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EFFECT OF HOT PRESSING TEMPERATURE ON THE PERFORMANCE OF PROTON EXCHANGE MEMBRANE FUEL CELL BASED ON GAS DIFFUSION ELECTRODE CARBON PAPER AND CARBON CLOTH

Yuyun Irmawati, Indriyati and Achiar Oemry
Research Center for Physics, Indonesian Institute of Sciences
Jl. Cisitu No.21/154D, Bandung 40135
e-mail: indriyati@lipi.go.id

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ABSTRACT

EFFECT OF HOT PRESSING TEMPERATURE ON THE PERFORMANCE OF PROTON EXCHANGE MEMBRANE FUEL CELL BASED ON GAS DIFFUSION ELECTRODE CARBON PAPER AND CARBON CLOTH. This paper investigates the effect of hot pressing temperature on the performance of Membrane Electrode Assembly (MEA) and to examine the performance differences between Proton Exchange Membrane Fuel Cell (PEMFC) that used Gas Diffusion Electrode (GDE) based on Carbon Cloth (CC) and Carbon Paper (CP). The temperature during hot-pressing was varied of 120 and 150 °C, while the other parameters, such as time and pressure were set steadily at 5 minute and 20 kgf/cm^2, respectively. By examining the polarization curves of PEMFC with active area of 50 cm^2 at pressure of 1 bar, temperature of 25 °C, and excess gas flow rate of pure H_2 and O_2, CC was found to have better performance than CP when pressing at 120 °C, while CP has higher performance at 150 °C. Further investigation on activation and ohmic losses using empirical equation revealed that hot pressing temperature just affects the ohmic losses for the CC, while for CP, both activation and ohmic regions considerably changed. The different performances are mainly due to the structural differences such as surface roughness and porosity between CC and CP. Maximum power of 1.53 watt was obtained from GDE based on CC hot pressed at 120 °C, followed by GDE based on CP hot pressed at 150 °C with maximum power of 1.45 watt.

Keywords: Gas diffusion electrode, Carbon cloth, Carbon paper, MEA, Polarization curve

ABSTRAK

PENGARUH SUHU PRESS TERHADAP KINERJA *PROTON EXCHANGE MEMBRANE FUEL CELL* YANG MENGGUNAKAN GAS DIFFUSION ELECTRODE BERBASIS *CARBON CLOTH* DAN *CARBON PAPER*. Tujuan dari penelitian ini adalah untuk mengetahui efek suhu saat pembuatan *Membrane Electrode Assembly* (*MEA*) dengan teknik *hot press* terhadap kinerja *Proton Exchange Membrane Fuel Cell* (*PEMFC*) dan mengevaluasi perbedaan kinerja antara *Gas Diffusion Electrode* (*GDE*) berbasis kain karbon (*CC*) dan kertas karbon (*CP*). Suhu proses pembuatan dipilih 120 °C dan 150 °C, sedangkan waktu dan tekanan di*set* konstan pada 5 menit dan 20 kgf/cm^2. Uji kinerja *stack PEMFC* dengan daerah aktif 50 cm^2 dilakukan pada kondisi operasional tekanan 1 bar dan suhu 25 °C dengan mengalirkan gas H_2 dan O_2 murni. Dari evaluasi kurva polarisasi, kinerja *PEMFC* berbasis *CC* lebih bagus dari *CP* pada suhu *press* 120 °C, sedangkan kinerja *PEMFC* berbasis *CP* lebih bagus pada suhu *press* 150 °C. Pengolahan data menggunakan persamaan empiris pada daerah overpotensial aktivasi dan overpotensial ohmik menunjukkan bahwa suhu *hot press* hanya mempengaruhi daerah ohmik untuk kasus *CC*, tetapi mempengaruhi daerah aktivasi dan ohmik untuk *CP*. Perbedaan kinerja *fuel cell* berbasis *CC* dan *CP* terjadi karena perbedaan struktur *CC* dan *CP* seperti derajat porositas dan tingkat kekasaran permukaan. Daya maksimum sebesar 1,53 watt diperoleh dari *GDE* berbasis CC yang di*hot press* pada suhu 120 °C, diikuti oleh *GDE* berbasis *CP* yang di*hot press* pada suhu 150 °C dengan daya maksimum 1,45 watt.

Kata Kunci: *Gas diffusion electrode, Carbon cloth, Carbon paper, MEA*, Kurva polarisasi

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INTRODUCTION

Proton Exchange Membrane Fuel Cell (PEMFC) has high potential to reduce the needs of fossil fuel energy and pollutant emissions because it only has water in the by-product. In order to gain high durability and performance and reduce the cost production for commercial applications [1], the development of Membrane Electrode Assembly (MEA), where the electrochemical reactions actually occur, must be optimized. As the heart of PEMFC, MEA consists of a proton exchange membrane and two Gas Diffusion Electrodes (GDEs) for anode and cathode as can be seen in Figure 1. GDE functions as electrical connector, media for electrochemical reaction and reactant diffusion, and mechanical support to the membrane [2-5].

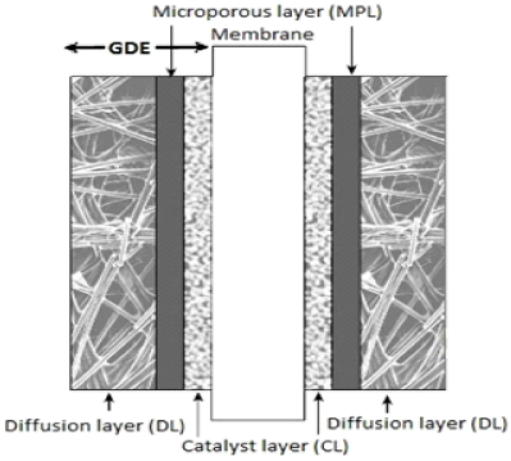

Figure 1. Schematic of MEA and its components [5]

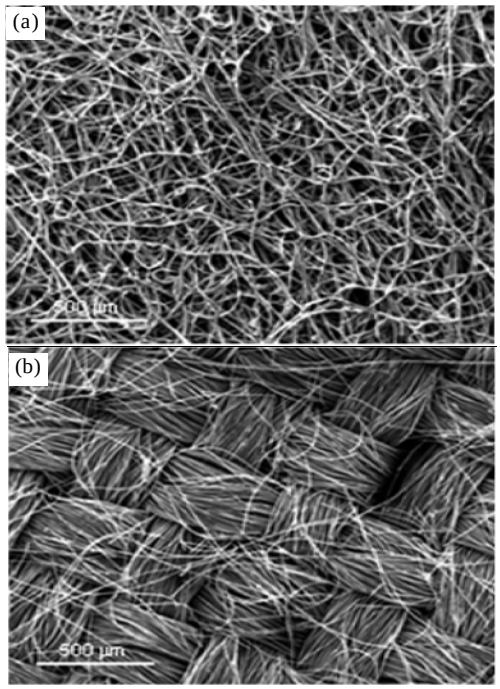

Figure 2. SEM micrographs for substrate of (a). Carbon Paper and (b). Carbon Cloth [3]

There are two types of GDE, both are commercially available, that are commonly used in PEMFC: GDE employing carbon paper and GDE employing carbon cloth as the Gas Diffusion Layer (GDL) [3,4]. Carbon Paper (CP) is non-woven carbon-fiber-based porous materials, while the Carbon Cloth (CC) is woven fabric. The structural differences between CP and CC can be seen in Figure 2 [3]. The porous nature of the GDL material ensures effective diffusion of each reactant gas to the catalyst on the MEA [6].

Several researchers have demonstrated that CC and CP give different effects on the fuel cell performance at low and high humidity [2,7-9]. At high humidity and high current density, CC led higher performance than CP, whereas CP showed better performance at low humidity due to the differences in their structural and mechanical properties. Moreover, through neutron radiography investigation, it is observed the differences of water content in CC and CP [9].

In order to fabricate MEA, hot pressing is a simple way to assemble anode, cathode, and membrane. This process results in a good interfacial contact between the electrodes and membrane that can improve cell performance [6,7,10]. Several hot-pressing techniques that combining parameters of temperature, pressure, time, and Nafion solution loading have been employed by researchers to fabricate in-house MEA [11-13]. In particular, a MEA based on Nafion 1100 series membranes is fabricated by hot-pressing at the temperature range of 100-160 °C [11,14-16] which is selected between the glass transition tempertature (T_g = 115 °C) of the Nafion and the decomposition temperature (T_d > 280 °C) of the Nafion 1100 series [17]. At temperature above Tg, the Nafion membrane is softened and can be attached to the electrode under a high pressure. At temperature much higher than Tg, the Nafion membrane will undergo a micro-structural and physical properties change, which leads to a lower proton conductivity [15,17-18].

Although several studies have investigated and compared the role of CC and CP in PEMFC, research on the influence of hot pressing parameters in the performance of PEMFC employing GDE based on CP and CC has not been published in literature extensively. The objectives of this work are to characterize fuel cell's performance and to examine how hot pressing temperature gives different effects on the performance of the MEAs using CP and CC, by evaluating their polarisation curves. Further investigation on the effect of the hot-pressing temperature on cell performances, especially on the activation and ohmic losses, will be conducted using empirical equation. A better understanding about the commercial GDE whether using CC or CP will be useful for reaching the optimum performance of PEMFC.

EXPERIMENTAL METHOD

MEA Fabrication

Prior to fabricating the MEAs, proton exchange membranes (PEM, Nafion 117, DuPont) were treated according to the standard procedure of 1 h in 3 wt.% H_2O_2 solution at 70-80 °C, 1 h in distilled water at 80 °C, 1 h in 0.5 M H_2SO_4 solution at 70-80 °C, and finally wash in distilled water until reached pH of 7. Subsequently, pre-treated membranes were stored in de-ionized water at room temperature. Two commercially available catalyzed GDE, based on CC and CP (20 wt.%Pt/C, 0.5 mg/cm2 Pt, ELAT) were used as the anode and cathode for all fuel cell tests. Nafion solution was brushed thinly onto GDE's surface area and dried at room temperature for about 15 min. The pre-treated Nafion membrane was sandwiched between two GDEs and hot-pressed at 120 °C and 150 °C under pressure of 20 kgf/cm^2 and time of 5 minutes. Two teflon sheets covered the MEA in order to avoid the membrane sticky. The arrangement in the hot-pressing process can be seen on the Figure 3.

Fuel Cell Measurement

Single cells were assembled with the prepared MEAs and graphite plates with parallel flow channels. The PEMFC stack was operated at room temperature using pure H_2 and O_2 (99.9%), an operational pressure of 1 bar, and excess gas flow in order to minimize the effect of stoichiometry. The gases were not humidified before being fed into the cell. Performance of the single cell was evaluated by measuring polarization curve.

RESULTS AND DISCUSSION

Figure 4 shows the polarization (a) and power (b) curves, for both MEAs based on CC and CP prepared at the hot-pressing temperature of 120 °C and 150 °C. It is clearly seen that hot-pressing temperature gives different effect on the performance of CC and CP in fuel cell, under identical test condition of

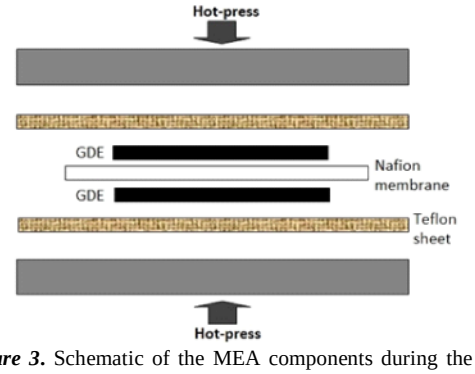

Figure 3. Schematic of the MEA components during the hot-pressing process

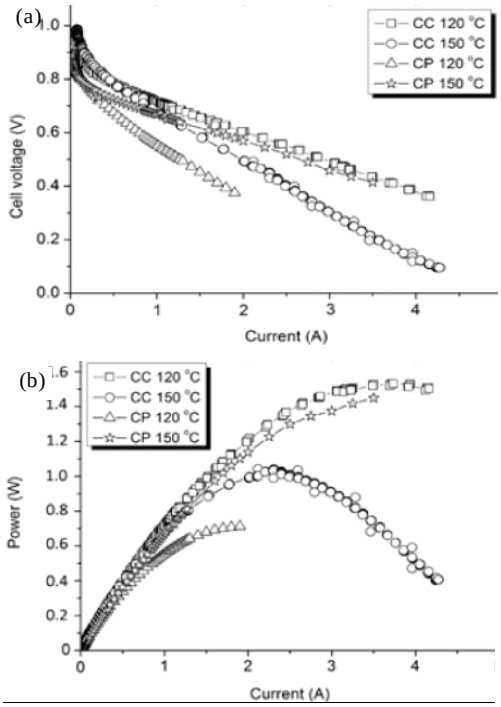

Figure 4. Cell voltage (a) and power (b) curve for CC and CP GDEs with different hot-pressing temperature

Table 1. Performance parameters in different types of GDE

Parameter	CP	CP	CC	CC
T_{press} (^oC)	120	150	120	150
I_{op}(A)	0.8	1.7	1.98	1.52
P_{op} (W)	0.48	0.97	1.18	0.91
P_{max}(W)	0.71	1.45	1.53	1.04
I_{max} (A)	1.9	3.5	3.73	2.31
V_{max} (V)	0.37	0.41	0.41	0.45

H_2/O_2. PEMFC based on CP shows an increase in the performance as hot-pressing temperature goes up, while PEMFC employing CC experiences a downward trend. As illustrated in Figure 4, the lowest power is obtained from the PEMFC employing CP at hot-pressing temperature of 120 ^{o}C, which is 0.71 W at 1.9 A and 0.37 V (Table 1).

When increasing the hot-pressing temeperature, its power doubles to 1.45 W (3.5 A; 0.41 V). On the contrary, the CC performance decline considerably as the hot-pressing temperature rises. At lower temperature, the maximum power of CC is 1.53 W (3.73 A; 0.41V), which was the highest power, and then it reduces by nearly 50% at higher hot-pressing temperature. It is noted that this experiment was conducted at dry reactant gases or no humidification. Decrease in the power mainly causes by the increasing of ohmic resistance of the membrane that is clearly seen from the gradation of the linear region of polarisation curve in Figure 4 (a). The different trends of CP and CC reveal variation effect of the hot-pressing temperature on the MEA structure and morphology.

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The structural differences (non-woven versus woven fabric) as shown in Figure 1, result in two major quantifiable differences [2]. One is the GDL tortuosity, where CC is more porous and less tortuous than CP. The second is in controlling water droplet attachment or water coverage on the GDL surface, with CC being rougher and hence less liquid water coverage than CP.

Further investigation on the effect of the hot-pressing temperature on cell performances, especially on the activation and ohmic losses, is done by using empirical Equation (1) and (2) [19],

$$E_i = E_{oc} - b \ln(I) - IR \quad \text{..... (1)}$$

$$E_{oc} = E_i - b \ln(I_o) - IR \quad \text{..... (2)}$$

Here, E_i is potential from experimental observation, E_r is reversible potential, b and I_o are Tafel slope and exchange current density, respectively, and R represents the ohmic resistance. The actual performance of PEMFC is decreased from its ideal voltage (E_{oc}), 1.23 volt, because of three main losses: activation, ohmic, and diffusion overpotential. Activation losses are caused by sluggish electrode kinetics and these appear for overpotential 50-100 mV [20]. Ohmic losses that is seen at linear region of polarisation curve are dominated by electrical and ionic conductivity losses, while diffusion losses are caused by mass transport limitations of the reactants to electrode [5,20].

Using Equations (1) and (2), the trend of activation and ohmic losses change can be described, and then illustrated in Figure 5 for both CC (a) and CP (b). It is noticeable that hot-pressing temperature just affects the ohmic losses of MEAs employing CC, whereas both activation and ohmic regions considerably change in MEAs based on CP. In order to get the trend of hot-pressing temperature effect on the activation losses (b and I_o), qualitative approach of equation (2) is used.

From Figure 5(a), the Tafel curves of CC for both hot-pressing temperature of 120 °C and 150 °C at the activation region, delta voltage less than 100 mV, almost coincide. Therefore, in the case of CC, hot-pressing temperatures do not significantly change its electrochemical rate reaction. In addition, log I intercepts as the representative of exchange current density (I_o) for both temperatures are almost the same. On the other hand, activation losses for MEAs based on CP, Figure 5 (b), show a significant change as a function of hot pressing temperature. From the slope of tafel curve in Figure 5 (b), it is known that I_o for CP at hot-pressing temperature of 150 °C is much less than that of CP at lower temperature. Having less I_o indicates slower electrochemical reaction [5]. This is probably attributed of high penetration of conductive layer into catalyst sites due to hot pressed process. At high hot pressing temperature, the conductive layer easily penetrated into active layer. This means that there is a high possibility that Pt/C particles are forced into the conductive layer

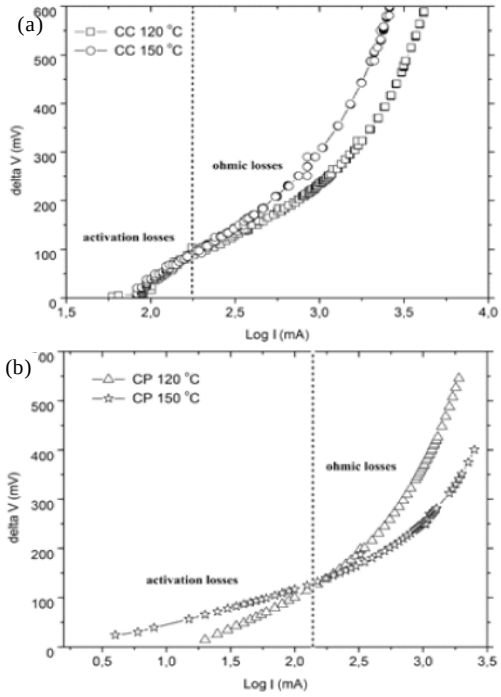

Figure 5. Tafel plot of both GDE based on (a). carbon cloth and (b). carbon paper

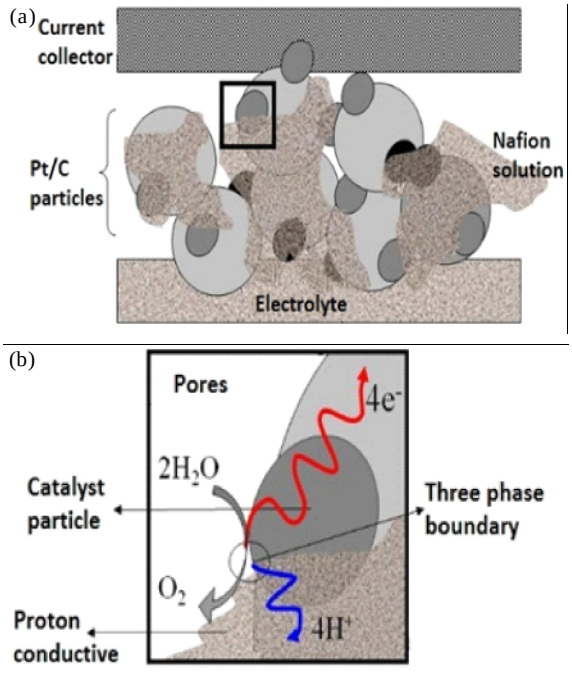

Figure 6. Schematic overview of (a). cell cross-section and (b). three-phase boundary [21]

and covered by ionomer, Nafion solution, thus reducing the number of available reaction sites. Increasing covered Pt/C particles also reduce three phase boundary that will resist access to ionic and electric conductors, catalyst, and reactant gas as seen in Figure 6 [21].

Furthermore, from the polarisation curve fitting at linear region using equation (1), as shown in Table 2, the ohmic resistance of CC at 120 °C is 114 mΩ, which is nearly a half of the ohmic resistance of CC at 150 °C,

Table 2. Ohmic resistance for all CC and CP at two different hot-pressing temperature

Parameter	CP	CP	CC	CC
T_{press} (°C)	120	150	120	150
R (mΩ)	199	100	114	182

which is 182 mΩ. An increase of CC ohmic resistance as the hot-pressing temperature goes up is also clearly seen from the gradient of linear curve at Figure 5 (a) when log current is more than 2.5 mA. It can be a result of the reduction in the electrical connection of Pt/C to the diffusion layer due to penetration of conductive layer [11]. This effect will be also seen when use high ratio of Nafion solution loading [13]. A decrease in the contact of catalyst particles to the diffusion layer will also hinder the diffusion of hydrogen and oxygen, so diffusion losses rise that is noticeable from a sudden decline in the power of CC at hot-pressing temperature of 150 °C when the current higher than 3 A, Figure 4 (b). A downward trend of CC performance with hot-pressing temperature is also found in the previous research [11].

In contrast, increasing the hot-pressing temperature enhance the performance of GDE based on CP because it decreases the ohmic resistance, from 199 to 100 mΩ at hot pressing temperature of 120 and 150 °C, respectively. Similar result was also performed in previous research [10]. It is believed that the inner structure and the activity of the MEAs can be changed during hot pressing process [22]. Higher temperature of hot pressed process would result in a better compact electrode, hence decreases MEAs resistance. Moreover, higher temperature would result in a thinner Nafion membrane, which leads to improve the performance of MEAs [23].

CONCLUSION

The performance of single Proton Exchange Membrane Fuel Cell (PEMFC) prepared from conventional hot pressing Membrane Electrode Assembly (MEA) employing Carbon Cloth (CC) and Carbon Paper (CP) was studied using polarization curves. From this study, it is known that hot pressing temperature gives different effects on the cell performance based on Gas Diffusion Electrodes (GDE) of CC and CP. When CP shows better performance as the temperature increases, CC illustrates an opposite trend. Investigation on activation and ohmic losses using empirical equation shows that the hot-pressing temperature plays important role in ohmic losses for both types of GDE, while in the case of CP, activation region also changed as hot pressing temperature changed. Decreasing in exchange current density of CP as the hot pressing temperature increased is probably due to penetration of Pt/C particles into the conductive layer and that were covered by Nafion solution. The best performance is achieved from the CC at hot-pressing temperature of 120 °C (1.53 watt) which is slightly the same as the power of CP prepared at 150 °C (1.45 watt).

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