

Water permeability study of Membrane Electrode Assembly (MEA) fabrication using X-Y robotic sprayer machine

**Abdul Amir H. Kadhum, Abu Bakar Mohamad, Wan Ramli Wan Daud
and Ramli Sitanggang**

*Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600
UKM Bangi Selangor Darul Ehsan, Malaysia, Tel: 03-89216410 Fax: 03-892916148
e-mail: ramlisi@vlsi.eng.ukm.my*

Abstract

The fabrication of MEA is conducted using an in-house robotic sprayer machine capable of adjusting its X-Y motions. The MEA produced was analyzed for porosity, distributions pore and water flux using BET and SEM based on the water permeability methodology. The results of the MEA shown that the pore geometry of MEA has a tortuosity parameter which is greater than the MEA's thickness while the permeability coefficient parameter of water is $9.10^{-5} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ or the tortuosity of 2. These results were then compared to the ones available from the commercial MEA.

Keyword : Permeability coefficient, membrane electrode assembly

1. Introduction

Membrane Electrode Assemblies (MEA) is the core component of fuel cell. It consists of the electrolyte membrane, anode and cathode electrodes. The electrochemical reactions occur when a fuel and oxidant are applied to the anode and cathode sides of the MEA. There are several fabrication methods of MEA were reported, such as rolling, screen printing, casting, and spraying. Each of these types produces different MEA's structure. One of the recent research in sprayer as what we interested in our laboratory, used one or multi nozzle (Blore et al., 2002, Jun, 2001, Chun, 2001). The most important parameter in MEA is the water flux, usually named as water transport phenomenon. The water flux itself depends on electro osmotic behavior, diffusion and permeability coefficient, and proton movement (Eikerling, 1998, Hu, 2004). Some of researchers have approached the water transport phenomenon in one, two and three dimensional (Minggru, 2004, Jun, 2001, Chen, 2003). Based on the mechanism of hydrogen bridge within membrane (Bansal, 1998), we observed that the water flux is pressure dependent. The balancing of humidity has to be insured with restricted crucially on the empty volume of MEA to avoid the floods of water and dehydration that will cause an ohmic losses. The minimizing of ohmic losses suggested by many researchers by achieving various compositions of materials and reconstructing of size of diffusion layer of electrode. In this research, we observed the permeability coefficient of MEA by setting the slope of water flux in a certain value.

2. Methodology

MEA consists of three component gas diffusion layer (GDL), gas diffusion electrode (GDE), and membrane. The fabrication process of GDL and GDE was made using in-house robotic sprayer machine adopted the Chun's method (2001). The permeability coefficient of the fabricated electrode was characterized. We assuming the water mass transfer represents by the simplest equation as follows (Middleman,1997, Muider, 1991, Baker,2000, Frank,2003)

$$N = \kappa \cdot \Delta P_{eff} \quad (1)$$

Where K is the membrane permeability coefficient that depends on the porosity, pore radius, viscosity and turtocity factor, effective pressure difference (ΔP_{eff}) and N permeate flux.

The System configuration in our study is an in-house robotic sprayer machine. Data of workpiece is controlled. The post processor converts the spray coating carbon ink path-line to the robot control command to move the sprayer in X-Y direction. Such spraying system will produce an even GDL. The GDE is produced by spraying the GDL with a similar process as mentioned above but with difference formulation of material such as carbon ink-platinum. The produced MEA is substrates to hot pressing in a sandwich form of GDE with membrane inside in high temperature and high pressure (Chun, 2001). After that we activate the MEA using treatment method (Kwak, 2000), and then boiled it to avoid water and gases inside the pore. Next, we characterize the dimension of pore of MEA, GDL and GDE using BET and SEM by analyzing the permeate and the slope of water flux. The analyzed permeate was done using continuous membrane system method and the analyzing of the slope water flux by linear fitting curve against pressure difference as in eq. (1). Permeability coefficient and MEA performance was investigated using FCTS.

3. Experiment

Activated carbon with 400 mesh was laminated on carbon cloth. Polytetrafluoroethylene (PTFE), nafion liquid by Aldrich Chemical Company and DuPont Fluoroproducts. Moderate polar of mix solute from water and isopropyl alcohol as was used as medium for carbon mobility and the membrane used in this observation is Nafion 117 produced by DuPont.

The fabrication process of MEA consists of three steps; the logging of GDL, GDE, membrane activation and assembly of membrane electrodes (MEA). In the GDL fabrication step, admixture of the activated carbon, alcohol, water, Nafion and PTPE are stirred for 10 minutes. The slurry produced has viscosity for about 1.17 cp and usually

called as carbon ink. The carbon ink is sprayed on carbon cloth with flow of spraying as 0.5 ccs, 6 bar air pressure through spraying nozzle, with pattern 4 cm, and the standing position of nozzle is perpendicular with the object, with 10 times moving period. The fabricated GDL must be dried using vacuum dryer in room temperature for about 2 hours and then will be subjected to BET, SEM and permeate test characterization, the profile and permeability coefficient of the material, was tested also.

In case of the fabrication of GDE, the GDL must be sprayed with another mixed material that consists of C-Pt, water, alcohol. Nafion, PTPE. The such materials must be mixed on 5 minutes, and the result is namely as carbon ink C-Pt and has 1.16 cp viscosity. The procedures of spraying after mixing process are similar as we mentioned above.

The third material that we used is membrane nafion 117. Membrane were cleaned to remove any trace of impurities and stored in deionized water for future use. The MEA, GDE and membrane will sandwich together using hot pressing, the MEA, GDE and membrane will sandwich together using hot pressing. Produced electrode will be rinsed with 0.5 M H_2SO_4 and have to be dried in vacuum dryer in room temperature and 2 hours. The result then has to be characterized using permeability test and FCT.

4. Result and discussion

4.1. Characterization

The fabrication process of GDE was repeated seven times in insure reproducibility to characterized the crack and the roughness of the GDE surface. From the SEM characterization of experimental a) and b) (see Fig. 2), the results still has crack, and in experimental b) (see Fig. 2b) the result is free of crack. Experimental b) also has similar surface roughness with commercial GDE (see Fig. 2c).

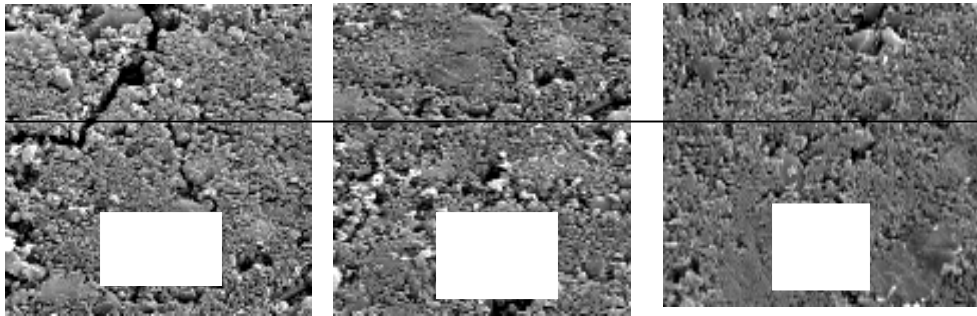


Fig. 2 Surface Microscope Scanning of a) First trial b) After modified c) Reference

For the next observation, we will focus on fig.2a that has activated carbon as 1.05 g cm^{-2} and 0.53 g cm^{-2} PTFE, 0.51 g cm^{-2} C-Pt and the scale characteristic as mentioned in Table 1.

Table 1
BET analysis

Property	GDE a)	GDE b)	MEA a)	MEA b)	MEA c)
Diameter pore (Å)	34.31	41.15	34.41	39.41	68.2
Surface area (m ² /g)	472	451	410	450	220
Volume pore (cc/g)	0.097	0.157	0.060	0.102	0.081

Using pore dimension point of view within micropore scale, fig 2a and fig 2b have mesopore characteristics. Another advantage of fig 2b is that it has greater adsorption capacity and pore capability than the other experimental in our observation (Ruthven,1997). After assembly the membrane with electrode of fig. 2b, the pore dimension of MEA remains similar with GDE fig 2b stand alone. We could conclude that the fig.2b is appropriate as a material for fabricating fuel cell.

4.2. Permeability coefficient

Within MEA fuel cell, the GDL has a function to distribute humidity water and evacuate water from electrode part, meanwhile the electrode is used to distribute humidity water and will use for triggering the reaction between Pt and CO. The membrane also has task to bond water for bridging hydrogen and sweeping out the electron (Mikko, 2003). If we flow water through the layers within MEA, then the water flux inside each layer will depend on the channel structure.

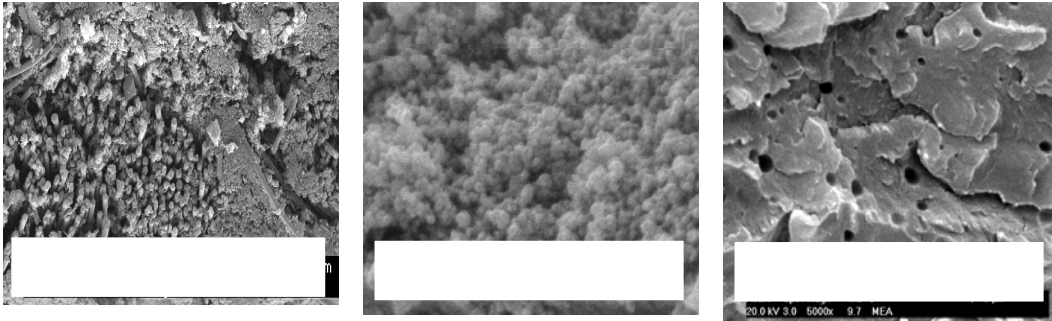


Fig 3. Surface of GDE

For GDL, the water flux will be affected by channel that has been built within the carbon cloth (see Fig. 3a), meanwhile the water flux inside the electrode will be affected by channel that has been built by the mesopore.

Figure 3c illustrates good profile of pore within membrane to make possible water flux flow through it. Such kind of pore profile is usually called as porosity and turtosity.

To build better understand about what we mentioned above, we will explain more detail about the capability of MEA to flow water flux as follow

$$N = 3.10^{-4} \Delta P_{eff} \quad (2)$$

$$N = 10^{-4} \Delta P_{eff} \quad (3)$$

$$N = 2.10^{-4} \Delta P_{eff} \quad (4)$$

Eq. (2) is developed from eq. (1) with κ for about $3.10^{-4} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ that has been found using Figure 4, and ΔP_{eff} indicates the pressure differences of water flux. Using turtosity table we got 1.1 for 3.10^{-4} permeability coefficient. It means that the length of channel for flowing water within GDL is greater than the thickness of GDL itself. Furthermore, for calculating the capability of electrode to flow water follows Eq. (3) as shown in Figure 4b. with $10^{-4} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ of permeability coefficient it is similar with 1.7 turtosity. It also means that the channel for flowing water within electrode greater than the thickness of electrode itself. From the calculation of water flux as mentioned above, we could emphasize that the flow resistance of water within electrode is greater than within GDL. It means that GDL is capable to distribute and evacuate water easier and electrode could flow in or out water faster.

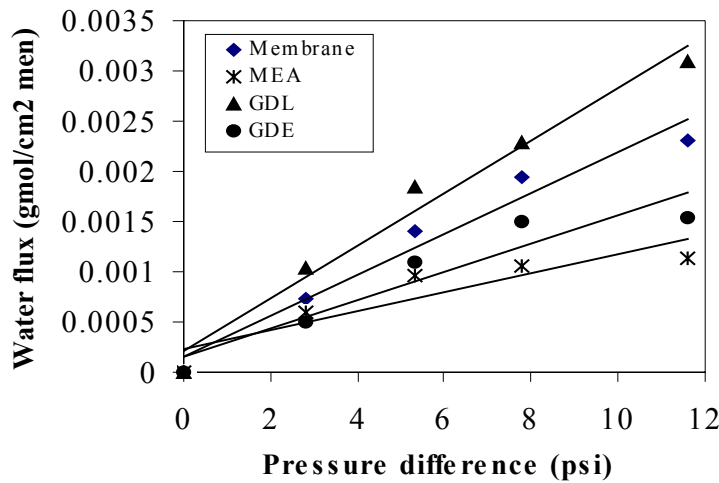


Fig 4. Characteristic of Water Permeability

For calculating the water flux within membrane Nafion 117, we use Eq. (4) with permeability coefficient of $2.10^{-4} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ or 1.4 turtosity, it means that the channel length within membrane is also greater than its thickness.

From these three layers discussed above, we could conclude that water resistance as follows

$$\text{GDL} < \text{membrane} < \text{electrode} \quad (5)$$

After assembly of membrane and electrodes on 35 kgfcm⁻² pressure and 130 °C temperature, we get water flux as in Eq. (6).

$$N = 9.10^{-5} \Delta P_{eff} \quad (6)$$

The capability of MEA to distribute water is proportional with the pressure difference that is attached to MEA. With 2.8 psia pressure differences, MEA could flow water around $3.3 \cdot 10^{-5} \text{ gmol cm}^{-2} \text{ min}^{-1}$ and restore around $3.6 \cdot 10^{-4} \text{ gmol cm}^{-2}$. The permeability coefficient of water within MEA is around $9.10^{-5} \text{ gcm}^{-1} \text{ men}^{-1} \text{ psia}^{-1}$ or with tortuosity greater than 2. Therefore we could modify Eq. (5) to

$$\text{GDL} < \text{membrane} < \text{electrode} < \text{MEA} \quad (7)$$

Electrode has greatest water resistance, it means that to fabricate MEA, we have to modify electrode layer to control the water distribution and evacuation properties. Including the commercial MEA (with $2.10^{-6} \text{ gcm}^{-1} \text{ men}^{-1} \text{ psia}^{-1}$ permeability coefficient), Eq. (7) will have to modify to

$$\text{GDL} < \text{membrane} < \text{electrode} < \text{MEA} < \text{MEA Com} \quad (8)$$

4.3. Performance of MEA fuel cell

In observing the MEA fuel cell with single stack, pressure at anode is set up greater than the pressure of oxygen. With pressure difference of 2.8 psi and flow rate of H₂ as 0.3 slpm, oxygen 0.4 slpm and flooding water is happened within membrane, then the performance of MEA fuel cell could be illustrated as in Figure 5.

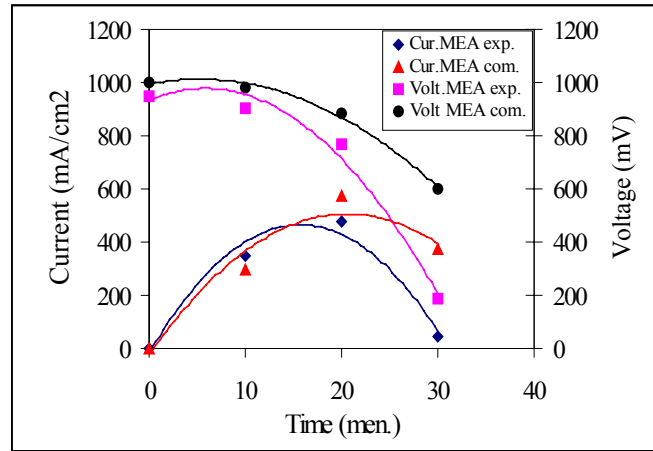


Fig 5. Performance of MEA fuel Cell

As can be seen in Figure 5, the MEA fuel cell with greater permeability coefficient will have less current density voltage. In this operation, the anode MEA fuel cell will be dehydrated and osmotic electron will be happened through the membrane. This osmotic electron or usually called as electron diffusion will cause ohmic losses inside the MEA fuel cell. In such condition, the changing of current within MEA tends to drop rapidly than the commercial MEA for 30 minutes operation times. This difference is due to the permeability coefficient of our MEA greater than the commercial MEA. If H_2 and O_2 suddenly drop out to zero, the MEA current will be discharged very rapidly than the commercial MEA. It means that MEA with very rapidly transient current (rise time and fall time) is good enough to control dehydration in low temperature without any drying process

5. Conclusion

From the discussion above, the water flux within the geometrical structure of MEA is influenced strongly by porosity and turtosity. The turtosity of the layer could be defined as $GDL < membrane < electrode$ or we got the permeability coefficient of DGL as $3 \cdot 10^{-4} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$, Electrode as $10^{-4} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ membrane as $2 \cdot 10^{-4}$, MEA as $9 \cdot 10^{-5} \text{ gcm}^{-1}\text{men}^{-1}\text{psia}^{-1}$ or turtosity greater than 2 for MEA. The MEA will occur ohmic losses using greater permeability coefficient.

References

- [1] Midleman S., "An Introduction to mass and heat transfer", John Wiley & Sons, Inc, (1997)

[2] Ruthven D., "Encyclopedia of Separation Technology", Vol 1., John Wley, New York (1997)

[3] Baker W.R., "Membrane technology and Applications", McGraw-Hill(2000)

[4] Chun, William; et al., "Direct deposit of catalyst on the membrane of direct fuel cell", California Institute of technology, california corporation (2001)

[5] Muider M., "Basic Principles of Membrane Technology", Center for membrane Science and Tecnology, Universitas of twente, the netherlands (1991)

[6] Frank M., Gerhart E., "Transport parameter for modelling of water transport ionomer membrane for PEM Fuel Cell", Electrochimica Acta in press (2004)

[7] Eikerling M., Kharkats Yu., Kornyshe A.A.,Volfkovich M., Electrochem J.. Soc.145(1998)2684

[8] Hu M., Zhu X., Minghua W., Gu K., Yu I., "Three dimensional, two phase flow mathematical model for PEM Fuel cell: Part II. Analysis and discussion of the internal transport mechanisms", Energy and management in press (2004) , Published by elsevier Ltd

[9] Bansal K., "Organic Reaction Mechanisms". Tata McGraw-Hill Publishing Company Limited(1998)

[10] Mikko Mikkola,"Membrane", Helsinki University of Technology (2003)

[11] Chen F., Su Y., Song C., Yan W., Chu. Transient behavior of water transport in membrane of a PEM fuel Cell. J. Electro analytical Chemistry, in press(2003)

[12] Kwak S.H., Peck D.H, "New Fabrication method of the composite membrane for polymer electrolyte membrane fuel cell", J.New Mat. Electrochem systems, 4,25-29(2001)