESISTIVIDAD IONIC OF THE IMPREGNATED MEMBRANES.

The impedance spectroscopy is an electrochemical technique which is applied an electrical interference of small amplitude sinusoidal form (potential or current) to different frequencies. If a $E = E_0 \sin \omega t$, where E_0 it is the amplitude, ω is angular frequency ($\omega = 2\pi f$, f is frequency) and $t = \text{time}$, sinusoidal potential is applied to the system, the current answer, also sinusoidal is $I = I_0 \sin(\omega t + \theta)$ I_0 it represents their amplitude and θ the phase difference with regard to E . In the figure 2 the outline in the four electrodes cell is observed, which was used to measure the electrochemical impedance of the impregnated membranes.

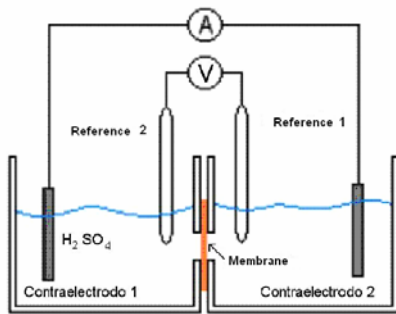


Figure 2 Four electrodes system used for electrochemical characterization.

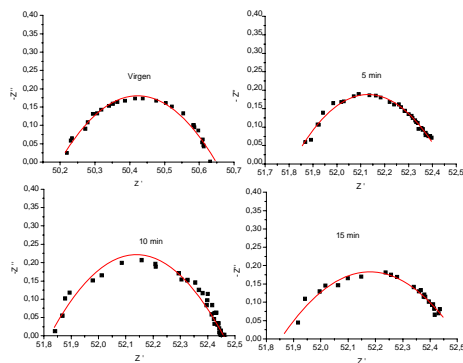


Figure 3 Impedance of the impregnated membranes at different immersion times.

The impregnated membranes at different deposited times (5, 10 and 15 minutes) were analyzed by the four electrodes technique, which they was obtained when the impregnation time increases in the colloidal dispersions of platinum, then an increment is presented in the resistance of the impregnated membranes, probably because it increases conform the impregnation time of the platinum nanoparticles is incorporate to the membrane and somehow it block the membrane active places, for that reason it is considered a good time of 5 minutes of impregnation to guarantee the minimum resistance of the membrane. The obtained resistance values are shown in the table 1.

Table 1 Resistance values of the impregnated membranes.

Time (min)	Resistance (Ohms)
Untreated	0.463
5	0.638
10	0.670
15	0.712

4.- AFM MEASUREMENTS.

In the following figures we present images of Atomic Force Microscopy (AFM) of a membrane with and without impregnation.

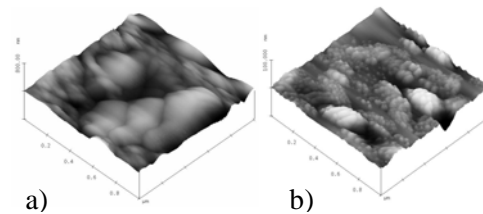


Figure 4 AFM Nafion number 117 imagines a) virgin and b) impregnated 10 min.

Images are possible to compare the Nafion virgin sample with the impregnated sample, in this it finishes a mass of the platinum nanoparticles it is

observed while the virgin sample is free of any material type.

4.- MEA IMPREGNATED.

Nafion 117 membrane was activated and impregnated later during 1 hr with a 2.61 mM colloidal dispersion Pt nanoparticles, the electrodes were carried out with pure coal. The active area of the one assembles manufactured was of 4 cm², the current density that was obtained around 34 mA/cm², which it is very small compared with the assemble with the conventional type. The smallest acting is attributed to two factors. The first one is that we don't know with accuracy the quantity of catalytic material that finally is adhered to the membrane, how much is probable they have been formed heaps that finally impede the step of the ions through the membrane, or that the quantity of stuck material is smaller to the final limit than it reports the literature for the reduction of the Pt load, the quantity for a monolayer that is of 0.54 g/cm², but this value should be increased if the Pt is in spherical particles form of around 5 nm, when 10% of all the atoms could be considered catalytic places, which also depends on the form of Pt particles dispersion and the surface structure [11].

5.- CONCLUSIONS.

Platinum particles of nanometric size were obtained on the surface of the Nafion membranes, one observes that it increases conforms the particles impregnation times are spread to increase the size but always in the nanometers order, and that tendency exists when the impregnation time increasing the nanoparticles quantity stuck to the membrane, this rebounds in the absorption, which also increases when the impregnation time is increased

to. In the case of the resistance, it was obtained that this it increases conform to it increases the impregnation time of the membranes.

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