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Effect of Humidifier Temperature and Hydrogen Flow Rate on MEA Performance of PEMFC Using Pt/C and Pd-Co/C Catalyst

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The tests on the effect of humidifier temperature and hydrogen gas flow rate on MEA performance of PEMFC has been done. This study used MEA with Pt/Ccatalyst at the anode and Pd-Co/C at the cathode. The MEA was characterized using the Cyclic Voltammetry (CV) method to determine the Electrochemical Active Surface Area (ECSA) and Electrochemical Impedance Spectroscopy (EIS) to determine the conductivity value. Then the MEA performance test was carried out based on the I-V and I-P curves on variations in humidifier temperature and hydrogen gas flow rate. Characterization and performance tests were carried out on PEMFC single stack. The results of the MEA characterization of Pt/C and Pd-Co/C with the CV method obtained an ECSA value of 1.8 cm^2/g. Meanwhile, using the EIS method, the conductivity value is 3.85×10^{-9} S/cm. The MEA humidifier temperature performance test obtained the best operating temperature at 40 °C with a power density of 3.192 mW/cm^2at a current density of 12 mA/cm^2 and the MEA performance test with variations in the hydrogen flow rate was the best at a flow rate of 200 mL/min with a power density of 3.192 mW/cm^2 at a current density of 12 mA/cm^2.

Keywords: PEMFC; humidifier temperature; hydrogen gas flow rate

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Fuel cell is an energy conversion device that converts chemical energy in fuel into electrical energy [1]. One type of fuel cell that uses hydrogen as a fuel is Proton Exchange Membrane Fuel Cell (PEMFC). PEMFC was chosen because it has high energy conversion efficiency, quiet operation, low emission, and low-temperature [2].

The important part of PEMFC is Membrane Electrode Assembly (MEA). MEA is composed of electrodes consisting of a cathode and anode [3]. The electro-chemical properties of the electrodes can affect the performance of MEA which is known by measuring its catalytic activity through Cyclic Voltammetry (CV) analysis based on the value of Electrochemical Surface Area (ECSA) [4] then the electrical conductivity is known by performing Electro-chemical Impendance Spectroscopy (EIS) analysis [5].

The part of the electrode that affects the performance of MEA is the catalyst. Fuel cells generally use platinum (Pt) and its alloys as hydrogen oxidation catalysts [6]. Currently, researchers continue to look for the best alternative to Pt, without compromising its catalyst performance by using non-platinum-based catalysts with catalyst properties similar to Pt such as Palladium (Pd) [7]. Pd has an electron configuration identical to Pt so it is considered capable of achieving high oxygen reduction reaction activity [8]. However, the catalytic activity of pure Pd is five times less than that of Pt. Therefore, researchers have tried to increase the catalytic activity of Pd by introducing different transition metals such as Co, Fe, Ni, Cu, Mo, Bi, Ir, and W [7].

One of the challenges for optimizing PEMFC performance is to maintain proper membrane humidity. Humidity plays an important role in fuel cells because the chemical reactions that occur are highly dependent on the presence of air in the membrane as a proton carrier [9]. Low humidity levels can accelerate the membrane degradation process which causes the membrane to become dehydrated. On the other hand, too high humidity can inhibit the movement of reactants due to the pores that are blocked by the formed molecules [10].

Zhang et al [11], reported that in addition to humidity, the flow rate can also affect fuel cell performance. Increasing the hydrogen flow rate can increase the supply of hydrogen/fuel at the anode. However, an excessive supply of hydrogen will lead

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to the wasteful use of hydrogen. Meanwhile, a small supply of hydrogen will cause a sudden power change problem which leads to a decrease in performance due to higher loading and damage to the MEA [12].

Explanation Based on the above, the performance of MEA was tested with Pt/C catalystat the anode and Pd-Co/C at the cathode at PEMFC on humidifier temperature and hydrogen flow rate, and the utilization of Pd-Co/C in PEMFC is the novelty of this research.

EXPERIMENTAL

Chemicals and Materials

Pd/C 40 wt% and Pt/C 40 wt% are used as Catalysts (Fuel Cell Store), 2-propanol (Merck) as solvent, ammonium hydroxide (NH_4OH), Carbon paper P75T CVSP (Fuel Cell Store) as backing layer, Carbon Vulkan XC-72R (Fuel Cell Store), cobalt(II) chloridehexa-hydrate ($CoCl_2.6H_2O$) as catalyst, polytetrafluoroetylen (PTFE) solutions (Dupont) as hydrophobic agents and Nafion-212 Dispersion (Fuel Cell Store).

Manufacturing Gas Diffusion Layer (GDL)

The certain amount of Carbon Vulcan XC-72R was activated by heating in an oven at a temperature of 115°C for 2 hours. The Carbon Vulcan was then added with 2-propanol and 27 mg of ammonium bicarbonate. Then, 412.5 mg of Teflon/PTFE solution was added and the resulting mixture was stirred in an ultrasonic stirrer for 15 minutes. The ink (We called Microporous Layer (MPL) ink) is put in a spray gun and then sprayed on carbon paper with a size of 5 x 5 cm^2 in the direction of the X and Y axes alternately. MPL attached to carbon paperis heated in a furnace at a temperature of 350°C for 3 hours so that it becomes a Gas Diffusion Layer (GDL) (Yulianti *et al.*, 2019).

Manufacturing Pd-Co/C Catalyst

12.62 mg of $CoCl_2.6H_2O$ was dissolved in 25 mL of distilled water, then impregnated with Pd/C, added 0.1 mL of ammonium hydroxide dropwise, and stirred for 24 hours to form NH_4Cl and $Co(OH)_2$ then the mixture was washed until neutral pH. The mixture was dried using an oven at a temperature of 110 °C for 2 hours, then calcined using a furnace at a temperature of 550 °C for 5 hours, and then reduced with hydrogen gas (H_2) at a rate of 1 mL/second at a temperature of 450 °C for 2 hours, the catalyst product will be obtained Pd-Co/C.

Manufacturing Electrode

Pd-Co/C was added with 1 mL of 2-propanol and Nafion solution then stirred for the first 20 minutes. Next, add Teflon emulsion and the mixture is stirred again for 5 minutes until Pd-Co/C ink is formed. The Pd-Co/C ink is then put into a spray gun and sprayed onto the GDL with an area of 25 cm^2 in a horizontal and vertical direction alternately until the ink runs out. The electrodes formed were then dried in a 350 °C furnace, to form a Pd-Co/C layer attached to the GDL.

Manufacturing Membrane Electrode Assembly (MEA)

Two electrodes of the cathode and anode are glued on both sides of the Nafion-212 membrane.Then coated with aluminum foil and clamped with aluminum plates. Furthermore, MEA was pressed using a hot press at a pressure of 2000 psi for 3 minutes at a temperature of 135 °C.

MEA Characterization using the Cyclic Voltammetry (CV) and Electrochemical Impedances Spectroscopy (EIS) Method

MEA characterization was carried out using the CV method to determine the electrochemical properties of the MEA from the calculation of the value of the Electrochemical Surface Area (ECSA), and EIS method was carried out to determine the value of the electrical conductivity which indicates the ability of MEA to conduct electricity. The characterization was carried out using a potentiostat/galvanostat tool Autolab Methrom PGSTAT 204.

MEA Testing on PEMFC Singlestack

The MEA performance test on PEMFC on the effect of humidifier temperature was carried outby varying the temperature of the humidifier at room temperature, 40, 60, and 80 °C with a constant flow rate of 200 mL/minute. The operating conditions of the best humidifier temperature were used to test the MEA performance at various hydrogen flow rates of 100, 200, 300 and 400 mL/minute by connecting a PEMFC singlestack to the WonATech Smart 2 Fuel cell Test Station.

Performance measurement is carried out by recording the voltage value for each additional load (current) until the MEA is unable to maintain its voltage value. The measurement data is then analyzed using the I-V polarization curve, which is a curve that showsthe relationship between voltage (V) on the y-axis and current density (I) on the x-axis, and theI-P curve, which is a curve that shows the relationship between voltage (V) on the y-axis and power density (P) on the x-axis obtained by multiplying the value of the current density by the voltage.

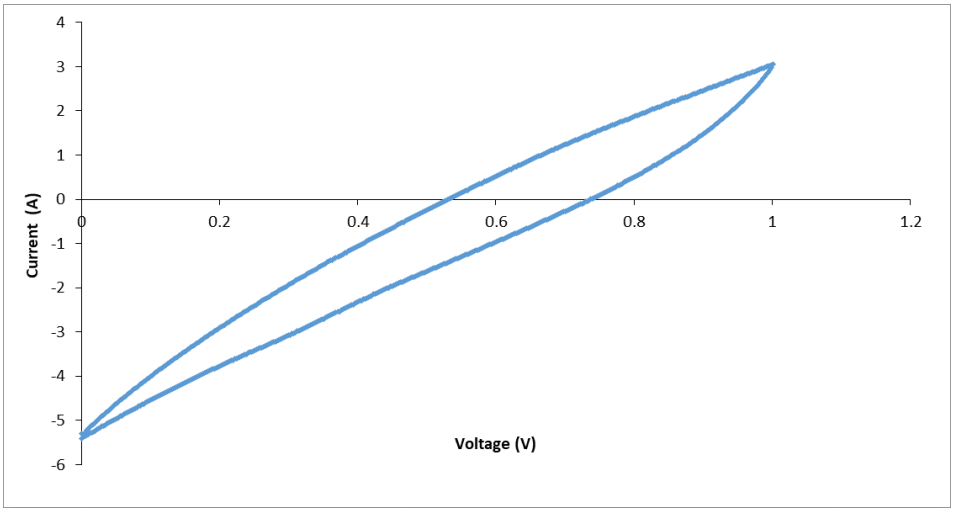

Figure 1. Voltammogram curve of MEA.

RESULTS AND DISCUSSION

MEA Characterization using Cyclic Voltammetry (CV) Method

The CV technique is used to determine the number of active catalyst sites on the surface which can be determined by the ECSA value [14-15]. Measurements by CV technique on MEA with Pt/C and Pd-Co/C catalyst were carried out at a scan rate of 25 mV/s. Measurements with the CV technique produce a curve of the relationship between current and potential which is depicted on the voltammogram curve shown in Figure 1.

Figure 1 shows the voltammogram curve from the results of CV characterization on MEA with Pt/C catalyst in anodeand Pd-Co/C in cathode. It can be seen that the anodic peak occurs at a voltage of 0.439 V and the cathodic peak at 0.803 V. The anodic peak is a response to the electron release reaction, while the cathodic peak indicates an electron capture reaction [13]. Based on the magnitude of the resulting peak, the ECSA value of MEA Pt/C and Pd-Co/C was obtained at 1.8 cm^2/g.

MEA Characterization using Electrochemical Impedances Spectroscopy (EIS) Method

The EIS method in this research is used to determine the electrical conductivity of the MEA [16]. Characterization using the EIS method produces an impedance spectrum which is plotted in the form of a Nyquist plot. The Nyquist plot shows the plot between the imaginary part (-Z") and the real part (Z') of the impedance at different frequencies [17-18]. The Nyquist plot of the results of the Pt/C and Pd-Co/C MEA characterization measurements is shown in Figure 2.

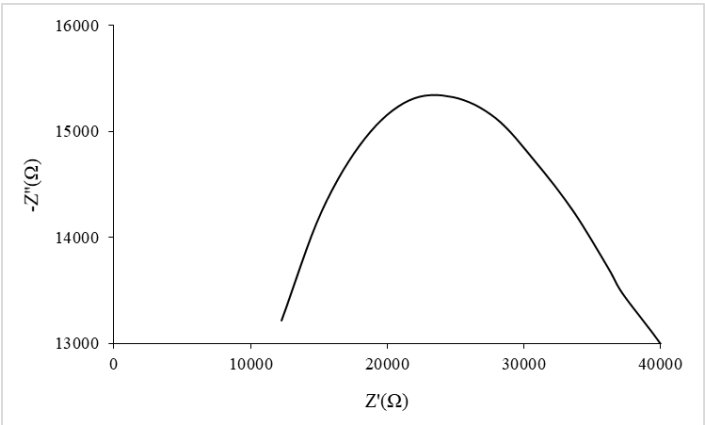

Figure 2. *Nyquist* plot of MEA.

Figure 2 shows the Nyquist plot of the characterization of MEA with Pt/C and Pd-Co/C catalysts in the form of a half arc in the low frequency range in the initial state and a quarter arc in the medium and high frequency ranges. The unbroken line on the plot is the result of the fitting process to get the value of Rp (Resistance Polarization) and Rs (Resistance Solution) [19] which can then be used to calculate the electrical conductivity value. The value of Rp and Rs from the analysis using NOVA 2.1.4 software on MEA Pt/C and Pd-Co/C was obtained at 725151 Ω and 18510 Ω. This relatively high value of Rp can provide better protection for MEA against corrosion [20].

The electrical conductivity value of MEA characterization using the EIS method was obtained at 3.85×10^{-9} S/cm. The resulting conductivity value is fairly low, this is because theresulting impedance is quite high. Laribi et al [21] say that the impedance value is inversely proportional to the conductivity value. The higher the impedance value, the lower the conductivity value.

MEA Performance Test on Humidifier Temperature Variations

The MEA performance test on PEMFC on humidifier temperature was carried out by varying the humidifier temperature, including room temperature, 40, 60, and 80°C with a constant flow rate of 200 mL/minute. The MEA performance test results with humidifier temperature variations can be seen in Figure 3.

Figure 3(a) depicts the relationship between voltage and current density (I-V) as a result of a humidifier temperature performance test on MEA Pt/C and Pd-Co/C. The humidifier temperature of 40°C provided the best MEA performance under operating conditions. This can be seen at each increase in current, MEA is better able to maintain its voltage compared to other humidifier temperature variations. At a humidifier temperature of 40°C is able to hydrate MEA better than at room temperature conditions. At room temperature operation, MEA is inconditions of low temperature or high humidity. High humidity can result in flooding at the electrodes and water molecules will block the pores and prevent the transport of reactants [10].

MEA performance decreased at humidifier temperature conditions of 60°C and 80°C because it was unable to maintain its voltage as well as MEA 40°C. Wilberforce *et al* (2019) [22] reported that at high humidifier temperature operating conditions, the membrane on the catalyst layer was not fully hydrated because the water in the membrane evaporated and then the membrane dried out. Dryness of the membrane can cause a decrease in the conductivity of the membrane as well as the active surface area of the catalyst so that the performance of MEA Pt/C and Pd-Co/C decreases [23].

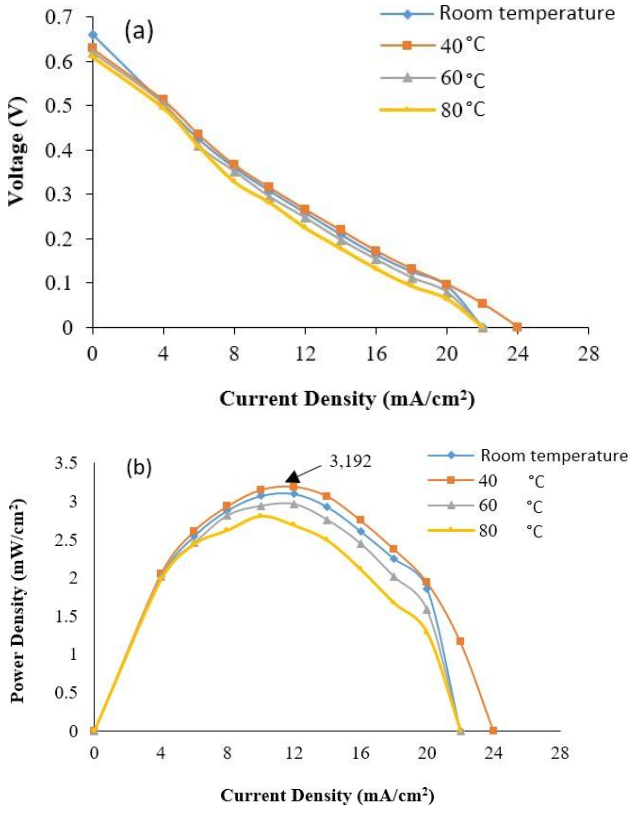

Figure 3. Humidifier temperature polarization curve (a) I-V (b) I-P.

The curve of the relationship between power density and current density from the MEA application with various humidifier temperatures is shown in Figure 3(b). Figure 3(b) depicts the maximum power density at 3.192 mW/cm^2 with a current density of 12 mA/cm^2 at a humidifier operating temperature of 40°C.

MEA Performance Test on Variation of Hydrogen Flow Rate

MEA performance testing on PEMFC on hydrogen gas flow rate was carried out at variations of 100, 200, 300, and 400 mL/minute with a constant humidifier temperature of 40 °C which is the temperature of the humidifier with the best performance. The results of the MEA performance test at various flow rates can be seen in Figure 4.

Figure 4 shows the performance of MEA at various hydrogen flow rates. Figure 4(a) shows that the best performance of MEA Pt/C and Pd-Co/C is at a hydrogen flow rate of 200 mL/min because, under these conditions, MEA is able to maintain a voltage against a larger current than the flow rate other variation hydrogens. Based on the I-V curve, it is also knownthat the best PEMFC performance results from an adequate supply of hydrogen. If the hydrogen flow rate is too high, the resulting fuel cell efficiency will be low because hydrogen will be wasted. However, if the hydrogen flow rate is too low, the performance of the fuel cell will decrease, which is indicated by a decrease in voltage along with an increase in load [24].

The performance of the 100 mL/minute hydrogen gas flow rate indicates that the supplied gas is not optimal. The phenomenon of inadequate reactant supply can lead to corrosion of the supporting carbon due to water accumulating in the pores of the electrode.This blockage results in the blocking of the GDL pores and prevents the reactants from reaching the catalyst [25]. Corrosion of the supporting carbon due to low hydrogen supply can also result in a decrease in the catalytically active surface area due to an increase in particle size [26]. However, at flow rates of 300 mL/min and 400 mL/min, performance decreased due to excess hydrogen supply.

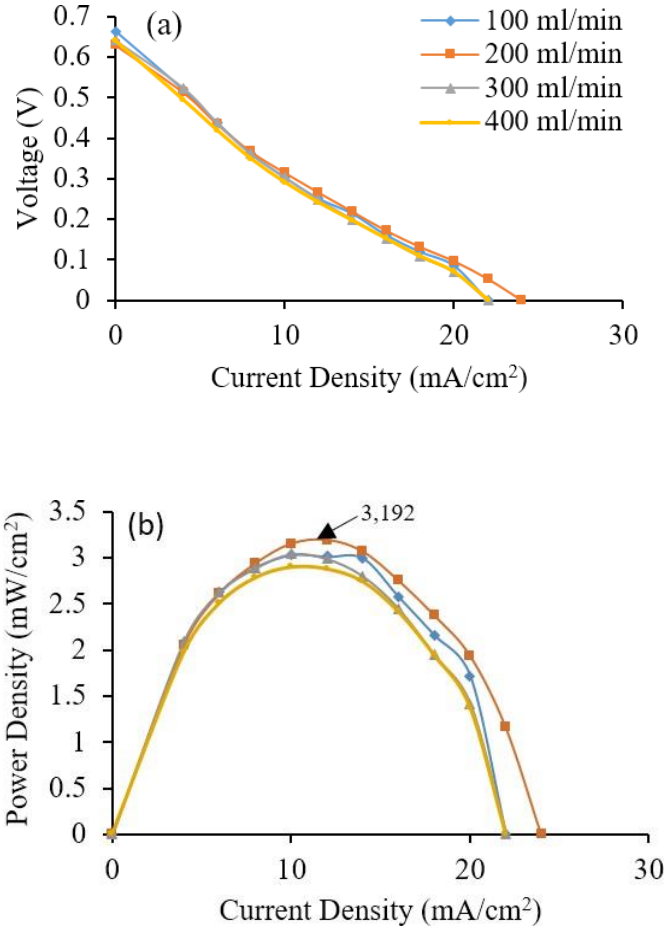

Figure 4. Hydrogen flow rate polarization curve (a) I-V (b) I-P.

The power density to current density (I-P) curve in Figure 4(b) can be used to see the ability of an MEA in PEMFC to achieve maximum power density [27]. MEA performance improved when the hydrogen flow rate was increased from 100 mL/min to 200 mL/min with a 5% increase in power density. Then it continued to decrease when the flow rate was increased to 300 mL/min and 400 mL/min with the resulting power densities of 3.04 mW/cm^2 and 2.9 mW/cm^2, respectively.

CONCLUSION

Based on the results of the MEA characterization measurements with Pt/C and Pd-Co/C catalysts using the Cyclic Voltammetry (CV) method, the ECSA value was 1.8 cm^2/g. Meanwhile, using the Electrochemical Impedance Spectroscopy (EIS) method, the electrical conductivity value was 3.85 × 10^{-9} S/cm.

The best operating humidifier temperature based on the I-V and I-P curves of MEA with Pt/C catalyst (Anode) and Pd-Co/C (Cathode) is at a temperature of 40°C with a power density of 3.192 mW/cm^2 at a current density of 12 mA/cm^2.

The best hydrogen flow rate based on the I-V and I-P curves of MEA with Pt/C catalyst (Anode) and Pd-Co/C (Cathode) is at a flow rate of 200 mL/min with a power density of 3.192 mW/cm^2 at a current density of 12 mA/cm^2.

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