Preparation and characterization of membrane electrode assembly (MEA) for PEMFC

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SUMMARY

Fuel cell is a system that converts chemical energy to electrical energy from an oxidation–reduction reaction of hydrogen and oxygen. In this study, Pt/C catalyst, solvent, and a binder agent were mixed to prepare catalyst ink. First, we applied carbon black ink to the carbon paper to supply hydrophobic and hydrophilic structure on its surface, which is called as microporous layer (MPL). Then catalyst ink was deposited on the treated carbon paper to form gas diffusion layers (GDLs) for anode and cathode side of the fuel cell. At this position, catalyst layer surfaces and carbon paper were analyzed by using scanning electron microscopy (SEM) and it was seen by energy dispersive spectroscopy (EDS) analysis that the catalysts were spread uniformly on a carbon paper. A membrane is fixed between GDLs and hot-pressed at 120 °C, 75 kg cm−2 to compose membrane electrode assembly (MEA). In a fuel cell test unit, MEA has internal resistance, which was evaluated by applying current interrupt method and current–voltage curve was drawn by load application. As a result of the test, I−V curves were formed and compared with characteristic curve of commercial MEA. It was seen that the shapes of the curves are similar. Maximum power values are 100, 275, and 390 mW for homemade MEA without MPL, with MPL, and commercial MEA, respectively. MEA without MPL was susceptible to flooding, especially at high-current values. MPL is helpful to increase the porosity of the diffusion layer and this effect can improve the oxygen transfer rate and lead to a higher performance.

Compared with commercial MEA, homemade MEA did not reach high-current and -power values due to lots of parameters which affects the fuel cell performance as catalyst activity, conditions of MEA preparation, and disorder of measurement conditions, etc. Copyright © 2010 John Wiley & Sons, Ltd.

KEY WORDS
PEMFC; catalyst ink; MEA; hydrogen energy

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1. INTRODUCTION

Fuel cells are a promising energy source on account of their high efficiency and low pollutant emission. There are two approaches to reduce the amount of platinum in fuel cell [1]. One method is to develop an alloyed catalyst based on platinum, which has a better catalytic activity, or to discover a new catalyst [2,3]. The other is to invent a new catalyst layer fabrication method such as pulse electrodeposition, electrospray technique, sputter deposition, pulsed laser deposition, and ion-beam deposition [4].

In a fuel cell system, the electrochemical reaction can only occur at ‘triple-phase boundaries’, where the electrolyte, reaction material, and electrically connected catalyst particles contact together in a membrane electrode assembly (MEA) [5]. The triple-phase-boundary area in turn depends significantly on the fabrication procedure of MEA in addition to other important parameters such as catalyst loading [6] and ionomer loading [7]. Two fabrication methods can be used to prepare MEAs, which are hot-press and catalyst-coated membrane (CCM) or CCM method [8]. In the case of MEA by hot-press method, the Pt/C catalyst mixing with a PTFE suspension is spread onto the porous carbon paper or cloth support, and sintered to produce the electrodes. The electrodes are sandwiched between a proton exchange membrane and then hot-pressed to form a MEA [9].
MEAs can also be prepared by a CCM method [10]. In the CCM method, the Nafion containing catalyst ink is spread on a Teflon support and then transferred to the proton exchange membrane by hot pressing. The Teflon support is then peeled away and the CCM is sandwiched between porous carbon paper or cloth supports [11]. MEAs prepared by the CCM method provides better power density due to an extended catalyst/ionomer interface and improvement of catalyst utilization [12].

The objective of this work was to study differences in fuel cell performance resulting from preparation procedure of homemade MEA’s and commercial MEA and to identify an optimized fabrication concept with regard to minimal performance, considering the previous optimized procedure.

2. EXPERIMENTAL

2.1. Ink preparation

Catalyst of 20 wt% Pt was supported on a conductive carbon black with a high surface area, which was used for anode and cathode. This was purchased from Alfa Aesar.

The catalyst ink was made by mixing Pt/C catalyst with 5 wt.% solubilized Nafion was prepared to provide the more intimate contact between the polymer electrolyte membrane and platinum clusters. The slurry containing Nafion and Pt/C was prepared by first thoroughly mixing the solution using a magnetic stirrer, followed by adding glycerol for solvent into the slurry. The protonated form of Nafion within the slurry was converted into the TBA+ form by the addition of 1 M TBAOH dissolved in water to give thermoplastic property to the constituting Nafion ionomer. About 50% excess TBAOH was added to minimize the thermal degradation of the ionomer. TBAOH solution was not added until the catalyst and Nafion solution were completely mixed (typically a few hours), because addition of more alkaline solutions directly to the solubilized Nafion results in some coagulation. The cathode ink was made by mixing Pt/C catalyst with the same procedure. The amount of Nafion in catalyst ink is an important parameter. This amount is calculated by Equation (1). In this equation, Nafion in ink is set to be 20(wt)% [13]

\[
\text{Nafion (wt)} = \frac{M_{\text{Naf}}}{M_{\text{Naf}}+M_{\text{Cat}}} \times 100 \quad (1)
\]

2.2. Preparation of Gas Diffusion Layer (GDL)

GDLs for anode and cathode were bare C-paper (Avecarb T-50). The GDLs were C-papers coated with the hydrophilic and hydrophobic microporous layer (MPL). The hydrophilic MPL for the anode comprised Vulcan XC-72R carbon black and 30 wt% of Nafion ionomer, and the hydrophobic MPL for the cathode comprised Vulcan XC-72R carbon black and 30 wt% of PTFE (Teflon solution). The loading of carbon black is 2 mg cm\(^{-2}\) for both the anode and the cathode [14].

In this study, commercial Pt/C catalyst was used as a catalyst for the anode and cathode side of the cell. As prepared, catalyst ink is deposited on to a carbon paper that is treated with carbon black. The deposition process took place gradually.

2.3. Fabrication of MEA

Nafion 117 polymer membrane (Alfa Aesar NR 117) was used to fabricate MEA. Before being applied to the electrodes, the membrane was pretreated in four steps to remove the organic and inorganic contaminants. First, membrane was boiled in 3 wt% \(\text{H}_2\text{O}_2\) solution followed by washing in a ultrapure water. Then, the membrane was boiled in 0.5mol\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution. Finally, the membrane was boiled again in the ultrapure water. Each step took about 1 h [15].

MEA was fabricated by hot-pressed MEA method for electrode preparation. To prepare the catalyst layer by the hot-pressed MEA method, the catalyst ink was applied to GDL by brush printing. Then, the Nafion membrane and catalyst-coated GDL were bonded together by hot pressing under conditions of 120°C, 75 kg cm\(^{-2}\) and 1.0 min. Fabrication of MEA was shown in Figure 1 [16]. Pt/C catalyst is deposited on anode and cathode side of cell as 1 mg cm\(^{-2}\). The deposition was carried out in stages. To improve the interface contact between the catalytic coated backing and the membrane, a thin layer of ionomer solution is brushed on the electrode surface. Active area of the MEA was 5 cm\(^2\). Commercial MEA with catalyst loading 1 mg cm\(^{-2}\) for anode and cathode was purchased from Electrochem (FC05-MEA).

3. RESULTS AND DISCUSSION

3.1. Current interrupt method (CIM)

A polarization curve provides useful but not sufficient information about fuel cell performance. Both flooding and drying of a cell would result in a loss of voltage, but a single polarization curve would not be able to distinguish between the two. In addition, polarization curve takes time and cannot be performed during normal operation of a fuel cell. A quick measurement of the cell resistance may provide more information about the cell’s performance. Drying of the membrane would result in resistance decrease. One of the methods to measure the resistance in an operational fuel cell is the CIM.

In this method, current is interrupted for a very short period, and the resulting voltage gain is observed. The difference between the cell voltage value before...
and after the current interrupt, divided by the current is the cell resistance \( R \) \([17]\). The graph of \( V-t \) was shown in Figure 2. Internal resistance was calculated with Equation (2). This value is very high. High internal resistance prevents high-current values and can cause voltage drops. The high-conductivity electrodes, battery connections, and bipolar plates are required to use in order to prevent cell resistance

\[
R = \frac{\Delta V}{I} = \frac{(0.87 - 0.05)(V)}{0.85(A)} = 0.964 \Omega \quad (2)
\]

3.2. Scanning electron microscopy (SEM–EDS)

Surface morphology of prepared GDLs with and without catalyst will be examined by scanning electron microscopy (SEM) analysis. EDS analysis is provided to understand whether a uniform dispersion of catalyst on the GDL is achieved or not and what the elemental composition of the catalyst is. The surface morphologies of the C-paper, MPL, and catalyst layer on the carbon paper that were made before the hot pressing of the MEA are shown in Figure 3(a–c).

Avcarb T-50 commercial carbon paper without any treatment was scanned by using SEM. Figure 3(a) shows the SEM image of carbon paper with a magnification of 1000 and there were macroscopic spaces between carbon fiber structures. Macroscopic gaps, which is on the carbon paper, were getting filled and to ensure the whole surface of the carbon paper has uniform micro-porosity, when carbon was deposited on to carbon paper. Deposition of carbon is performed by applying carbon ink, which is prepared by carbon black and appropriate percentage of Nafion solution, on the carbon paper. When MPL is deposited onto carbon paper, the catalyst layer will be prevented from entering macroscopic space. The interface with the adjacent catalyst layer may also be fitted with the MPL to ensure better electrical contacts as well as efficient water transport in and out of the diffusion layer. The amount of Nafion in catalyst ink and carbon black on the carbon paper are the important parameters for affecting cell performance.

In Figure 3(b), we can see that some small cracks and voids scattered on the surface of the MPL, whereas fewer cracks and voids are on the surface of the MPL (Figure 3(b)) than of the C-paper (Figure 3(a)) that have macroscopic voids.
Apparently, MPL is helpful to increase the porosity of the diffusion layer. This effect can improve the oxygen transfer rate and lead to a higher performance.

Micro porous layer consists of carbon particles mixed with Nafion binder. After applying this layer, small pore size occurs and it helps in improving the electrical contacts with the adjacent catalyst layer. The primary role of this layer is to facilitate effective wicking of liquid water from the cathode catalyst layer into the diffusion media, resulting in more
water droplets less likely to flood the gas diffusion mediabulk [17].

In Figure 3(c), we can see a uniform distribution on GDL, which was observed in the EDS spectrum. Deposit the catalyst layer on GDL homogeneously is an important parameter for using GDL effectively. Weight percentage of Pt/C catalyst that was deposited on GDL is shown in Table I. It can be seen in this spectrum that the Pt metal particles was spread uniformly on a carbon paper. Compared with SEM images of literature, it can be seen that similar images were obtained [18].

### 3.3. PEM fuel cell

\[ \text{H}_2(\text{g}) \rightarrow 2\text{H}^++2\text{e}^- \quad \text{(anode)} \quad (3) \]

\[ \frac{1}{2} \text{O}_2(\text{g})+2\text{H}^++2\text{e}^- \rightarrow \text{H}_2\text{O(s)} \quad \text{(cathode)} \quad (4) \]

\[ \text{H}_2(\text{g})+\frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(s)} \quad \text{(overall reaction)} \quad (5) \]

The electrochemical reactions in fuel cells happen simultaneously on both sides of the membrane—the anode and the cathode. The basic fuel cell reactions are shown in Equations (3)-(5). Electrochemical reactions happen at the surface of the catalyst, which is the interface between the electrolyte and the membrane. Hydrogen, which is fed on anode side of the membrane, splits into its primary constituents—protons and electrons. Each hydrogen atom consists of one electron and one proton. Protons travel through the membrane, whereas the electrons travel through electrically conductive electrodes, through current collectors, and through the outside circuit where they perform useful work, and come back through the other side of the membrane. At the catalyst sides between the membrane and the other electrode, they come in contact with the protons that went through the membrane and oxygen that is fed on the cathode side of the membrane. Water is created in the electrochemical reaction, and then pushed out of the cell with excess flow of oxygen. The net result of these reactions is the current of electrons through an external circuit—direct electrical current [17]. The performance curve for the PEMFC using hot-pressed MEA method is shown in Figure 4. The cell temperature was 75°C. H₂ flow was 50ml min⁻¹ at the anode side and O₂ flow was 150ml min⁻¹ at the cathode side. Relative humidity, which was calculated with the cell temperature value and humidification temperature value, was found to be 80.8%. This value is an important parameter that is used for performance of fuel cells. Stochiometric ratio was set at 3 with using flow rates. Back pressure was set at 2 atm.

Although the mechanisms of activation are not clear, they appear to be related to the changes of the catalytic activity and the pore structure of the electrodes [19]. The conditioning or activation of PEMFC and other fuel cells has been discussed by several authors [20,21].

In this study, each MEA was tested approximately 4 h per day to stabilize the cell performance and then the average of current and voltage values were recorded.

If the polarization curve is recorded in both directions, increasing and decreasing current, it may show hysteresis, that is, the two curves may not be at the top of each other. This typically points to either flooding or drying in the fuel cell. If the cell is flooding on the cathode side, then operation at high current density would only make the situation worse because additional water would be produced. The polarization curve recorded with decreasing current would show lower voltage at high currents than previously taken polarization curve with increasing current. Conversely, if the cell is drying on the cathode side, then the additional water produced at high current densities would be beneficial, resulting in higher cell potential in a backward polarization curve. Similar behavior may result in a fuel cell that is drying or flooding on the anode side. In order to distinguish between the anode drying and cathode flooding, additional information is needed, such as membrane resistance.

Figure 5 shows polarization curves of MEA’s with MPL and without MPL. It can be seen that the homemade MEA without MPL shows significant decrease in polarization curve. MEA without MPL was susceptible to flooding, especially at high current values.

There are different kinds of voltage losses in a fuel cell caused by kinetics of electrochemical reactions,
internal electronic and ionic resistance, difficulties in getting the reactants to reaction sites, internal currents, and crossover of reactants. Commercial MEA produce a rather symmetric power at high and low currents because of its stability, but the homemade MEA exhibits non-symmetric curves. Activation losses are caused by the reactions that proceeded slowly at electrode surface and needed more activation energy. Ohmic losses occur because of resistance to the flow of ions in the electrolyte and resistance to the flow of electrons through the electrically conductive fuel components. Nafion membrane is not electrically conductive but some electrons that passes through the membrane, can cause local shortcuts. Concentration polarization occurs when a reactant is rapidly consumed at the electrode by the electrochemical reaction [22]. This occurs at high current density. Voltage drop is proportional to the amount of current.

$I-V$ polarization curve of commercial MEA (Electrochem) is given at the same conditions in Figure 6. Compared commercial with homemade MEA’s, similar characteristics could be seen in the curves that were obtained. Commercial MEA is composed of anode and cathode electrode, which was deposited on 1 mg Pt/cm$^2$ as the catalyst material and Nafion 1135 as the membrane.

The power–current curves for the PEMFC’s are shown in Figure 7. Commercial MEA achieved a peak power value of 390 mW, which is greater than 275 mW measured using home-made MEA. It can be seen that when MEAs are compared with each other, homemade MEA shows ohmic losses because of internal resistance which is determined from CIM. Maximum power value is obtained by multiple current and voltage values. Thus, homemade MEA must be improved to reach high power values.

Homemade MEA without MPL reached 100 mW, which is lower than MEA with MPL. The polarization curves exhibit that the cell without MPL decreased the cell performance due to the difficulty in mass transport as seen in Figure 7.

The activation process increases the cell performance by ‘opening’ the mass transport routes and the ‘dead’ regions in the electrodes. The mass transport rates and the pore sizes in the electrode decrease, and the time required for the MEA activation increases after hot pressing.

4. CONCLUSIONS

With these studies;

1. Preparation of catalyst ink using the commercial Pt/C catalyst.
2. Preparation of the GDL.
3. Fabrication of MEA with hot-press method.
5. Calculate the internal resistance of homemade MEA during the flow-testing by applying CIM (CI method).
6. MEA’s were tested and drawing $I-V$ curves.
7. Compared with the commercial MEA, the power value of PEMFC with the home-made MEA was
reduced. On the other hand, home-made MEA with MPL exhibited a significantly higher power value than home-made MEA without MPL. The polarization curve of MEA without MPL exhibited low cell performance due to the difficulty for mass transport.

Maximum power values are 100, 275, and 390 mW for homemade MEA without MPL, with MPL, and commercial MEA, respectively. There various reasons for voltage losses. The catalyst activity, MEA preparation conditions such as temperature and pressure, irregularities in the testing phase, percentage of humidification, and cell temperature affect the performance of fuel cells. The next work will be focused on reducing the internal cell resistance of the cell with the new MPL and optimizing the new MPL structure and parameters to further upgrade the cell performance.

REFERENCES