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Comparison of The Performance of Proton Exchange Membrane Fuel Cell (PEMFC) Electrodes with Different Carbon Powder Content and Methods of Manufacture

D. Rohendi[1], E.H. Majlan[2,], A.B. Mohamad[2], L.K. Shyuan[2] , J. Raharjo[3]

[1]*Dept. of Chemistry, Faculty of Mathematic and Sciences, Sriwijaya University, Inderalaya, Indonesia*
[2]*Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor DE, Malaysia*
[3]*Center of Materials Technology, Agency for the Assessment and Application of technology, Puspitek 224 building, Tangerang Selatan, Indonesia*
[*]*Corresponding Author: rohendi19@gmail.com*

Abstract

Carbon powder in the gas diffusion layer (GDL) contained in the membrane electrode assembly (MEA) has an important role in the flow of electrons and reactant gas. Meanwhile, the method of making the electrode is one of the many studies conducted to determine the most appropriate method to use. Comparative study of the performance of proton exchange membrane fuel cell (PEMFC) electrodes with different carbon powder content (vulcan XC-72) in the GDL and methods of manufacture of the electrode between casting and spraying method has been carried out. The spraying method consists of one layer and three layer of catalyst layer (CL). The content of carbon powder in the GDL as much as 3 mg cm^{-2} has a better performance compared to 1.5 mg cm^{-2} with an increase of 177.78% current density at 0.6 V. Meanwhile, the manufacture of CL with three-layer spraying method has better performance compared with one-layer spraying and casting method.

Keywords: *casting method, spraying method, catalyst layer (CL), GDL*

Abstrak (Indonesian)

Serbuk karbon pada lapisan difusi gas (LDG) yang menyusun elektroda membran memiliki peran penting dalam mengatur aliran elektron dan gas reaktan. Pada sisi lain metoda pembuatan elektroda adalah salah satu dari banyak studi yang dilakukan untuk menentukan metoda yang paling sesuai yang dapat dikerjakan. Telah dikerjakan studi komparatif kinerja membran penukar proton pada elektroda sel bahan bakar dengan kandungan serbuk karbon (vulcan XC-72) dalam LDG yang bervariasi dan studi komparasi metoda pembuatan elektroda secara tuang dan semprot. Metoda semprot dikerjakan dalam dua variasi yakni pembuatan lapisan katalis (LK) satu dan tiga lapisan. Kandungan serbuk karbon dalam LDG hingga 3 mg cm^{-2} memiliki kinerja lebih baik dibanding 1,5 mg cm^{-2} dengan peningkatan kerapatan arus 17,78% pada 0,6 V. Pembuatan LK dengan metoda semprot tiga lapisan memperlihatkan kinerja terbaik dibanding metoda semprot satu lapisan dan metoda tuang.

Keywords: metode casting, metode spraying, katalis layer, GDL

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INTRODUCTION

Fuel cells are electrochemical devices that convert the chemical energy in the fuel and oxidant into electrical energy. Research on fuel cells is developed in line with the requirements of clean and efficient energy sources. Fuel cell technology is a promising technology to produce energy sufficient in quality and quantity as well as environmentally friendly.

Proton exchange membrane fuel cells (Proton Exchange Membrane Fuel Cell, PEMFC) is one of the many types of fuel cells reviewed. PEMFC is widely used as a promising energy conversion devices for vehicles, stationary power, and portable power systems because it can show high power density, energy efficiency, zero pollutant emissions and low operating temperature [1].

MEA is one of the most important component in PEMFC system. Three important processes occurring in the MEA. First, the transport of electrons from the anode to the cathode through an external circuit and the current collector, second, the transport of protons from the anode to the cathode through the membrane, and third, the gas transport of reactants to the catalyst (catalyst layer/ CL) [2]. The MEA consists of two electrodes, a cathode (reduction of oxygen site) and the anode (oxidation of hydrogen site). Both electrodes are located on both sides of the polymer membrane that normally use Nafion or composite of Nafion membrane with other compounds. Electrode structure consists of gas diffusion media (GDM) or backing layer (BL) (usually using carbon paper or carbon cloth), a layer of micro porosity (microporous layer, MPL) and CL. Combination of MPL and BL called gas diffusion layer (GDL) [3]. GDL not only must be conductive but also hydrophobic. Therefore, the BL and the MPL contains carbon as conductive components and Polytetrafluoroethylene (PTFE) as a hydrophobic component. The function of hydrophobicity of GDL is to increase the flow of water through the pores of the carbon substrate to prevent the risk of flooding [4]. Convergence study of three components of electrodes (BL, MPL and CL) and membrane electrolyte is important to get the MEA with a high current density.

Carbon powder has a critical role in the PEMFC, especially because of the characteristics of high conductivity, resistance to corrosion and high surface area [5]. In addition to being a very good matrix for catalyst support [6], carbon powder is used as filler material in MPL.

EXPERIMENTAL SECTION

MPL ink components for GDL consists of Vulcan XC72 carbon powder, Isopropyl alcohol (IPA), ammonium hydrogen carbonate (NH_4HCO_3, ABC) and PTFE with specific content. MPL was made by spraying method using a manual sprayer that suitable for small scale with simple operation and can reduce ink wastage. Method of casting also carried out in the manufacture of MPL and CL. for comparison purpose.

In addition to compare the manufacturing method, this research also used MPL ink with different content of carbon powder i.e. 1.5 mg cm^{-2} and 3 mg cm^{-2}. Carbon powder content of 1.5 mg cm^{-2} was referred to previous studies [7, 8], while the content of 3 mg cm^{-2} was chosen based on other reference [9] using the vapor grown carbon fiber casting methods and using carbon cloth [10]. In this section, the manufacture of MP was conducted using casting methods with PTFE and ABC content that adapts to the content of carbon powder.

In this study, the PTFE content in the MPL is 30% by weight of carbon black powder refered to the results of previous investigators [11]. Based on Tsai [12], 30 wt% PTFE content have a better performance compared with the 40% for gas transport to facilitate the reaction and diffusion of water back from the cathode to the anode. Low content of PTFE will result in the production and flow of water is not effective, while if it is high PTFE content might close the pores.

Carbon black powder used in this study is carbon Vulcan XC72 which refer to the results of previous work [13, 14]. Carbon Vulcan XC72 was proved to be effective for used in the MPL to provide uniform micropores hence improve mass transportation capabilities and reduce the possibility of flooding. In addition to its effectivity, the carbon Vulcan XC72 also has a high level of electron conductivity.

Catalyst layer was made of a mixture of a platinum catalyst (Pt), PTFE and Nafion solution. Catalyst Layer is usually made of only one layer but here we made the CL in this study used three layers. The first layer, CL which is sprayed onto MPL containing catalyst and PTFE solution. The addition of PTFE to reduce the resistance of the interface between the CL and MPL. Moreover, the addition of PTFE aimed to improve hydrophobicity and assist management of water. CL second layer consists of a mixture of a platinum catalyst and Nafion solution. Nafion in the second layer had function to reduce the resistance of the interface layer between second layer and third layer and help the flow of H^+ ion out of the anode. Finally, the third layer consists of Nafion solution, the solvent and the remaining catalyst. The third layer had roled as connector whic also reduce the interfacial resistance of CL with electrolyte membrane. The comparison of performance between CL single layer and three layers was the main focus in this study.

RESULT AND DISCUSSION

The Influence of Carbon Powder Content in MPL

The performance of MEA with different carbon powder content of MPL is shown in Figure 1. MEA with 3 mg cm^{-2} carbon powder content in the MPL has a better performance compared with the content of carbon black 1.5 mg cm^{-2} (Figure 1).

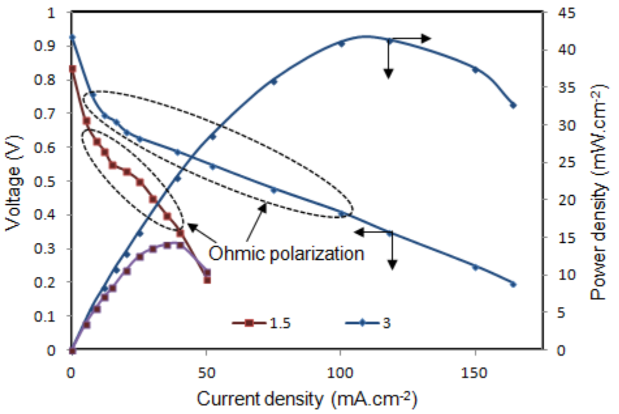

Figure 1. The comparison of the performance of MEA with different carbon powder content in MPL (mg cm^{-2}).

Both MPL made by casting methods showed that the content of carbon black powder 3 mg cm^{-2} increased current density as high as 177.78% at 0.6 V compared to 1.5 mg cm^{-2}. This improved performance was associated with an increase in the thickness of the MPL due to the addition of carbon powder content. MPL with a thickness sufficient to be able to reduce the polarization by reducing the ohmic contact resistance between the GDL and the CL interface [15]. MEA with carbon powder containing 3 mg cm^{-2} in the MPL is able to survive better in the ohmic polarization compared with 1.5 mg cm^{-2} content. Voltage drop at ohmic polarization area causes the power density of MEA with 1.5 mg cm^{-2} carbon content is much lower than 3 mg cm^{-2}.

The influence of carbon powder content to the thickness of GDL and electrode with different catalyst content are shown in figure 2. The overall thickness of the electrode give effect on electron flow and transport of reactant gas and water.

The average thickness of the electrodes is measured from SEM images; it increases with increasing catalyst content (Figure 2). The addition of catalyst will increase content of carbon powder and contribute to increase of thickness, because platinum is added in the form of Pt/C. For comparison, the thickness of the BL and the GDL is also shown. Increasing in thickness of the GDL is cause by the addition of MPL containing carbon powder with 3 mg cm^{-2} content. Based on the figure 2, the thickness of the MPL is ± 58.5 μm, which is obtained from the subtraction of the BL thickness of GDL. MPL with the content of carbon powder 3 mg cm^{-2} made by spraying method leads to an average thickness of GDL increased 302.5 μm as shown in Figure 2. GDL thickness above 300 μm proved to have a better impact on the performance of the MEA with a thickness below it [9].

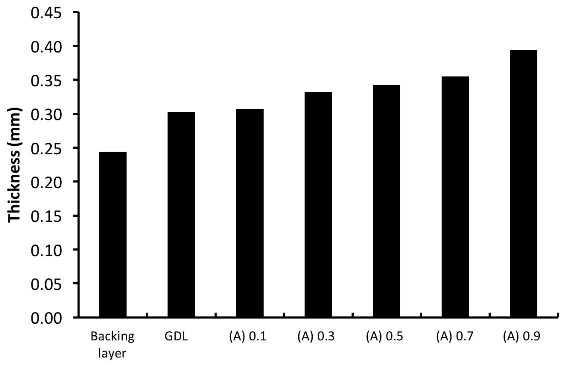

Figure 2. The thickness of BL, GDL and anode (A) at various catalyst content (0.1, 0.3, 0.5, 0.7 dan 0.9 mg cm^{-2})

MEA performance as a result of the influence of the thickness of the electrodes has already gained the attention of researchers. If the electrode is too thin, it will lead to increased electrical resistance due to lack of smooth surface and not enough time for the gas to spread on the entire surface of the electrode. But, if it is too thick; it will complicate the transport of gas to get into CL [3]. Therefore, the thickness of middle size electrode is selected option. The setting is done by adjusting the thickness of the electrode thickness of MPL [11].

Comparison of Manufacturing of MPL and CL

Many researchers have conducted research on the method of manufacture MPL and CL. However, research results are highly dependent on the circumstances and the type of material used. Even though, previous research results can be a reference to the materials used and the circumstances are appropriate. One method of making the MPL and CL simple and quite effective is spraying method as used in this study. In addition to the spraying method, manufacturing MPL and CL by casting methods have been performed in this study for comparison. Meanwhile, making the CL with the spraying method is done by two methods, namely the method of spraying single catalyst layer and three layers of catalyst. The purpose of utilizing different methods is to find a method that produces better performance. MEA performance with different MPL and CL manufacturing methods are shown in Figure 3.

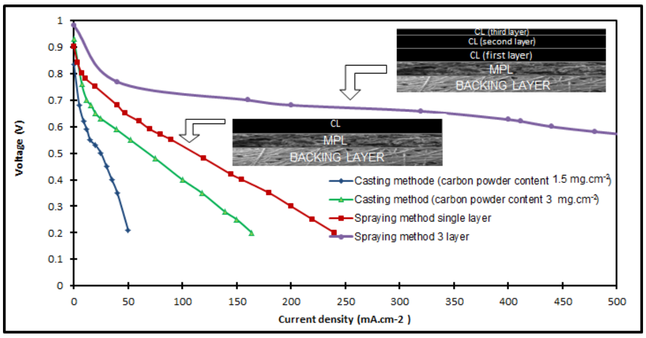

Figure 3. Comparison of the performance of the MEA between casting methods (containing carbon powder 1.5 mg cm^{-2} and 3 mg cm^{-2}), method of spraying with single layer and three layers of catalyst content 0.3 mg cm^{-2}

Spraying method with single layer has a better performance compared with the casting method, and spraying method with a three-layer method is a method selected from the three methods (Figure 3). MEA made with three layers of spraying method is able to maintain its performance in the ohmic polarization region that has much higher performance than either method of casting or spray with single layer. This prove that three-layer spraying method is capable to reduce the resistance of the interface, whether the interface between CL and MPL or CL and the electrolyte membrane. CL with a three-layer structure consisting of: (1) a mixture of catalyst Pt/C with PTFE sprayed on the MPL as the first layer. The addition of PTFE aims to reduce resistance interface with MPL CL which also contains PTFE. (2) The second layer consists of mixed catalysts Pt / C with Nafion solution, and (3) the third layer consists of a solution of Nafion and residual catalyst from the second layer. The presence of Nafion ionomer in the second layer will reduce the interface resistance with the third layer and the third layer will reduce the interface resistance CL with Nafion membrane. The addition of Nafion in the second and third layers is meant as an agent for the resulting flow of ions H^+ CL towards the membrane. Some research results indicate that the optimum content of Nafion ionomer in the CL is in the range of 15-36% [16], but generally is more than 30% [17]. In this research, the content of Nafion ionomer in the CL is 35% by weight for anode and 30% by weight of the cathode for each distributed into two parts for the second layer and the third layer CL.

The casting methods suffered difficulty in attaching the catalyst layer on the MPL and harder if the catalyst is composed of three layers. In addition, the surface structure consists of casting methods subtler and even (figure 4) less favorable in terms of attaching ink to surface CL compared with coarse surface from spraying method.

The morphological structure of MPL surface from casting method and spraying methods is shown in figure 4.

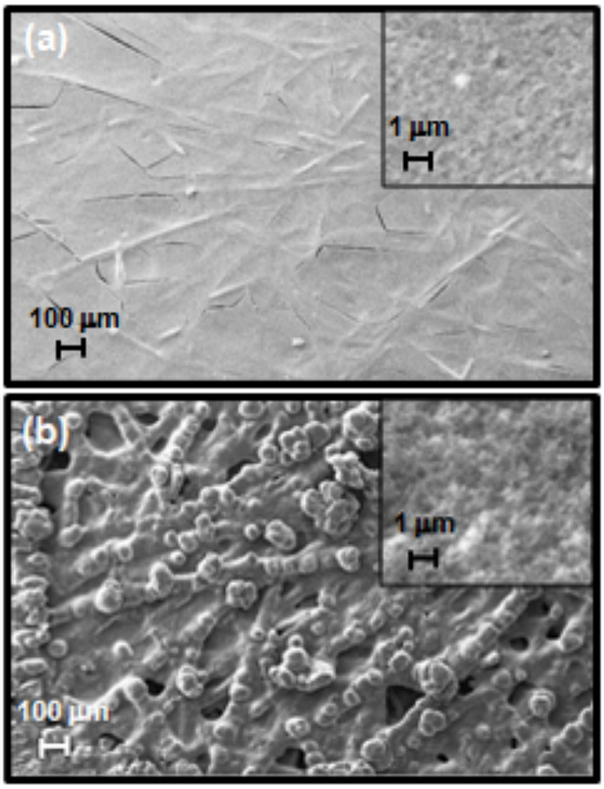

Figure 4.The comparison surface structure of MPL between casting method (a) and spraying method (b)with 100 x magnification (inset, 10,000x magnification).

Referring to the results of Figure 4, the MPL surface structure that made by the casting method is more smooth and dense compared with the spraying method, but applies the cracks as a result of differences in the coefficient of expansion of the MPL during the sintering process. Surface cracks occur because the casting methods in manufacturing process is done with pressure on the ink so that the structure is more compact. MPL surface more clearly shown by inset image (10,000x magnification) that show the size of the pores closer and hampers the flow of gas and water. Another point of weakness of the casting method is allows mixed it between MPL and CL due to the casting process repeatedly.

The results of previous research [11] have tried to compare the performance of the spraying and brushing method and get the results that the spraying method has better performance, especially in the addition of a solution of Nafion. According to Lee et al. [11], the addition of Nafion in the spraying method will reduce the charge transfer resistance and increase the three phases in the CL.

The structure of cross section of MEA, electrode and Cl with three layer and single layer spraying method is shown by figure 5.

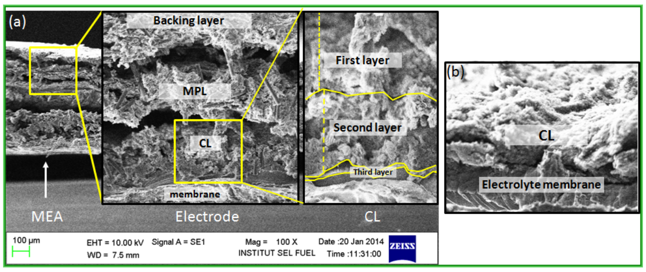

Figure 5. SEM image of a cross section of MEA, the electrode and the CL and CL cross-sectional comparison between the spray method (a) three-layer and (b) single layer

Image in figure 5 (a) regarding the structure of MEA, electrode and CL with three-layer spraying method and (b) the structure of electrode with single layer uses spraying method. There are obvious differences between two methods. In single layer spraying method, the component of carbon powder, PTFE and Nafion is mixed and sprayed in one layer, until CL structure is homogeneous. While in three-layer spraying method, PTFE and Nafion are on different layers so that the difference between layers is apparent. The main weakness of the single layer spraying method comes from mixing the component of PTFE and Nafion while both of them have different functions. Results Figure 5 reinforces again the difference between the spray of one layer with three layers.

Figure 6 shows the thickness of the MEA in a variety of manufacturing methods and a variety of content. MEA with MPL and CL is made by casting methods has a thickness much lower compared to other methods. This is understandable because at the time of making the MPL and CL, the catalyst ink is being pressed so that can attach to the layer below. Meanwhile, the MEA with the single layer spraying method has highest of coating thickness compared with other methods. This is due to the manufacturing process of the electrode, the mixture is sprayed ink all over the MPL, then be pressed with the roller shaft. In the spraying method of three layers, the emphasis will be on each layer. Interestingly, the thickness of the MEA made with three layers of spraying method is almost as though the contents of the different Pt catalyst. This is due to the hot press on making the MEA with the same method.

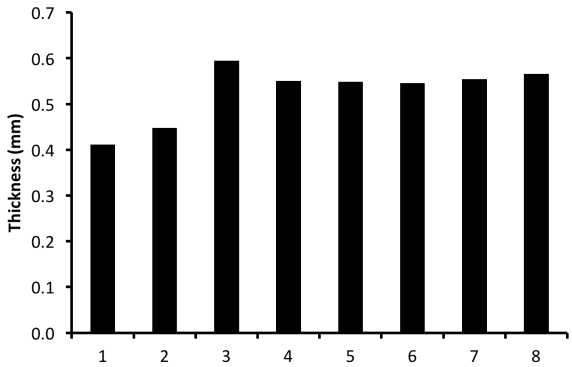

Figure 6. The thickness of the various MEA (1) Casting Method; (2) Commercial; (3) The method of spraying single layer; (4) 0.1 mg cm^{-2}; (5) 0.3 mg cm^{-2}; (6) 0.5 mg cm^{-2}; (7) 0.7 mg cm^{-2}; (8) 0.9 mg cm^{-2} (numbers 4-8 were spraying method with three layers with different catalyst content)

CONCLUSION

Based on the results of a comparative study of manufacturing methods MPL and CL, we can conclude that MEA with carbon black powder content in the MPL of 3 mg cm^{-2} has a better performance compared with the content of carbon black MPL 1.5 mg cm^{-2} with an increase in current density as high as 177.78% at 0.6 V. Spraying method with three layers is considered as the method that produces the best performance to be selective method than either method of spraying or casting methods. The MPL structure surface made by casting methods is closer to the surface of the pore size smaller than the pore structure and surface spraying method. The structure of CL with three layers has the advantage of reducing the resistance of the interface, whether the interface between CL and MPL or CL with the membrane.

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