Obtention of polymeric membrane fuel cells by low pressure plasma technique: Evaluation of total cell efficiency by function on the amount of platinum and the thickness of the deposited carbon support

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Abstract. This work aimed to obtain catalytic support over polymeric membrane building a fuel cell using low pressure plasma technique. For this, polymeric membranes were coated with carbon layer and platinum nanoparticles. The procedures were performed in separate steps in order to obtain firstly carbon layer and catalytic platinum nanoparticles. In the first step, the plasma processes were carried methane in order to obtain carbon layer over the polymeric membrane. At this stage, in order to obtain different thicknesses, were made several processes, reaching a thickness of 0,36μm to 1,4μm. The second step was to get the platinum nanoparticles on the carbon layer. For this, was used a platinum solid source and argon plasma. The study relied primarily on assessing the influence of the carbon layer on the performance of fuel cell. Compared with the commercial processes, it was observed that the results for fuel cells obtained by plasma have a better electric contact on three cell layers (catalyst – electrolyte – reagent). By electrochemical activity test was possible observe increase of reverse voltage of 0.8 volts to 1.24 volts according to increase the thickness of the carbon layer. The same behavior was also observed in the analysis of total efficiency, which was limited to 50% of maximum efficiency of commercial cell due the thickness of the carbon layer deposited during the preparation of this study, indicating a greater thickness with carbon it is possible to achieve the same efficiency of cells better than commercial.

1. Introduction
Fuel cells are electrochemical cells that directly convert the variation of Gibbs free energy of a redox reaction (reduction / oxidation) in electrical energy [1]. Currently, due to increasing demand of energy needed to manage the large amount of technological equipment put on the market, and the growing concern with nature as well as the depletion in renewable, make the fuel cell should be studied more intensively. The subject of intense research is that the problems caused by pollutants such as CO, SO\textsubscript{2} and CO\textsubscript{2} eliminated by fossil fuels are greatly reduced with the use of fuel cell [2].

A fuel cell consists basically of: bipolar plate or interconnector; diffusion electrodes and electrolytes [1, 2]. The hydrogen electrode is the anode or the negative terminal of the fuel cell in which hydrogen enters through channels on the plate [1, 3], and the oxygen electrode or cathode is the positive terminal of the cell. The catalyst turn covers the electrolyte and causes the breakdown of the hydrogen molecule (H\textsubscript{2})
in ions (H\(^+\)) and electrons [1, 2, 3]. The electrons generates the electric current and water is generates by ions H\(^+\) and oxygen molecules from cathode.

The main catalytic material used in this system is platinum particles, but their cost is high, resulting in studies to reduce the amount used in fuel cell. One study refers to developing new technologies to reduce the dimensions of these particles, and thus ensure greater contact area with less platinum [2, 3]. Another responsible for the fuel cell performance is the gas diffusion layer (GDL). The GDL is disposed between the catalyst layer and the bipolar plate channels. The main purpose of this layer is to facilitate the reactants flows and products through the channels and interstices, ensuring contact with the bipolar plate. The electrons need to be guided to the catalyst channels of the plates, which are guaranteed by gas diffusion layer. The GDL also serves to maintain a proper draining of water levels, avoiding lose performance [1, 4, 5].

The polymeric ionic membrane is the main component in the PEMFC (Polymeric Membrane Fuel Cells). The most promising PEMFC use perfluorinated ionomer, among which stands out the Nafion®, first membrane of this type, developed by Du Pont in the 70s [6]. The proton exchange membrane is responsible for conducting protons from the anode to the cathode, electrical isolation between the electrodes and gas barrier between bipolar plates.

The catalysts have properties that vary according to the nanoscale size, improving the catalytic effect when lower is the particle [2, 6]. Catalysts of Pt / carbon have been widely used as electrode materials for converting chemical energy in electricity through electrochemical reactions. The catalyst consists of small platinum particles (about 50 nm) on a surface of carbon particles. The effective contact area of the catalyst increases due to carbon structure and must be in simultaneous contact with the reactants, with the membrane and the GDL which in turn are in contact with the bipolar plates. The catalyst must be attached to the membrane in order to promote contact with the conducting electrons and protons. The interstices of proton conduction consist of a finely divided carbon particles on the Nafion film [1, 7].

The performance maximization of PEMFC results of increase from active surface of catalyst in electrolyte. However when catalyst area is excessive, increases the catalytic layer thickness, promoting a progressive reduction of the mass transfer. The catalyst when produced should balance the platinum on carbon, keeping a thinnest layer possible deposited directly on polymer or gas diffusion layer [8, 9]. The distribution of catalytic particles should be such that homogeneous phase region electrolyte - catalyst - reactant is maximized [7].

2. Material

The platinum nanoparticles and carbon support was obtained in a home building parallel plate plasma reactor (figure 1). The plasma was generated by a radio frequency generator at 13.56 MHz. The catalysts were produced using a 99.98% pure platinum wire. The platinum wire was assembled in grid on aluminum rim. The carbon layers were obtained using methane (CH\(_4\)) 99.5% of purity. Pure nitrogen gas was used for opening and closing the chamber. Nafion® was used as the electrolyte; the sample was 50 x 50 mm area and 1mm thickness. The fuel gases were hydrogen (H\(_2\)) 5.0 (99.999%) and oxygen (O\(_2\)) 4.0 (99.99%). The membrane was actived using sulfuric acid (H\(_2\)SO\(_4\)) MOS grade, hydrogen peroxide (H\(_2\)O\(_2\)) MOS grade and deionized water (18MΩ.cm). The samples were observed by a scanning electron microscope with field emission gun Nova NanoSEM 400 FEI Company. The catalytic metal was analyzed by X-ray diffractometer PANalytical XRD Empyrean and the layer thickness was measured by High step meter model 3030 from Dektak - Sloan.
3. Methodology

The fuel cell was prepared in two steps. The first step was carbon layers deposition in both sides of polymeric membrane and in different thickness. After that, were realized the platinum nanoparticles deposition also in both sides of polymeric membrane. After fuel cells preparation, followed the assembled and efficiency tests. The procedure steps are described bellow:

3.1. Carbon layer deposition

For carbon layer deposition was used methane 99.5 % of purity which was inserted inside of the chamber at low pressure. To fill only the useful area was used an aluminum rim with 100 x 100 mm of size. In the center of this aluminum rim was made an aperture of 30 x 30 mm. The polymeric membrane was positioned on the aluminum electrode (150 mm diameter) and the aluminum rim was placed immediately over it (figure 1). Therefore, besides to fill just the useful area of fuel cell, the aluminum rim kept the polymeric membrane positioned on electrode center, improving the thermic contact from polymeric membrane with the cooled electrode and thus avoiding polymeric membrane damage by high temperature caused by plasma process. The parameters were set up to 300 mTorr of pressure, 200 watts of RF power and the methane gas flow used was 72 sccm. The time for all process was 5 minutes. For the reach different layers thicknesses the processes were made in different steps. For one carbon layer, the time process was 5 minutes in each polymeric membrane side, in other words, ten minutes of total process to both sides. For two carbon layers were made two processes, in other words, was made five minutes of process in each polymeric membrane side and after that, the process was repeated again, totaling twenty minutes of total process deposition. For other carbon layers following the same steps which means the process was repeated three times for three carbon layers, four times to four carbon layer increasing the processes amount until the eight carbon layers. The last process the total time was eighty minutes for eight carbon layers deposition.

The purpose for using only 5 minutes each plasma process was avoid to damage the polymeric membrane because the temperature inside of the chamber caused by plasma effects. The time between each process is enough to decrease the temperature on the electrode and keep to near the room temperature.

3.2. Platinum nanoparticles deposition

The second step was platinum nanoparticles deposition over the carbon layers obtained in previous step.
The platinum nanoparticles were obtained by platinum grid. The same situation was used for reach to platinum nanoparticle just on useful area of fuel cell. Some platinum wires were cut and assembled over an aluminum rim prepared like in carbon layer deposition process, but in this case, the platinum wires were placed on aperture crossing and forming a grid. The purpose of this platinum grid was to fill all useful area of fuel cell using low radio frequency power and lower time process, thus, the amount of platinum nanoparticle deposited on polymeric membrane would be much lower than commercial process, besides the shape and size would be more controlled. In this process the polymeric membrane containing the carbon layers were placed over the electrode and below the platinum grid. After reduce the chamber pressure near to 1 mTorr, was injected inside of the chamber argon 99.995% of purity at flow of 45 scem and pressure of 500 mTorr. After set up these parameters was controlled the Radio frequency power in 100 watts and so followed the process for 30 seconds each side of polymeric membrane.

3.3. Preparation of polymeric membrane
After the deposition of nanoparticles in the polymeric membrane, the following step was the preparation of the membrane to application in the fuel cell. For the preparation of the cell, chemical cleaning processes were carried out to activate the cell. The following steps were taken: Bath in a hydrogen peroxide solution 3 vol at 80 °C for 1 hour, then three deionized water baths were performed for three hours each at 80 °C and then one sulfuric acid bath also for one hour at 80 °C. Finally more three baths in deionized water for one hour each at 80 °C.

3.4. Tests of electrochemical activities
After all deposition processes and the preparation of polymeric membrane by chemical cleaning, the fuel cells were assembled in a half-cells experimental parker fuel cell in order to verify the total efficiency evaluating mainly the influence of carbon layer thickness. The gases used were hydrogen 99.995% of purity and oxygen 99.995% of purity. In order to keep the membrane humidity was used deionized water at 18 mega ohm. The load was simulated by resistors connected in parallel with the fuel cell. The gases were controlled by mass flow controllers. For comparison test was used a total efficiency commercial cell like reference.

4. Results and discussions
The results of carbon layers thickness measured shown an increase of thickness from 1 to five layers, but after the fifth layer does not have any more increase of thickness (table 1). This can be explained by plasma system build which works like corrosion plasma system. In other words, mean that after a thickness given, the carbon film does not have a good adherence over the previous carbon layer film and then, the plasma corrosion is started over the last carbon layer.

| Thickness of carbon layers (μm) | Commercial fuel cell | Produced by plasma technique |
|--------------------------------|----------------------|-----------------------------|
| 1 layer                        | 0.361                | 3 layers 0.578              |
| 2 layers                       | 0.455                | 4 layers 0.623              |
| 3 layers                       | 0.578                | 5 layers 1.435              |
| 4 layers                       | 0.623                | 6 layers 1.368              |
| 5 layers                       | 1.435                | 7 layers 1.249              |
| 6 layers                       | 1.368                | 8 layers 1.138              |
| 7 layers                       |                      |                             |
| 8 layers                       |                      |                             |
By table 1 is possible to observe that the maximum of carbon layer reached by plasma technique was 1% of commercial fuel cell carbon layer. Although the carbon layer thickness had lower than commercial fuel cell, the electric contact of fuel cell produced by plasma technique was better due the film adherence on the polymeric membrane. By other hand the gas diffusion layer (GDL) was very thin and this hindered the fuel diffusion which decreases the performance of fuel cell.

By figure 2 is possible to see that after five carbon layer, the thickness start to decrease due the corrosion process. By extrapolation, continuing the carbon layer deposition process, each process, the carbon layer would decrease more and more, implying limitation of plasma process in five carbon layers maximum.

![Figure 2: Graphic of carbon layer thickness x number of carbon layers deposited by plasma technique](image)

The platinum nanoparticles obtained by plasma technique shown homogeneous size and shape (figure 3). The shape and size homogenization, besides better distribution over the membrane, improves the performance of fuel cell, so that can be use lower amount of catalizer. Thus the platinum mass deposited on polymeric membrane was 2.16 mg. That mass corresponds to 30% of total platinum mass used in commercial fuel cell.

![Figure 3: Platinum nanoparticles over carbon film](image)
By the figure 3 can observe that platinum nanoparticles are evenly distributed in the substrate. The nanoparticles size obtained was 50 nm and which is possible to see the uniformity for all particles deposited by plasma technique.

By activity electrochemical test was possible verify the fuel cell efficiency in relation at thickness of the carbon film. Thus was kept the same processes parameters for all platinum nanoparticles deposition, in other words, kept the amount of platinum mass deposited approximately in the same value for all fuel cell produced by plasma technique, changing just the GDL thickness.

So, was to be expecting different results for fuel cells with different carbon layer thickness. This way, when higher the thickness better would the fuel cell performance. Firstly for calculate the total efficiency of fuel cell, was measured the voltage and current (figure 4 and 5).

![Figure 4: Graphic showing the influence of carbon layer in the voltage](image1)

The figure 4 shows the voltage reached by electrochemical activity test. By comparison is possible to see the difference voltages of cells. The commercial cell simulates the conditions of voltage for parameters applied and can see that how much higher the thickness higher the voltage reached.

![Figure 5: Graphic showing the influence of carbon layer in the current](image2)
The evaluation of current shows the operations of cells upon load applied. It is possible to see that the behaviors of the current curves are the same for all cells. Although the curves behaviors of current are the same, the values of current are different, with small difference between the cells for high load and bigger difference when applied small load, reaching around to 62 mA for commercial cell and 20 mA for cell produced by plasma with carbon film higher than 5 layers.

This shows that how much higher the carbon thickness better is the performance of fuel cell. The performance of fuel cell was compared by polarization curve graphic [figure 6].

Figure 6: Polarization curve showing the performance of fuel cell according to layer carbon deposited

It’s possible to observe in the figure 6 that for the first carbon layers the performance of fuel cell is far below from measured in commercial fuel cell, but as carbon layer thickness increase, the fuel cell performance improves, approaching of commercial fuel cell value and reaching the maximum limit for the fifth carbon layer.

From these graphics was possible calculate the total efficiency of fuel cells [figure7]

Figure 7: Total efficiency of fuel cell according to layer carbon deposition
The total efficiency was showed in the figure 7 and can be observed the curve behavior is the same for all fuel cell, although measures have been smaller than obtained in commercial fuel cell. By comparison the total efficiency for commercial fuel cell was near to 60 % while the fuel cell produced by plasma technique was near to 30%. Mean to say that using 70% less platinum than commercial fuel cell, was possible achieve almost 50% of total efficiency of a commercial fuel cell even with a thin GDL. The results suggest that with increase of carbon layer thickness the efficiency also increase, this way the cost of fuel cell production decrease because the amount of metal used would be 70 % less.

5. Conclusions
The carbon layer has a great influence on the fuel cell performance, so the higher the carbon layer thickness higher performance. The results obtained in this work show that the carbon layer thickness deposited by plasma although very thin, got a relative efficiency, which is not higher because the limitation of carbon layer thickness deposition by plasma process which occurs due the corrosion on carbon film after some plasma processes. In the other hand the phase region electrolyte - catalyst - reactant was better than commercial fuel cell due the total adherence of carbon film on polymeric membrane. The possibility of control all processes parameters allows different setups, implying to adjust the deposition process of carbon to increase its thickness in reduced times, avoiding damage to polymeric membrane and increasing the efficiency of the fuel cell, besides, allows to control the size and shape of platinum nanoparticles and consequently decreasing the total mass of platinum applied on fuel cells without lose the efficiency. This way the results obtained in this work suggest with increase of carbon layer thickness the efficiency also increase, reducing the cost of fuel cell production because the amount of metal used would be 70 % less.

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