Platinum nanoparticle deposition on polymeric membranes for fuel cell applications

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Abstract. This work aimed to show an alternative to produce platinum nanoparticles directly on a polymeric membrane using plasma technique, in order to make these nanoparticles adhere to the membrane, in size, shape and homogeneity controlled by the process without damaging the polymeric material. In this manner the cell’s production time is reduced since the catalyst is directly deposited on the polymeric membrane; the time of the process is approximately five minutes for each side of the membrane, and the total time for each membrane is 10 minutes. With this exposure time, and the advantage of controlling the other parameters such as pressure, RF power, gas flow rate and temperature of the electrode, it was possible to obtain platinum nanoparticles with dimensions of about 50 nm scattered homogenously on the membrane, without damaging the structure of the polymeric material and, consequently, affecting its performance. Together with platinum nanoparticles were also deposited carbon nanoparticles, so that these acted as catalyst support, avoiding self poisoning. Electrochemical activity tests were performed to test the efficiency of the cell where it was exposed to different pressures and flow rates of O2 and H2, reaching open-circuit voltage of 750 mVolts.

1. Introduction
Nowadays there is a great concern about the generation of energy due to the emission of pollutants that greatly contribute to air pollution and environmental disasters caused by fossils and nuclear fuels [1]. A technology that has been studied in depth recently is the process that involves fuel cells, which not only is a source of renewable energy but also contributes to reducing pollution and threats to nature. An example of fuel cell is one that uses the proton exchange membrane technology. A catalyst (usually a platinum nanoparticle) is added to this membrane. The platinum is a rare metal and tends to become increasingly scarce due to its various applications. Thus, studies are conducted to reduce the amount of platinum used in fuel cells. One way to reduce the quantity of the metal and not affect the performance of the cell is to also reduce the size of these nanoparticles. Just as the nanoparticles are reduced the effects of size and surface are increasingly noticeable. Researchers have observed in metallic and semiconducting nanoparticles for example that by reducing the size of nanoparticles is a confinement of electrons is achieved. This confinement causes a quantum effect in the material. This is observed through the magnetic and optical properties, as well as the electronic conduction which are different in a larger size nanoparticle. The size also affects the thermodynamic properties such as heat capacity [2]. As to the surface effects, there is an increase in the surface free energy, which is caused by incomplete chemical bonds of atoms at the surface, since these are less tied than the atoms of the nanoparticles. These effects affect surface properties such as melting temperature, chemical reactivity.
and optical absorption. The melting temperature of platinum for example, falls from 1,773 °C in solid volume to 600 °C, for nanoparticle size 8 nm [3].

The particle shape also changes as it approaches the nanometer scale. This makes the knowledge of the properties of these nanoparticles very important for the application of this technology whatever the area it is applied to [1,4,5,6].

The techniques used to obtain nanoparticles vary according to the availability of resources, as well as the desired final application, and range from simple processes as the dissolution of the liquid phase wet via to a process more expensive and complicated processes.

This present work aimed to show the attainment of platinum nanoparticles using a physicochemical process, in which plasma equipment was employed.

The plasma technique for obtaining carbon nanotubes and nanoparticles in general has increased significantly due to its reproducibility, uniformity of size and shape of particles and nanotubes generated as well as the quickness of the procedures. In catalysts, studies have been developed to generate metal nanoparticles directly on carbon particles, allowing an increase in catalyst efficiency [7,8]. Studies using capacitive-coupled plasma equipment showed that by submitting a platinum target to argon plasma it is possible to extract the platinum particles from the raw metal and deposit them on a support inside the reactor. And also if these platinum nanoparticles mixed with a gas containing carbon, it is possible to generate carbon particles decorated with platinum nanoparticles, which in turn can significantly increase the performance of a fuel cell [9].

In the case of proton exchange fuel cell, the carbon support is critical for the proper functioning of the cell because it will cause this exchange to take place efficiently and it will avoid the self poisoning of platinum nanoparticle. The polymer membrane fuel cell operates at low temperature between 60 and 100 °C. Its operation requires highly pure hydrogen in order to avoid the poisoning of the electrolyte. It consists of two electrodes (hydrogen and oxygen) separated by an electrolyte and electrically connected to an external circuit through which the electrical current flows. Electrolytes are coated by the catalyst, which is platinum in the majority of cases. This serves to accelerate the reactions in electrolytes and break the hydrogen molecules [10,11]. These functions may vary depending on the nanoscale size, as stated previously, and this can directly affect the catalytic activity [2]. One of the materials commonly used as electrolyte is Nafton®, which is obtained by copolymerization of perfluorinated vinyl ether, which has as its terminal group the SO₂F, with tetrafluoroethylene. The performance of this electrolyte will depend on their physicochemical characteristics like: high ionic conductivity, chemical stability, low permeability to the driver and oxidant, low electro-osmotic flow and thermal stability. The proton conductivity through the Nafton® membrane, is one of most important properties for the application in fuel cells, because stopping the flow of proton across the membrane, would cause the cell's circuit to be interrupted and thus the cell to stop working. Another important factor is the transport of water through the membrane while keeping the cell always in optimal humidity condition. If this condition is not satisfactory, the cell’s performance can be affected in three ways: 1- Dehydratin of the regions of the membrane on the cathode side and affecting the proton conductivity through the membrane. 2- Accumulation of water in the cathode hinders the diffusion of oxygen to the catalyst. 3- Minimization of the negative electro-osmotic effects by the diffusion of the water returning from the cathodes to the anode. These considerations are important when dealing with material processed at low pressure plasma, because the conditions within the chamber such as humidity, pressure, temperature, U.V. radiation and ion bombardment can modify physicochemical or even structural properties, compromising the performance of the cell [11].

The most common methods of coating these electrolytes involve using sheets of carbon as support, where platinum nanoparticles are then deposited. When ready, these catalysts are hot pressed to the Nafton® membrane on both sides, then coating the electrolyte [12].

The purpose of this study was to produce platinum nanoparticles directly on the Nafton® membrane, so that these nanoparticles were homogeneously scattered, within the nanoscale and homogeneous shape without compromising the electrolyte in both its structure and its performance.
2. Material
The plasma equipment used to obtain the nanoparticles was parallel plate plasma with arc system, with a volume chamber of approximately 3.5 liters. The plasma was generated by a radio frequency generator operating at 13.56 MHz. The catalysts were produced using a 99.98 % pure platinum wire, and it was assembled in the form of a coil with five turns. The diameter of each turn was 10 mm approximately and spaced at approximately 0.5 mm. The gases used for plasma generation were industrial acetylene (C₂H₄) and argon (Ar). The acetylene gas was the source used to produce the carbon support and the argon gas was used to increase the ion bombardment on the platinum wire pulling particles and directing them towards the catalytic support. 99.999% pure nitrogen gas was used for opening and closing the chamber. Nafion® was used as the electrolyte; it was 50×50 mm² and 1 mm thick. The gases used as fuel were hydrogen (H₂) 5.0 (99.999% pure) and oxygen (O₂) 4.0 (99.99%). The membrane was prepared after obtaining the catalysts, using sulfuric acid (H₂SO₄) MOS grade, hydrogen peroxide (H₂O₂) MOS grade and deionized water level 18MΩ.cm. The samples were observed through a scanning electron microscope with field emission gun Nova NanoSEM 400 FEI Company. The metal deposition was observed through an Energy Dispersive Spectroscopy (EDS) Noran System Six of Thermo Electron Corporation, by SEM 6460LV of JEOI and an x-ray diffractometer PANalytical XRD Empyrean and the electrical resistance of the material deposited on the membrane was measured by four point probe FPP 5000 of VEECO Instruments INC.

3. Methodology

3.1. Assembling the platinum coil inside the plasma reactor
The previously molded platinum coil was connected to the plasma electrode through at the ends of the rods which acted as a support sustaining the coil at a high of approximately 10 mm (figure 1). This way, the membrane can be placed between the coil and the electrode causing the metal particles to be directed towards the electrolyte during the process.

Additionally it was also inserted between the coil and the membrane an aluminum mold with an opening that corresponds to the cell’s work area in the center of the mold, causing the released particles to reach only the cell’s work area, leaving the sides of the electrolyte free for assembling.

![Figure 1. Assembling of platinum coil inside plasma reactor.](image)

3.2. Obtention of nanoparticles deposition by plasma process
After assembling the platinum coil on the electrode, the polymeric membrane was inserted in the reactor, between the electrode and the coil. The aluminum mold was placed on the membrane so that the nanoparticles were deposited exclusively in the cell’s work region.
After assembling the cell in the chamber, the lid of the reactor was closed, the valves were opened and the system was evacuated until 1mTorr of pressure. So, with the reduced pressure, the gases of the processes were inserted at flows of 18 sccm for the acetylene and 45 sccm for the argon. Then the total system work pressure was controlled in 500 mTorr.

Once the flow and pressure were controlled the RF power was adjusted to 200 Watts. These conditions provided the heating of the electrode, which can harm the membrane [11], so the electrode’s temperature was reduced to 10°C and after five minutes, the power was turned off. After that the valves were closed and the gas pressure was reduced again in order to clean the chamber.

With the pressure close to 1 mTorr, the vacuum pump valves were closed and then the nitrogen gas was inserted to open the chamber. With the chamber opened the membrane was moved for deposition on the other side.

3.3. Preparation of polymeric membrane
After the deposition of nanoparticles in the polymer 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. Assembling of the fuel cell
After preparing the membrane, it was then assembled in an experimental parker fuel cell. After fixing the membrane in half-cells, these were closed and proceeded to be tested for leakage. The cell was inserted into a water container and the system was pressurized. After observing that there was no leakage in the system, the electrolyte was moistened with deionized water through the method of dragging for 15 minutes.

3.5. Tests of electrochemical activities
The oxygen and hydrogen gases were connected to the fuel cell and monitored by pressure gauges, so that it was possible to observe the effects of gas pressure variation in the voltage measurements achieved. This voltage was taken as a function of pressure up to a point where it reached the maximum for the designed cell.

4. Results and discussions
In order to evaluate the shape of the platinum nanoparticles and carbon deposition, as well as the coverage area of the deposition of these particles, tests were performed on 10×10 mm² glass laminas. Thus it was possible to adjust the parameters of RF power, pressure, gas flow rate and exposure time to reach homogeneous shape and sizes of platinum nanoparticles and carbon deposition. These tests also served to check the influence of the plasma temperature on the sample, which would hinder the application of this process on polymeric material. The distance between the coil and the substrate was set as this is also an important factor in heating the substrate, that is: during the process, the coil heats up due the effects of generating the plasma, such as current and ionic bombardment. This temperature can cause irreversible damages to the membrane. On the other hand, if the distance is too large, the dispersion of the particles may not be enough to ensure good homogenization, and may not generate the plasma within the coil, especially if the coil is out of the sheath region of the plasma, which would hinder the release of the platinum particles. The process time was 5 minutes, so that the substrate temperature was near to room temperature and there was a deposition of homogeneously shaped and sized nanoparticles scattered in the substrate (figure 2).

In these images it was possible to observe that the platinum nanoparticles did not overlap each other as they were deposited on the carbon film, which led to infer that in a polymeric membrane these nanoparticles would be well scattered and would contribute to good cell performance. Observing these
images it was also possible to calculate by extrapolating the amount of platinum nanoparticle deposited, and in this way a result of 200 nanoparticles/mm² was reached. Some of these samples in glass were analyzed by EDS, and the results obtained showed the presence of platinum (figure 3). With this information, the plasma process on the polymeric material was then carried out.

![Figure 2. Deposition of platinum nanoparticles and carbon on glass substrate.](image)

![Figure 3. Analysis by EDS showed the presence of platinum on the substrate.](image)

The next step was to submit the polymeric membrane to the plasma process in order to evaluate if the platinum nanoparticle generated and the carbon film would be reproducible in this material, and if the material would support the process conditions. The Nafion® membrane was then placed in the
reactor and exposed to the process under the same conditions of pressure, gas flow, power and process time, and also the cooling of the electrode. In the case of the membrane the difference was in the process time, because this had to be done in two stages, in a total of 10 minutes (5 minute each side of the membrane). However, by adjusting the temperature of the electrode to 10 °C, the opening time of the chamber already cools the electrode enough so that when the process is restarted on the other side of the membrane, the temperature inside the reactor does not damage the material. After the process was performed on both sides, it was possible to observe the fuel cell’s work area filled with the deposited material (figure 4).

Figure 4. Polymeric membrane with the work area filled with nanoparticle of platinum and carbon.

The polymeric membranes have properties that may be altered when exposed to certain conditions of pressure, humidity, temperature, etc. This issue was observed when the sample was exposed to the low plasma process. Although the temperature was controlled, a dry membrane was found. This was due to the lack of moisture inside the chamber. To avoid this problem, the membrane was fixed in the aluminum support being stretched and enabling the deposition in the entire region of the polymeric membrane. The images obtained by SEM-FEG show that the parameters used both in the glass and in the polymeric material, were not in a matter of reproductive size, but the shape and homogeneity of the dispersion on the substrate was satisfactory. The nanoparticle size increased to approximately 250 nm, but the format remained rounded (figure 5). The increase in size of the nanoparticles can be explained by the relief of the substrate, which makes the smaller nanoparticles grains accumulate until the end of the process generating the larger grains.

An indication that the substrate relief influences in nanoparticles dispersion, is that the larger nanoparticles were founded in the furrows of the material, and in the same sample were also found smaller nanoparticles on the surface (figure 6). It can also be observed that the shape of nanoparticles generated on the surface does not correspond to what was obtained in the glass sample. This may be due to the fact that during the plasma process very small grains are stripped off the platinum wire and deposited on the material, because of the energy and amount of grains removed, the grains join together with other grains already deposited in the cavities of the membrane, thus forming larger and rounded grains. The smaller rod-shaped grains have a smaller amount of added platinum grains, since there is a greater chance of dispersion of these grains on the surface of the sample. This can be clearly observed on the glass, as the surface is flat and the grains are dispersed in small sizes. But this apparently not so homogeneous distribution of nanoparticles did not cause a discrepancy in the measurement of electric resistance of the sample, it was measured an average of 13.45 Ω, and the difference between the five points measured in the sample was 0.67 Ω, which proves that the concentration of particles was well distributed on the work region of the fuel cell.

As mentioned earlier, the humidity of the membrane is an important factor. During the process low level of moisture may cause the pores of the membrane create furrows.

These furrows cause the nanoparticles to deposit unevenly, with higher concentrations in some regions and more scattered and in others. But, in general, the whole work area of the fuel cell was covered with the material of the catalysis, enabling its application in the fuel cell. It is noteworthy that
these furrows were not caused by the plasma process exclusively, but that the membrane already has these cavities in its construction. What happens is that during the plasma process these furrows tend to get bigger due to lack of moisture in the chamber. To try and solve this problem, the membrane was stretched, and the area of furrow formation was reduced and the nanoparticles deposition was more evenly distributed.

![Figure 5. Platinum nanoparticles on the Nafion® membrane.](image)

![Figure 6. Nanoparticles on Nafion® (surface region).](image)

The x-ray analysis performed on Nafion® processed samples by plasma confirmed the presence of platinum (figure 8), among other constituents of the material, and of other materials present in the construction of the reactor. Comparing the plasma process on the polymeric membrane with platinum wire (raw material) and platinum deposition plasma process on a glass sample, it was possible to see the difference between the elements present in the two sample (glass and polymeric membrane), besides to separate the position platinum point. So, the figure 9 shows the analysis of platinum wire.
without plasma exposition. This material was put directly on x-ray support, for platinum position definition.

**Figure 7.** Polymeric membrane furrows.

**Figure 8.** X-ray analysis showing the presence of platinum in Nafion® membrane.

Figure 10 shows the glass sample after platinum plasma process deposition in the same condition of polymeric membrane process. The noise shows the chemical elements present on the sample. Not all chemical elements observed on the noise are contaminants, and almost all belong to the material construction. It is possible to observe in the figures that the platinum peaks were higher than noise which represent the contaminants, which leads to inferring that the interference in the cell’s performance is very low, further showcasing the viability of this process directly on polymeric membrane for obtaining nanoparticles. These results of the plasma process on the membrane were tested for electro-chemical activity. Firstly, the membrane was chemically activated, for it to come into the appropriate operating system, enabling the pores and the channels, responsible for the electro-osmotic flow. Moreover, it was observed that during the production of nanoparticles there was strong membrane dehydration which could potentially affect its proton conductivity, so watering was necessary.
Figure 9. X-ray analysis on wire platinum showing the platinum peak.

Figure 10. X-ray analysis on glass sample after plasma process.
During the activation process and hydration of the membrane the roughness of the membrane’s surface disappeared, showing a good recovery of the material when hydrated.

It is known that the water flow affects the performance of fuel cells. So dehydration of the membrane on the side of the cathode and the accumulation of water were avoided.

The results of electro-chemical activity of the cell were obtained by altering the pressure of the oxygen and hydrogen (table 1), the maximum voltage was 750 mVolts, until the circuit was open. The purpose of this was to achieve the maximum voltage before the membrane was fully compressed, thereby reducing the pores and channels and expelling water from the polymeric matrix.

| Pressure | Voltage (mVolts) | 380 | 700 | 750 | 680 | 400 | 300 |
|----------|-----------------|-----|-----|-----|-----|-----|-----|
| Oxygen   | 0               | 0.5 | 1.0 | 2.0 | 2.0 | 3.0 |
| Hydrogen | 0.5             | 1.0 | 1.0 | 2.0 | 2.0 |

The results show that maximum voltage was reached for pressures of hydrogen and oxygen in equal proportions, and that the cell’s performance levels drop as more oxygen than hydrogen is provided. This is due to the compression cell undergoes in the anode region, preventing $H^+$ ions move and form water. With higher pressure of hydrogen than oxygen $H^+$ ions were expected to move and the cell’s performance to be of the highest voltage. Although every effort has been made to maintain good hydration in the membrane, and avoid external contamination, the result was not completely satisfactory and the voltage has not been high enough. Another factor to be considered is in the amount of platinum deposited on the sample it was higher than expected (200 particles/µm²) and this larger quantity of nanoparticles may have caused a self poisoning that caused the decrease of performance. As noted in previous tests, this problem can be avoided by reducing the process time. This way the prevention of possible damage to the cell is also obtained since it is exposed to the effects of plasma for less time.

5. Conclusions

Although the maximum voltage achieved is still relatively low, the results obtained in this work showed the possibility of using plasma for direct platinum nanoparticles deposition on polymeric membranes. It was observed that the temperature does not damage the polymeric matrix and that the nanoparticles are deposited along its entire length. This is an important factor for good catalytic action. Nevertheless the amount of nanoparticles deposited should be reduced, thus preventing self the poisoning of the cell.

Another possibility observed in this work was the formation of nanoparticles of other material along with platinum, in order to be used as a support for platinum. In this way, platinum can be used in smaller quantities, saving material without losing efficiency of the catalyst.

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