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A NOVEL SPUTTERING TECHNIQUE FOR REDUCING PLATINUM LOADING IN PEM FUEL CELLS

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ABSTRACT

Hydrogen is considered as the alternate fuel for the next generation vehicles. Thus PEM fuel cells which are used as the conversion devices from chemical energy to electrical energy have large potential in vehicle market. It uses Platinum as the catalyst, the cost and availability of Platinum is one of the major contributors to the commercialization of PEM fuel cell. Conventional technologies of Pt deposition such as spraying, brushing, decal layer etc. require 0.3-0.5 mg/cm^2 of catalyst on carbon support for effective catalyst utilization. The attempt to reduce the Pt loading below 0.1 mg/cm2 results in drastic degradation of performance due to low catalyst utilization. It is desired to have the high concentration of 3-5 nm Pt nano particles adjacent to the membrane as well as in contact with the carbon so as to satisfy the necessary criteria of three phase boundary. Here we use a novel sputtering method for reducing the platinum loading in PEM fuel cells

Keywords: Platinum loading, Sputtering, PEM Fuel Cells.

INTRODUCTION

Fuel cells are emerging as the power source of the future. PEM fuel cells [1] which are used as the conversion devices from chemical energy to electrical energy have large potential in meeting future energy needs. It uses Platinum as the catalyst, the cost and availability of Platinum is one of the major contributors to the commercialization of PEM fuel cell. Conventional technologies of Pt deposition [2] such as spraying, brushing, decal layer etc. require 0.3-0.5 mg/cm^2 of catalyst on carbon support for effective catalyst utilization [3]. The attempt to reduce the Pt loading below 0.1 mg/cm^2 results in drastic degradation of performance due to low catalyst utilization. It is desired to have the high concentration of 3-5 nm Pt nano particles adjacent to the membrane as well as in contact with the carbon so as to satisfy the necessary criteria of three phase boundary as shown in figure 1.

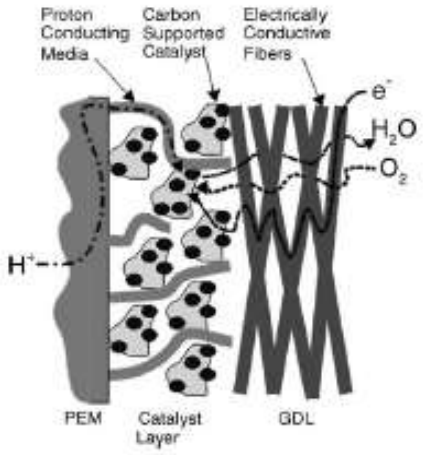

Figure 1. Diagram showing three phase boundary in the catalyst layer

Sputtering is a process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic particles. It is commonly used for thin-film deposition, etching and analytical techniques .Physical sputtering is driven by momentum exchange between the ions and atoms in the materials, due to collisions.

To attain good performance, a sputter-deposited catalyst layer must satisfy the following requirements. First, it should maximize the available amount of three-phase zone, where the gas reactants, proton conducting phase, and the catalytically active electrically conductive phase are all present together. Second, it should be thin so as to minimize gas diffusion losses and aid in water removal. Third, the catalyst layer should adhere strongly to the membrane in order to reduce ohmic losses and to support the high mechanical stresses produced during operation. Since state-of-the-art powder supported catalyst layers contain platinum particles in the 10 nm range, sputtering techniques need to provide platinum domains of a comparable size or smaller in order to be competitive. A unique advantage of the direct sputtering technique is that the catalyst deposit is highly localized directly at the membrane interface. This results in an extremely high platinum utilization, which somewhat compensates for the ultra-low loading levels.

Several authors [4] have reported the sputtering of platinum directly on the membrane with ultralow loadings of 0.01 mg/cm^2 in the form of thin films of 15- 100 nm in thickness. Studies have also reported the sputtering of Pt on GDL before hot pressing it on the membrane. Authors[5] have also reported the co-deposition of Pt and carbon simultaneously on the GDL. . Since the platinum particles are sputtered onto the Nafion, problem with this kind of sputtering process is that the MEA performance is degraded after 3-4 cycles of testing.

The novelty of the technique using sputtered platinum for fabrication of MEA described here is that it retains the conventional protocol of three phase boundary, while maintaining the high concentration of Pt nano particles in contact with the membrane. Two kind of sputtering processes are carried out to find out the advantage of novel sputtering process over the conventional one. A decal layer of carbon bonded with Nafion is formed on the Teflon sheet, the surface layer of Nafion is removed by plasma ashing process so as to expose the surface of carbon particles onto which the Pt sputtering is performed by RF magnetron sputtering method. The contact angle

measurements show the controlled removal of Nafion from the decal layer. SEM micrographs confirmed the Pt particles of 5- 10 nm in diameter directly on the carbon. The measured Pt loading was 0.03 mg/cm^2. The performance was studied for varying ashing times. The performance of the MEA is comparable to that reported in the literature but very little degradation is observed even after testing the cell for 10 cycles.

Experimental

The decal layer was prepared by coating the mixture of Nafion (10wt%) and Vulcan XC-72 carbon on the PTFE sheet. The DECAL process involves the steps as shown in figure 2

1. Coating the catalyst ink to a blank substrate (e.g. a PTFE film) (In chemistry, polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer of tetrafluoroethylene which finds numerous applications. PTFE is most well known by the DuPont brand name Teflon.)
2. Transferring the coat onto the membrane

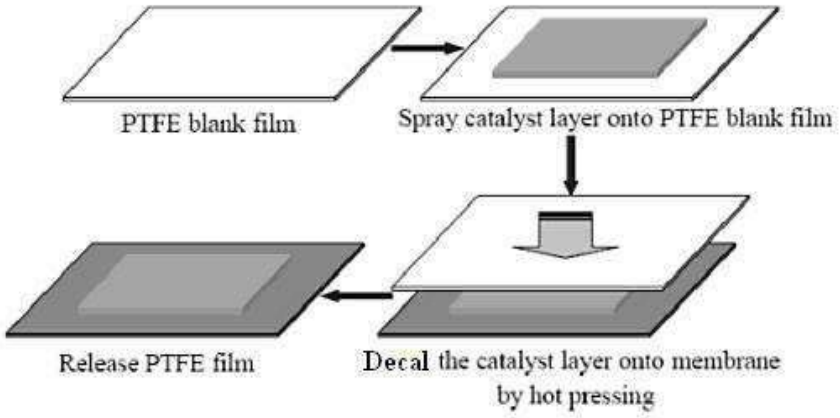

Figure 2. Decal layer preparation

A conventional MEA fabrication process for Decal layer is as follows

1. Prepare a uniformly distributed hydrophilic ink (Carbon, Nafion solution and Water/ glycerol as a solvent.) The weight ratio of Carbon, Water, and Glycerol is about 1:5:20.
2. Paint the PTFE film with a layer of ink and then bake this uncatalyzed film in an oven until dry.
3. Sputter the platinum onto this layer.
4. Decal the coated layer onto a polymer electrolyte membrane by a hot pressing process (i.e. press at 70-90 atm. for 90 sec at 140 degree Celsius)
5. Cool it down and then release the blank substrate from the coating film, leaving the film adhered to the membrane surface.
6. Place Gas diffusion layers against the catalyzed film to from the MEA.

In our proposed system, the above described process is modified after step 2 as follows

The Nafion removal from the layer coated in step 2 is carried out in oxygen plasma in in-house developed plasma asher system. The chamber is evacuated down to 10-5 mbar. The

oxygen (99.999%) then passed through the system and maintained at the pressure of 0.2 mbar. Ashing is then carried out at 50 W input power for time varying from 8 to 60 seconds. The Pt films were deposited on the ashed substrates at room temperature by using a commercial NORDICO RF magnetron sputtering system. The distance between the target and the substrate was 5.0 cm. The sputtering deposition system used for the experiments consists of a stainless steel chamber, which was evacuated down to 8×10 -5 Pa with a cryogenic pump backed up by a rotary pump. Before sputtering deposition, the Pt target (4 inch diameter, purity 99.95%) was sputter cleaned in pure Ar. The Ar working pressure (2.8×10^{-2} Pa), the power applied was 100 W. Deposition was carried out for varying sputtering time of 20, 40, 60 seconds.

The resulting Pt deposited decal is then transferred onto the Nafion 115 membrane by hot pressing the membrane between two decals at 130 degree and 1 ton pressure for 5 minutes. The MEA was then tested in Arbin Instruments fuel cell test station by passing fully humidified H_2 and O_2 gas at 0.2 slpm. The temperature of the cell was maintained at 60 degree.

RESULTS

Figure 3 shows the SEM image of the Decal layer without ashing of Nafion in the absence of platinum. SEM image shown in figure 4 has platinum sputtered on to the Decal layer for 20 seconds by above method. Platinum thin film spread on the Nafion layer broken into small size of 5-10 nm can be clearly seen in figure 3.

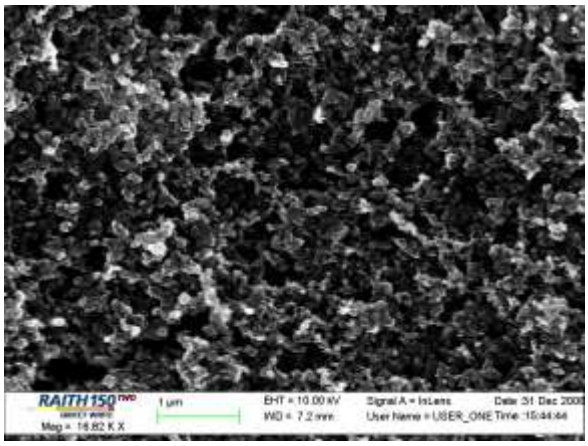

Figure 3. Decal layer without platinum

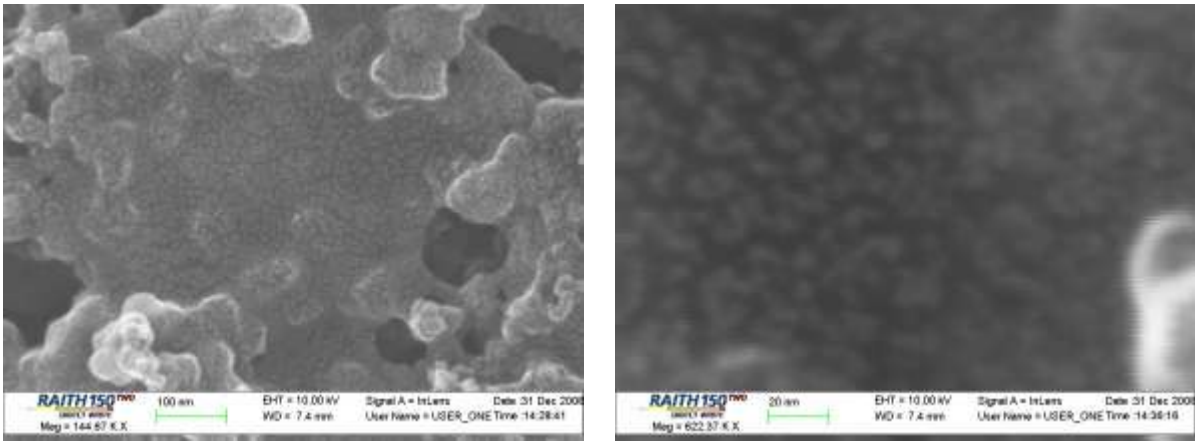

Figure 4. Decal layer with sputtered platinum for 20 seconds

Figure 5 shows the platinum sputtered on as prepared Decal layer for 40 seconds. A very thick platinum film with almost continuous morphology is observed which corresponds to high platinum loading of around 0.1 mg/cm^2. Hence it was decided to keep sputtering time of 20 seconds for various ashing time of Decal layer.

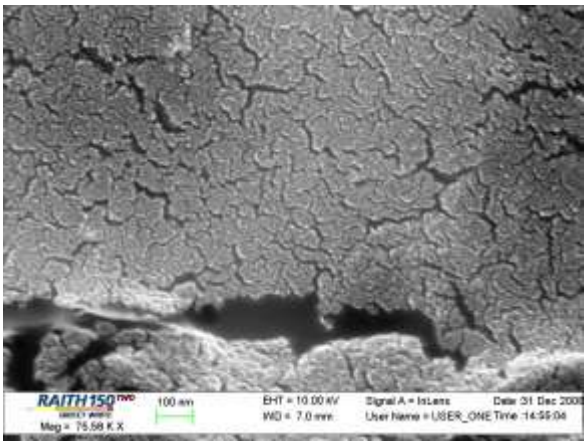

Figure 5. SEM micrograph of Platinum film formation for sputtering time of 40 seconds

Images shown in figure 6 are of pt sputtered for 20 seconds on the Decal layer modified with plasma ashing for 10 seconds. It can be seen that plasma ashing in oxygen atmosphere has removed the Nafion layer from the surface of the catalyst layer.

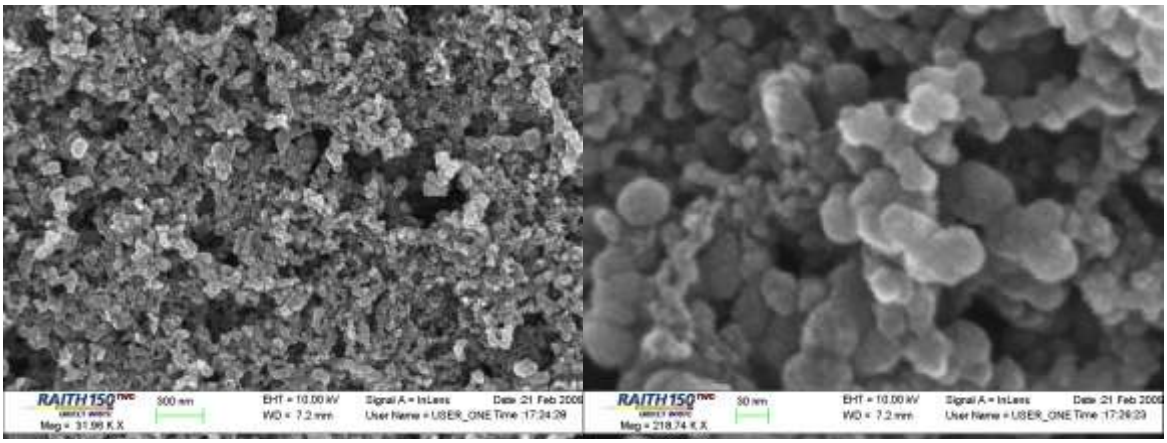

Figure 6. SEM micrographs of the Decal layer with platinum sputtered for 20 seconds after partial removal of Nafion for 10 seconds ashing time

Contact angle measurement

The following table 1 shows the relationship on contact angle of Decal film (carbon+Nafion) with ashing time at 50 W of oxygen plasma and 0.2 mbar oxygen pressure.

Table 1. Contact angle variation with ashing time

Ashing time in seconds	Contact angle in degrees
8	86
13	71.3
20	57.8
60	46

Nafion is completely hydrophobic and carbon is hydrophilic in nature. Change in contact angle with ashing time indicates that Nafion if getting partially removed from the Decal layer. If ashed beyond one minute the nearly all the Nafion gets removed from the layer and sample becomes hydrophilic in nature.

MEA performance

Figure 7 shows the polarization curves obtained for varying Pt sputtering times of the plasma ashed Decal layer for 10 seconds. Slight increase in the current density is observed with decrease in the sputtering time. This may be attributed to the increase in the platinum film thickness which increases the platinum particle size which in turn reduces the porosity of the film. This causes increase in the mass transport resistance at higher current densities as can be seen from the polarization curve.

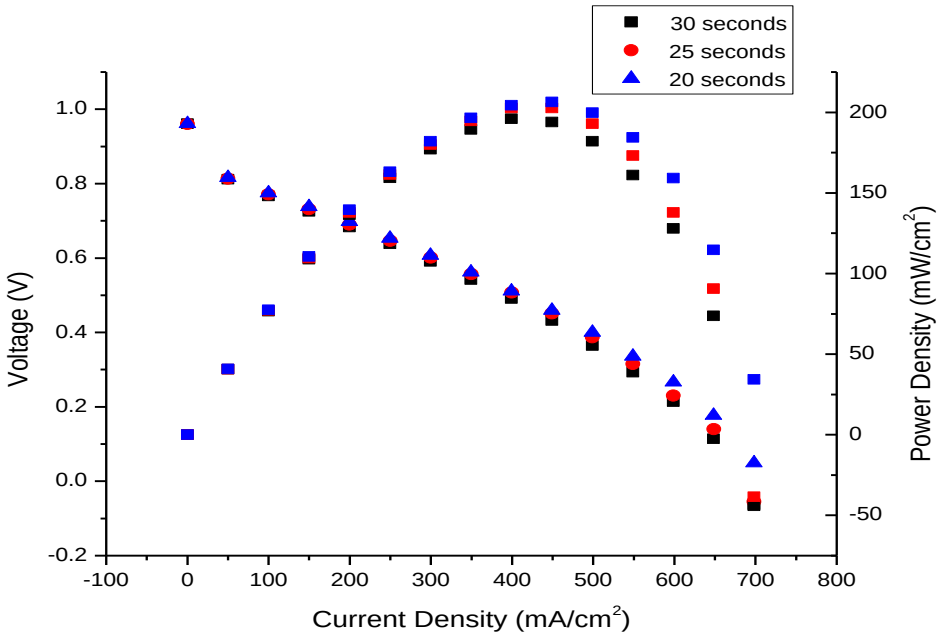

Figure 7. MEA performance curve for various platinum sputtering times

CONCLUSION

A power density of 200 mW/cm^2 was obtained for a sputtering time of 20 seconds. Slight increase in the fuel cell current density was observed with decrease in the sputtering time. This may be attributed to the increase in the platinum film thickness which increases the platinum particle size which in turn reduces the porosity of the film. This causes increase in the mass transport resistance at higher current densities as can be seen from the polarization curve.

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