Structural Effect of Cathode Catalyst Layer on the Performance of PEFC*

Hidetoshi MATSUDA**, Kazuyoshi FUSHINOBU**, Atsushi OHMA***, and Ken OKAZAKI**

**Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo, Japan
E-mail: fushinok@mech.titech.ac.jp
***Nissan Motor Company
Atsugi, Kanagawa, Japan

Abstract

The structure of cathode catalyst layer (CCL) has strong relationship with the performance of polymer electrolyte fuel cells (PEFCs). We investigated the relationship between the catalyst layer structure and the cell performance experimentally. Multi-layered CCL is used to investigate the effect of the layer design on the cell performance. Membrane side of CCL works, as a reaction area, more actively than the gas diffusion layer (GDL) side at low relative humidity (RH) due to the lower proton conductivity. On the other hand, when the cathode gas has less oxygen partial pressure at high RH, GDL side is more active than membrane side owing to low diffusivity of oxygen. We suggest that the volumetric catalyst concentration of the CCL membrane side should be higher at low RH, however at high RH with lower oxygen partial pressure in cathode gas, the GDL side should have higher concentration. Simple theoretical model is employed to see the behavior of the reaction distribution in the catalyst layer.

Key words: PEFC, Cathode Catalyst Layer, Structure, Pt Loading

1. Introduction

Polymer electrolyte fuel cell (PEFC) is a key technological element in hydrogen energy systems and is one of the most promising energy conversion devices because of its high power density and high efficiency. Compared with other fuel cells (FCs), PEFC can operate at lower temperatures with frequent power variation and can be downsized. Due to these advantages, PEFC is expected for automobiles, household co-generation systems and portable devices.

However, there are still various technical issues to be solved before they can be fully commercialized. Some of the serious issues include the expensive platinum catalyst and better cell performance by reducing the energy loss factors. The activation overpotential in the cathode electrode dominates the loss from very lower level of output current density. These requirements expect a development of novel catalyst layer that can achieve higher cell performance, lower activation overpotential with lower Pt loading.

For the performance, it is needed that the sufficient reactants are supplied to reaction site. The structure of cathode catalyst layer (CCL) has strong relationship with the performance of PEFC.

Importance of the catalyst layer structure on the performance of PEFC has been acknowledged recently. Boyer et al.\(^1\) presented simple mathematical expressions to optimize the fuel cell electrode structures. Neyerlin et al.\(^2\) conducted experimental study on the catalyst utilization. However the distribution of current density in the cathode electrode
has not been clear yet. Some studies were conducted to investigate the reaction distribution. Most of them, however, focused on the reaction distribution of in-plane direction\textsuperscript{(3)-(5)}. Although oxygen partial pressure has been measured in the thickness-wise\textsuperscript{(6)}, reaction distribution has not been examined. Some of the design parameters of CCLs are experimentally examined with a multi-layer catalyst layer\textsuperscript{(7)}, and one-dimensional theoretical study is conducted to assist electrode development\textsuperscript{(8)}. These studies are either experimental or theoretical, and the effects of major design and operation parameters have not been investigated yet. Parametric studies that explain the relation between the cell performance and the thickness-wise reaction distribution at various operating conditions cannot be acknowledged.

The authors have investigated the reaction and transport phenomena in PEFCs, including the characteristics in the catalyst layer\textsuperscript{(9)-(11)}. In this study, we investigate the relationship between the structure and performance of the cathode catalyst layer by means of multi-layered cathode catalyst layer to survey the reaction distribution of the thickness direction. Experimental study reveals the effect of the catalyst layer structure on the cell performance. Simple theoretical model is deployed in order to examine the reaction distribution in the catalyst layer.

### 2. Nomenclature

- $E_{\text{cell}}$: observed cell voltage, V
- $I_0$: current density defined as total current over reaction area, A/cm$^2$
- $R_e$: contact and bulk electronic resistance, $\Omega$ cm$^2$
- $R_{\text{mem}}$: membrane proton resistance, $\Omega$ cm$^2$
- $E_{\text{IR-free}}$: IR-free voltage defined as the observed cell voltage plus ohmic loss of electronic and membrane proton resistance, V
- $E_{\text{th}}$: apparent electromotive force, V
- $\eta_m$: overpotential at position “m”, V
- $R_{\text{H}^+}$: proton resistance in cathode catalyst layer, $\Omega$ cm$^2$
- $i_m$: reaction current density per real surface area at position “m”, A/cm$^2$
- $i_0$: exchange current density, A/cm$^2_{\text{Pt}}$
- $S$: roughness factor, cm$^2_{\text{Pt}}$/cm$^2_{\text{MEA}}$
- $C_m$: concentration of oxygen at position “m”, mol/cm$^3$
- $C^*$: bulk concentration of oxygen, mol/cm$^3$
- $\alpha$: transfer coefficient, mol/cm$^2$
- $n$: the number of electron involved in the electrode reaction
- $F$: faraday constant, C/mol
- $R$: universal gas constant, J/(mol K)
- $T$: absolute temperature, K
- $i(x)$: local proton current density, A/cm$^2$
- $D^{\text{eff}}_{\text{O}_2}$: effective oxygen diffusion coefficient, cm$^2$/s
- $D_{\text{Kn}}$: Knudsen diffusion coefficient, cm$^2$/s
- $\varepsilon$: porosity
- $\gamma$: tortuosity
- $M$: molecular weight of the reactant gases
- $L$: thickness of cathode catalyst layer, cm
3. Experimental

Fabrication of MEA and Cell preparation

Figure 1 shows a schematic of multi-layered cathode catalyst layer (CCL) used in this study. The CCL consists of multi layers of catalyst layers with different concentration of Pt loading, carbon support and ionomer. In this work, we use bi-layered CCL as shown in Fig. 1 where, for instance, the catalyst concentration of GDL (Gas Diffusion Layer) side is lower in CCL-1. On the other hand, the catalyst concentration of the membrane side is lower in the GDL side in CCL-2.

Catalyst inks are prepared by mixing Pt Catalyst (TEC10E30E or TEC10E50E, Tanaka kikinzoku kogyo) and Nafion solution (5% Nafion® DE520 CS type, Wako Pure Chemical Industries.) The ink is prepared on a Nafion212 membrane and is hot-pressed twice so that the CCL consists of two different layers with different fabrication parameters.

Figure 1. A Schematic of the Bi-layered Cathode Catalyst layer: The catalyst concentration of CCL-1 (left) is lower in the GDL side, and is lower in the membrane side of CCL-2 (right).

Anode Pt loading is ~ 0.3 mgPt/cm². Table 1 shows the Pt loadings of each cathode catalyst layer. Pt catalysts of 45.7 wt % are used for the layer whose Pt loading is 0.24 ~ 0.25 mgPt/cm² in Table 1 and of 28.2 wt% are used for the layer whose Pt loading is 0.10 ~ 0.11 mgPt/cm² in Table 1. All anodes and cathodes have the I/C (ionomer/carbon) weight ratio of 0.78/1. Membrane Electrode Assembly (MEA) is fabricated by sandwiching CCM between Gas diffusion layers (GDLs) with thickness of 200 µm (CARBEL®-CFP, Japan Gore-Tex). Fifteen channels and fourteen ribs with the width of 0.6 mm each are used. Thus total length of channels and ribs are 17.4 mm for 4 cm² reaction area.

Table 1. Catalyst loading in each layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer-1 (Membrane side)</th>
<th>Layer-2 (GDL side)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCL-1</td>
<td>0.24 mgpt/cm²</td>
<td>0.10 mgpt/cm²</td>
</tr>
<tr>
<td>CCL-2</td>
<td>0.10 mgpt/cm²</td>
<td>0.25 mgpt/cm²</td>
</tr>
</tbody>
</table>

Operating conditions

The fuel cell test station consists of a constant temperature bath, mass-flow controller, backpressure regulator, liquid source vaporization system (Horiba STEC), AC m-ohm tester (3566-05, Tsuruga Electric Co.) and Galvanostat (HZ-5000, Hokuto denko). The cell is operated in a constant temperature bath kept at 80°C. Pure H2 is supplied to the anode and pure O2 or diluted O2 with N2 is supplied to the cathode. Before obtaining polarization curves, the cell is operated at 600 mA/cm² for pure O2 supply condition, or 400 mA/cm² for
diluted O₂ supply condition for an hour until a steady state is reached. The anode and the cathode inlet gas flow are controlled at 500 ml/min and are humidified at 30%RH, 60%RH or 90%RH (anode/cathode). Each current density is kept for 5 min, and the measured voltage is averaged over the last 2 min to obtain the polarization curve.

4. Result and Discussion

Effect of oxygen gas concentration

Figure 2 shows the polarization curves at 90%RH with different O₂ concentration in the cathode gas. The horizontal axis shows the current density. In this study, we define the current density as the observed cell current over Pt loading. This definition of the current density is used in order to compare the performance of CCLs with different Pt loading. The vertical axis shows IR-free voltage, $E_{\text{IR-free}}$, and is defined as

$$E_{\text{IR-free}} = E_{\text{cell}} + I_0 \cdot (R_e + R_{\text{mem}})$$

where $E_{\text{cell}}$ is the observed cell voltage of PEFC, $I_0$ is the current density which is defined as total current over reaction area 4 cm², $R_e$ is the contact and bulk electronic resistance and $R_{\text{mem}}$ is the membrane proton resistance. Both $R_e$ and $R_{\text{mem}}$ can be obtained by AC m-ohm tester due to their high electric conductivity. They are measured for each MEA in each condition. It can be seen from the figures that the performance of CCL-1 becomes lower than that of CCL-2 at lower current density by increasing the degree of O₂ dilution. These results indicate that the decrease of oxygen concentration prevents the effective supply of oxygen to the catalyst on the membrane side, resulting in reduced performance in CCL-1 case. More reaction is expected in the GDL side of the catalyst layer. The discrepancy between CCL-1 and CCL-2 becomes smaller at higher current density, and CCL-1 shows slightly higher value of cell voltage. In this regime, relatively higher water production in the GDL side in CCL-2 may cause larger resistance to the oxygen supply than that of CCL-1 in which the produced water can relatively moves toward the membrane side.

![Figure 2. Effect of oxygen concentration](image-url)
Effect of the RH of supply gas

Figure 3 shows the cell performance at various relative humidity with pure oxygen. The clear trend is observed that the cell performance degrades with the decreasing RH value, and the performance of CCL-2 at lower current density becomes worse compared with CCL-1 case with decreasing relative humidity. This result suggests that more reaction is taking place in the membrane side of the CCL where less Pt is loaded in CCL-2 case.

Modeling of current density distribution with simple equivalent circuit model

In order to understand the experimental results and to predict the local transport-reaction field, we calculate the current density distribution in CCL with a simple equivalent circuit model (12). Figure 4 shows the equivalent circuit model for cathode catalyst layer. It is assumed in this model that the condition is steady state and that the electronic resistance in cathode electrode is negligible. Each layer of the bi-layered catalyst is divided into 150 meshes; so one CCL is divided into 300 meshes for calculation. Left-hand side of Fig. 4 is the membrane side, and right-hand side is the GDL side. $E_{th}$ is apparent electromotive force, $\eta_m$ is the overpotential at position “m,” and $R_{H+}$ is the proton resistance in CCL. The variable $i_m$ the reaction current density per real surface area at position “m”, is described as Eq. (2) by Butler-Volmer’s equation.
**Figure 4.** A Simple equivalent circuit model for CCL

\[ i_m = i_0 S \frac{C_m}{C^*} \exp \left( \frac{-mF\eta_m}{RT} \right) \]  

(2)

where \( i_0 \) is the exchange current density, \( S \) is the roughness factor, \( C_m \) is the concentration of oxygen at position “m,” \( C^* \) is the bulk concentration of oxygen, \( \alpha \) is the transfer coefficient, \( n \) is the number of electron involved in the electrode reaction, \( F \) is the faraday constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature and \( \eta_m \) is the overpotential at position “m”.

The relationship between the proton resistance \( (R_{H^+}) \) and \( \eta_i \) is described by Ohm’s low,

\[ \frac{d\eta_m}{dx} = i(x)R_{H^+} \]  

(3)

where \( i(x) \) is the local proton current density. The oxygen flux through the catalyst layer is assumed to be driven by the concentration gradient. It is determined by the Fick’s law of diffusion as

\[ D_{O_2}^{eff} \frac{dC_m}{dx} = \frac{I_0 - i(x)}{4F} \]  

(4)

where \( D_{O_2}^{eff} \) is an effective oxygen diffusion coefficient and \( I_0 \) is the total current density.

The effective diffusion coefficient of a porous body is written as a following equation (13),

\[ D_{O_2}^{eff} = D_{O_2} \cdot \varepsilon^\gamma \]  

(5)

where \( D_{O_2} \) is the Knudsen diffusion coefficient, \( \varepsilon \) is the porosity, \( \gamma \) is the tortuosity. The Knudsen diffusion coefficient of the pore with radius \( r \) is (14),

\[ D_{O_2} = \frac{2r}{3} \sqrt{\frac{8RT}{\pi M}} \]  

(6)

where \( M \) is molecular weight of the reactant gases. Since the pore size in the catalyst layers distributes randomly, the average of pore size is used, which is estimated from SEM pictures. Values of \( \varepsilon = 0.58 \), \( \gamma = 1.5 \) and \( r = 50 \) nm are used in calculations considering literatures and images. Value of exchange current density is determined to best fit the experiments, and is 3.31x10^{-9} A/cm² Pt for CCL-1 and 3.10x10^{-9} A/cm² Pt for CCL-2 respectively at pure O₂ with 90%RH case.

The set of boundary conditions is

\[ x = 0 \quad i(x = 0) = I_0 \quad \frac{dC_m}{dx} = 0 \]  

(7)

\[ x = L \quad i(x = L) = 0 \quad C_m = C_m^* \]  

(8)
where \( L \) is the thickness of CCL and \( C_m^- \) is the oxygen concentration at the interface between GDL and CCL.

Figure 5 shows a comparison between the experiments and the calculated \( i-V \) characteristics. As seen from the figures, the model can quantitatively explain the \( i-V \) curve at relatively lower current density. The discrepancy becomes larger with the increasing current density presumably due to the presence of produced water.

![Figure 5. Calculated (Calc.) and experimental (Exp.) \( i-V \) curve](image)

Figure 6 shows the result of above calculation with pure \( O_2 \) at 90%RH for CCLs. The horizontal axis shows the distance from the membrane. The vertical axis shows the distribution of dimensionless local current density that is defined as the local reaction current density over total (cell) current density. Cell current of 100 mA corresponds to 0.291 A/mgPt for CCL-1 and 0.279 A/mgPt for CCL-2, respectively. In the figures, local reaction current density is denoted as local current density. Distribution of the dimensionless local current density shows the position-wise distribution of the actively reacting area in the catalyst layer. The reaction, namely the local current density, of the membrane side is more active than that of the GDL side at the high humidification case, 90%RH in the figure, for both CCLs. This result shows that the proton transport resistance dominates the cell performance for the case of pure \( O_2 \) supply condition.

![Figure 6. The Reaction rate in CCLs with pure oxygen at 90%RH](image)
Figure 7 shows the calculation results with diluted O₂ (10% oxygen concentration) at 90%RH. It is seen in Fig. 7(a) that the position of actively reacting area moves toward the GDL side by increasing the dimensionless local current density at the GDL side with the increase of the cell current density. This implies that at higher cell current density, the oxygen supply shortage becomes significant, although the proton is sufficiently supplied. In this situation, the membrane side of the catalyst layer is not fully working as an electrochemically active area compared with the case of pure O₂ supply. Figure 8 shows the distribution of overpotential in CCL with diluted O₂ (10% oxygen concentration) at 90%RH. The value of $\eta$ at 0 distance from membrane corresponds to the cell overpotential. It is seen from the figure that the cell overpotential of CCL-1 is larger than CCL-2. The trend is due to the oxygen concentration discussed above.

![Figure 7](image1.png)

**Figure 7.** Effect of oxygen concentration: supply of 10% oxygen at 90%RH

![Figure 8](image2.png)

**Figure 8.** Distribution of overpotential: supply of 10% oxygen at 90%RH

Figure 9 shows the results at lower humidity, 30%RH. It is seen in Fig. 9, by comparing with Fig. 7, that the actively reacting area clearly moves toward membrane side (left-hand side of the figures) by decreasing the value of RH. It can also be seen that the dimensionless local current density decreases in GDL side (right-hand side of the figures) with the increase of the current density. This implies that a part of the Pt catalyst in GDL side is no more effectively used. Especially the dimensionless local current density in GDL side dramatically decreases in CCL-2. Figure 10 shows the distribution of overpotential in CCL with pure O₂ at 30%RH. It can be seen that the overpotential of CCL-1 becomes lower than
that of CCL-2. It is also understood from Figs 8 and 10 that the cell performance of CCL-2 becomes lower than CCL-1 due to the decrease of relative humidity.

Above discussions showed that the relative humidity has more serious impact on the reaction distribution than the oxygen concentration. As seen in Fig. 9(b), dimensionless local current density in GDL side is higher than the membrane side at lower current density, and the relation reverses at higher current densities. In Fig. 7, dimensionless local current density in membrane side decreases in CCL-1, but the amount of decrease in current density is less than Fig. 9(b). Relation between the reaction distribution and the Pt loading is suggested to have a strong influence on the cell performance. These results explain the larger performance difference between CCL-1 and CCL-2 in Fig. 3 than that in Fig. 2. The difference between Fig. 8 and Fig. 10 also account for the cell performance difference of experiments.

![Figure 9. Effect of relative humidity: supply of pure oxygen at 30%RH](image)

![Figure 10. Distribution of overpotential: supply of pure oxygen at 30%RH](image)

5. Conclusion

Bi-layered catalyst layer is fabricated in order to examine the effect of the catalyst layer structure on the cell performance. The experimental results showed the performance dependence of the structure at various operation conditions. Simple theoretical model showed the reaction distribution in the catalyst layer at various conditions. Results suggest the importance of structural design parameters.
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References


