Effect of PTFE contents in the Gas Diffusion Layers of Polymer Electrolyte-based Unitized Reversible Fuel Cells


Abstract – Polymer electrolyte-based unitized reversible fuel cells (URFCs) combine the functionality of a fuel cell and an electrolyzer in a single device. In this study, the influence of hydrophobic agent in the gas diffusion layer (GDL) of URFC was investigated. The titanium (Ti)-felt GDL which treated with different percent of PTFE emulsion was intensively tested with various humidification temperature conditions in the single cell of URFC. I-V performance curves and divided three overpotentials were compared and analyzed in the fuel cell mode. The electrolyzer performances were also evaluated with the I-V curves. Experimental results showed that the GDLs with high PTFE contents have better performance in the dry conditions. On the other hand, the increased PTFE contents accelerate flooding problem in the wet condition and it is related with rising concentration overpotential. The electrolyzer performances are almost same with different PTFE contents of GDL.

Keywords: Proton Exchange Membrane, Unitized Reversible Fuel cell, Gas Diffusion Layer, Titanium felt, Water Management

1. Introduction

Polymer electrolyte-based unitized reversible fuel cells (URFCs) combine the functionality of a fuel cell and an electrolyzer in a single device [1], [2]. Gas diffusion layer (GDL) is one of the important components of URFC. Two main roles of GDLs are electric conduction between the electrode and the bipolar plates and efficient gas transport between the electrode and the flow channels. There are two major differences in the GDL conditions between the operations of PEMFC and URFC. The first difference is the hydration state of the GDLs. During fuel cell operation mode of a URFC, humidified gases humidify the membrane as they do in a PEMFC. However, excess liquid water in the GDL hinders gas transport, especially in the oxygen electrode, thus inducing loss in mass transport. Under typical PEMFC conditions, the estimated ratio of liquid water saturation in the GDL ranges from 0.1 to 0.3 [3], which is the same as that during fuel cell mode in a URFC. In contrast, during electrolysis mode in a URFC, the GDLs are actually fully saturated by liquid water. Thus, a pre-switching gas purge to dry the GDL is needed for smooth switching from electrolysis mode to fuel cell mode during actual operation of a URFC [4]. The second difference is the potential at the oxygen electrode. For a typical PEMFC, carbon paper or carbon cloth is used as the GDL at both sides of the electrodes. However, for the oxygen electrode of a URFC, carbon material is unsuitable for not only the electrode but also for the GDL, because the potential of the oxygen electrode during electrolysis mode is so cathodic that carbon material tends to corrode. In a PEM electrolyzer as the same as PEMFC, stable electrical conductance and gas transport are required by the GDL (current collector), such as sintered porous metal, expanded metal mesh, or metal felt. Grigoriev et al. [5] examined an optimum pore size of GDL from both experimental and modeling approaches from the view point of mass transport. They used a plate of sintered Ti-powder as the GDL of electrolyzer, and concluded the optimum pore size is 12-13μm. For the GDL of the oxygen electrode, we use a titanium (Ti)-felt (nonwoven fabric) in which Ti fiber is bonded and sintered without adhesives.

A hydrophobic agent such as PTFE is usually added to the GDL substrate to enhance the hydrophobicity of the GDL. However, Lin et al. [6] reported that the PTFE content in the GDL substrate has no noticeable effect on...
fuel cell performance and the PTFE effect on fuel cell performance remains unclear. Gostick et al. [7], [8] measured the saturation curve versus capillary pressure using a carbon paper substrate with or without PTFE treatment. Ioroi et al. [9] examined the relationship between the PTFE loading amount on Ti-felt and the URFC performance when Ti-felt is used as the GDL of a URFC. However, in their experiments, the flow rate of supplied gas during fuel cell mode was constant and the stoichiometric ratio of gas was relatively high (5.6 at 500 mA cm\(^{-2}\) for oxygen).

Therefore, complete understanding of the relation between liquid water transport and PTFE content in the Ti-felt GDL is necessary to improve URFC performance. The objective of our work is to verify the influence of the PTFE contents in oxygen side Ti-felt GDL substrate for improving liquid water and oxygen gas transport under practical condition of gas flow rate.

### 2. Experiment

The MEA used here was specially designed for URFC and developed through collaboration between Takasago Thermal Engineering Co. and Daiki Ataka Engineering Co. The catalytic electrodes were hot pressed to both surfaces of the membrane. Nafion 115 was used as the PEM. Iridium oxide (IrO\(_2\)) and platinum (Pt) mixed-electrocatalyst was used for the oxygen electrode, and Pt catalyst for the hydrogen electrode. Fig. 1 shows micrographs of the carbon paper (Toray 090) and Ti-felt (Bekinit) used for the GDLs. Both substrates had similar structure of an unwoven fabric made of fine fibers. The carbon fibers were about 10\(\mu\)m in diameter. The fiber diameter of this Ti-felt substrate was 20\(\mu\)m which is the minimum diameter that we could obtain. There is no adhesive in the Ti-felt substrate, while a certain amount of adhesive is included in the carbon paper substrate. Thus the pore diameter of the Ti-felt was larger than that of the carbon paper. Various Ti-felt GDLs and carbon paper GDLs with different PTFE content (Table 1) were prepared for the oxygen electrode for the URFC performance tests. The mean pore diameter of each GDL substrate (Ti-felt and carbon paper) were measured by a capillary flow porometer (PSM165, Yuasa-Ionics) using the bubble point technique [10]. In the U2, U3, and F2, F3 cells, PTFE was loaded on the GDL substrate as follows. After each GDL substrate was dipped in a given PTFE emulsion (D-210C, Daikin), first it was dried at 120°C for 1 hour to evaporate the remaining solvent, and then sintered at 360°C in an vacuum atmosphere for 1 hour. The PTFE content in the GDL can be controlled by adjusting the PTFE concentration in the emulsion, and is approximately the same in both the carbon paper and Ti-felt substrates, based on external geometry. In this study, the U1 cell in Table 1 was considered the standard cell in which the Ti-felt GDL in the oxygen side had a fiber diameter of 20\(\mu\)m and a porosity of 0.75 without PTFE loading. The Ti-felt GDL of the U2 and U3 cells had the same properties as the U1 cell but were treated with different PTFE concentrations in the emulsion, namely, 10 and 20 wt.%, respectively. The carbon paper GDL (Toray 090) treated with 10 wt.% PTFE emulsion was used for the hydrogen electrode side.
### Table 1. Specification of constitution parts of URFC

<table>
<thead>
<tr>
<th>Cell</th>
<th>GDL(O2 side)</th>
<th>PTFE loading [wt% in emulsion]</th>
<th>Mean Pore Diameter [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>Ti-felt</td>
<td>-</td>
<td>45.0</td>
</tr>
<tr>
<td>U2</td>
<td>Ti-felt 10wt%</td>
<td>-</td>
<td>36.4</td>
</tr>
<tr>
<td>U3</td>
<td>Ti-felt 20wt%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F1</td>
<td>Carbon paper</td>
<td>-</td>
<td>26.4</td>
</tr>
<tr>
<td>F2</td>
<td>Carbon paper 10wt%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F3</td>
<td>Carbon paper 20wt%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The AC impedance of the cell was measured using a frequency response analyzer (FRA) (1255B, Solartron) and the load. The cell resistance ($Z_{\text{real}}$) was measured at 10 kHz frequency. The stoichiometric ratio of the supplied pure hydrogen and oxygen in the air was kept at 1.43 and 2.50, respectively, and the humidification temperatures of both were changed arbitrarily but were always the same for a given test. In the electrolysis mode, De-ionized liquid water supplied to the cell was heated to the same temperature as the cell by a preheating tank. Theoretically, water must be supplied only to the oxygen electrode side, because water molecules move to the hydrogen electrode with protons during electrolysis. In our experiments, however, water was circulated at a flow rate of 25ml/min at both sides of the electrodes to prevent membrane burn-out caused by lack of water. It is summarized three overpotentials; activation overpotential ($\eta_{\text{act}}$), concentration overpotential ($\eta_{\text{conc}}$), and ohmic overpotential ($\eta_{\text{ohm}}$) as same as the previous study [11].

3. Results

3.1 Electrolysis performance

![Fig. 2. Characteristics of current density ($i$) and voltage ($V$) of electrolysis with different PTFE content Ti-felt GDL of the oxygen electrode at a cell temperature ($T_{\text{cell}}$) of 80°C.](image)

During the electrolysis mode, because carbon paper cannot be used as the GDL of the oxygen electrode side, only cells with Ti-felt GDL for the oxygen side (U1-U3 cells in Table I) were used for the electrolysis performance test. Carbon paper GDL treated with 10wt.% PTFE emulsion was used for the hydrogen electrode side in this performance test. Fig. 2 shows the effect of PTFE content on the $i$-$V$ characteristics during the electrolysis mode by plotting the $i$-$V$ characteristics for the U1, U2, U3 cells. The PTFE loading on the GDL substrate (U2) caused the slight decrease in mean pore diameter of the porous media. However, no noticeable difference was detected in the performance of these 3 cells. The smooth supply of water and the efficient releasing of produced gas from the electrode are expected to be achieved at these cells.

3.2 Effect of humidification temperature on fuel cell performance

Fig. 3 shows the $i$-$V$ characteristics and divided overpotentials of U2 during the fuel cell mode at various humidification temperatures of the gases ($T_{\text{fuel}}$) when the cell temperature ($T_{\text{cell}}$) was 80°C. The relative humidity (RH) is determined by the ratio of $T_{\text{fuel}}$ and $T_{\text{cell}}$. The $T_{\text{fuel}}$ was the same for both hydrogen and air (between 60 to 80°C) and controlled by a bubble type humidifier. The curve for $T_{\text{fuel}} = 80°C$ at $i = 0.1$–$0.2$Acm$^{-2}$ and those for $T_{\text{fuel}} = 60°C$ and $65°C$ at $i = 0.3$–$0.45$Acm$^{-2}$ shown a rapid decrease in $V$. In contrast, the curves for $T_{\text{fuel}} = 70°C$ and $T_{\text{fuel}} = 75°C$ do not show such a rapid decrease, but rather a relatively good performance (as evidenced by a steady decrease) until a high $i$ (> 400 mAcm$^{-2}$).

The decrease in fuel cell performance at $T_{\text{fuel}} = 80°C$ was caused by an increase in concentration overpotential ($\eta_{\text{conc}}$). An increase of $\eta_{\text{conc}}$ is caused by a common phenomenon of flooding in GDL due to both the high humidity and produced water that blocks the fuel distribution in pores of the oxygen-side GDL. When $T_{\text{fuel}} = 60$ and 65°C, the decreased fuel cell performances were caused by an increase in ohmic overpotentials ($\eta_{\text{ohm}}$). An increase of cell resistance ($Z_{\text{real}}$) from the insufficient water supply to the membrane makes higher $\eta_{\text{ohm}}$. This $\eta_{\text{ohm}}$ can be expressed as follow;

$$\eta_{\text{ohm}} = Z_{\text{real}} \times i$$

An influence of activation overpotential ($\eta_{\text{act}}$) was relatively small in all humidification temperature.
Fig. 3. Characteristics of current density \(i\) and voltage \(V\) of fuel cell operation (A) and divided overpotentials (B) with “U2” cell at different humidification temperatures of gases (H\(_2\) and air) \(T_{\text{fuel}}\) at a cell temperature \(T_{\text{cell}}\) of 80°C.

3.3 Effect of PTFE contents in the GDL on fuel cell

Fig. 4. Characteristics of current density \(i\) - voltage \(V\) and current density \(i\) - cell resistance \(Z_{\text{real}}\) of fuel cell operation with U1, U2, U3 cells at different humidification temperatures of gases (H\(_2\) and air) \(T_{\text{fuel}}\) at a cell temperature \(T_{\text{cell}}\) of 80°C.
Fig. 4 shows the $i-V$ and $i-Z_{\text{real}}$ characteristics at $T_{\text{fuel}}=60$, 65, 70, 75 and 80°C for the U1, U2 and U3 fuel cells (Ti-felt GDL treated with 0, 10, or 20 wt.% PTFE emulsion, respectively). The hydration state of the electrode (i.e., catalyst layer) can be corresponded by $Z_{\text{real}}$. When $T_{\text{fuel}} = 60$ and 65°C (RH 42% and 53%), $Z_{\text{real}}$ was increased drastically from 0.3Ω cm$^2$. When $T_{\text{fuel}} = 70$, 75 and 80°C, $Z_{\text{real}}$ are stable and nearly constant around 0.1 to 0.15Ω cm$^2$.

Basically, the higher PTFE content was expected to enhance both the hydrophobicity of porous network and the discharge of liquid water from the electrode surface to the channel, and thus improve the fuel cell performance at high $i$ ($> 400$ mA cm$^{-2}$). However, our result showed an opposite trend, indicating that PTFE loading on the GDL substrate hinders the fuel cell performance at relatively wet condition. Fig. 4 (D) shows that higher PTFE content in the GDL caused a noticeable degradation in cell performance at $T_{\text{fuel}}=75$ °C. Degradation was also observed at $T_{\text{fuel}}=70$ °C (Fig. 4 (C)), although it was relatively small.

When $T_{\text{fuel}}=80$ °C, flooding problem was happen in low $i$ (< 200 mA cm$^{-2}$) because cell inside is fully wet condition (RH 100%). On the other hand, the PTFE content in the GDL substrate of the oxygen electrode was little effective for better $i-V$ performance during dry condition as shown in Fig. 4 (A, B). It is indicated that the PTFE content might prevent rising $Z_{\text{real}}$. The different $i-V$ performances and degradation on the Fig.4 (C, D) are possibly related with the concentration overpotential ($\eta_{\text{conc}}$) because $Z_{\text{real}}$ were nearly same among U1, U2, and U3. Therefore, the relation between $i-V$ performances and $\eta_{\text{conc}}$ should be discussed.

Fig. 5 shows $\eta_{\text{ohm}}$ (a) and $\eta_{\text{act}}$ (b) results according to $i$ for cells with different GDLs of the oxygen electrode (Table 1). When $T_{\text{fuel}}$ was 70 or 75°C, the difference in $\eta_{\text{ohm}}$ was small among these cells for either $T_{\text{fuel}}$ of 70 and 75°C. The $\eta_{\text{ohm}}$ is an index of hydration state of the membrane and strongly depends on $T_{\text{fuel}}$ but the electrical resistance is insignificant. The cell impedance was almost constant at the entire range of current densities. The difference in $\eta_{\text{act}}$ was small among these cells; the maximum difference was less than 20 mV at $i = 650$ mA cm$^{-2}$. Therefore, we focused only on the $i-V$ characteristics and $\eta_{\text{conc}}$ at $T_{\text{fuel}} = 70$ and 75°C in the following analysis.

Fig. 6. The result of concentration overvoltage comparison with 0%, 10%, 20% of PTFE impregnation carbon paper and Ti-felt GDL at 70°C and 75°C fuel temperature.
Fig. 6 shows the comparison of $\eta_{\text{conc}}$ at $T_{\text{fuel}} = 70$ and 75 °C calculated from the i-V curves shown in Fig. 4. In Fig. 6, $\eta_{\text{conc}}$ at $T_{\text{fuel}} = 75$ °C was larger than that at $T_{\text{fuel}} = 70$ °C, because the cell was relatively “wet” at $T_{\text{fuel}} = 75$ °C, and the excess water hindered the mass transport of oxygen gas to the electrode surface. In addition, $\eta_{\text{conc}}$ was higher at higher PTFE content in the Ti-felt GDL at the oxygen electrode, particularly at the wet condition when $T_{\text{fuel}} = 75$ °C compared with that at $T_{\text{fuel}} = 70$ °C as shown in Fig. 6(b). The cell performance represented as $\eta_{\text{conc}}$ at $T_{\text{fuel}} = 70$ and 75°C for the F1, F2, F3 cells (carbon-paper GDL without and with treatment of 10, 20 wt.% PTFE emulsion). It is similar to the results of Ti-felt (Fig. 6(b)), the negative effect of PTFE loading on the carbon-paper GDL is clearly evident at $T_{\text{fuel}} = 75$ °C. The negative effect of PTFE contents in the GDL can be explained by using literature.

Fig. 7. Liquid water saturation (s) versus capillary pressure (Pc) characteristics with the Toray 090 substrate presented by Gostick et al. [7]. Toray 090 without PTFE treatment and Toray 090 with PTFE 20 wt.%. 

Fig. 7 shows the liquid saturation (s) capillary pressure (Pc) curves of the PTFE treated and untreated GDL of Toray 090 (without MPL) measured by Gostick et al.[7]. The negative capillary pressure during water withdrawal from the PTFE treated substrate was smaller than that from the untreated one, whereas the positive capillary pressure for water injection at PTFE treated substrate was larger than that at the untreated one. It reveals that the loading of hydrophobic agents gives to GDL substrate the effect of disturbing the water injection and PTFE treated GDL is much higher amount of work required for forcing water into the GDL from membrane.

5. Conclusion

In this study, the effect of the PTFE contents on the oxygen side Ti-felt GDLs was verified in each humidification condition. The cell performances for both the fuel cell and electrolysis operating modes were evaluated based on the i-V characteristics and the analysis of overpotentials. Based on our results, conclusions about relation between the PTFE contents of Ti-felt GDLs and the cell performance are as follows:

URFC in electrolysis mode

The electrolysis performance is not noticeably affected by a change of PTFE contents in the oxygen side GDL even though porosity and hydrophobicity of GDL must be different because the water supply through the GDL is not much affected by different amount of PTFE contents and enough water can be supplied for all of cells.

URFC in fuel cell mode

The higher PTFE contents probably enhance to prevent dry of membrane and to keep humidity at relatively dry fuel condition ($T_{\text{fuel}} = 60$ and 65°C). However, the higher PTFE contents make degraded fuel cell performance at relatively wet condition ($T_{\text{fuel}} = 70$ and 75°C). This performance degradation is also shown as the carbon paper GDL and caused by increase of $\eta_{\text{conc}}$. The excess water in the GDL must have hindered the mass transport of oxygen gas from flow channel to electrode and catalyst surface. This result is consistent with previous reported results in the literature.

References


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