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OXYGEN CONCENTRATION IN THE CATHODE CHANNEL OF PEM FUEL CELL USING GAS CHROMATOGRAPH

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ABSTRACT–Because of the low temperature operation, proton exchange membrane (PEM) fuel cell has a water phase transition. Therefore, water management is an important operation issue in a PEM fuel cell because the liquid water in the fuel cell causes electrode flooding that can lower the cell performance under high current density conditions. In this study, in order to understand the reactant distributions in the cathode channels of the PEM fuel cell, an experimental technique that can measure the species concentrations of reactant gases by using gas chromatograph (GC) is applied for an operating PEM fuel cell. The oxygen distribution along the cathode flow channels of PEM fuel cell is mainly investigated with various operating conditions. Also, the relations between cathode flooding and oxygen concentrations and oxygen consumption pattern along the cathode channel configurations of the unit cell adopted for this study are discussed using GC measurement and visualization experiment of cathode flooding. It is found that the amount of oxygen consumption is very sensitive to various operating conditions of the fuel cell and was much affected by the flooding occurrence in cathode channels.

KEY WORDS : PEM fuel cell, Water management, Flooding, Gas chromatograph, Oxygen distribution, Oxygen consumption

1. INTRODUCTION

Recently, fuel cell will be expected to be one of the clean technologies that can keep in step fundamentally in circumstance that various environment regulation policies are worldwide outspread including Kyoto protocol. The fuel cell has been well known as a source of clean alternative power. Especially, it is recognized that proton exchange membrane (PEM) fuel cell is the most suitable fuel cell type for application to vehicles in terms of start ability, operating temperature, and quick response with load change etc. (Yang, 2000). However, for the PEM fuel cell to be commercially viable, the efficiency and performance should be much improved by proper engineering optimization and design work (Larminie and Dicks, 2000). The PEM in PEM fuel cell need to be well hydrated to maintain the ionic conductivity for proper fuel cell operation (Rajalakshmi *et al.*, 2004). The PEM fuel cell displays water phase transition because of its operating temperature below 100°C. Therefore, the formation and condensation of liquid water occur within the PEM fuel cell by excessive humidification, and it can cause the accumulation of liquid water in the cathode gas diffusion layer (GDL) and electrode, which can result in flooding (Hakenjos *et al.*, 2004; Tüber *et al.*, 2003). This can act as the main reason of lowering the cell performance at high current densities. An optimal removal of produced water is very important under the conditions of maintaining an adequate humidity (Yang *et al.*, 2004) inside the fuel cell. Therefore, an effective water management is essential not only for the efficiency improvement and performance of the PEM fuel cell and but also for robust operation and long life. Generally, a V-I (voltage-current density) polarization curve, which is estimated in the fuel cell test, can be mainly used to represent the global performance characteristics of fuel cell. However, it does not present the local performance of each part of a channel in a fuel cell. Especially, when flooding, dry-out phenomena, and mass transfer limitation occur at the same time in the fuel cell, a general V-I characteristic curve cannot provide enough information for understanding the efficiency and performance of a PEM fuel cell (Mench *et al.*, 2003). For these reasons, it is highly needed to understand the local distribution of reactant including liquid water within an operating PEM fuel cell.

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To describe the reactant distributions and water transport inside the PEM fuel cell, many researches have been conducted using experimental methods and modeling works (He *et al.*, 2003; Dong *et al.*, 2005; Yang *et al.*, 2005). However, scant quantitative data are presently available on detailed reactant distributions and water content. Nowadays, more attention is paid to obtaining the detailed information on species distribution, local current density, temperature, and resistance using various experimental techniques including gas chromatograph (GC), neutron imaging (Pekula *et al.*, 2005) and magnetic resonance imaging (MRI) (Tsushima *et al.*, 2005). Among the various diagnostics tools, GC, with its high accuracy, is recognized as one of the most suitable tools to measure the reactant distributions quantitatively. However, GC can measure species distributions in gas phase; hence it has much difficulty in measuring the liquid water quantity. Although the water content can be quantitatively measured by evaporating it, it is not easy to keep the water in gas phase from the sampling site to GC. Moreover, it is difficult to extract water from the flow channel of operating PEM fuel cell because of condensation and evaporation of water with the change in temperature. Since the reacted oxygen gases turn into water in case of PEM fuel cell, oxygen concentration can be alternatively measured using that basic principle of the fuel cell.

The purpose of the present work is to provide basic quantitative information on oxygen concentration distribution along the cathode flow channels in an operating PEM fuel cell. To this end, firstly, the oxygen concentrations along the flow channel with cell operating voltage, relative humidity are measured by using a GC. Secondly, the oxygen concentration distribution was analyzed combined with visualization study of water transport and flooding in cathode channel. That is, the change of oxygen concentration according to the location in the channel of the cathode side of a PEM fuel cell and its relation with operating temperature, humidity condition and cathode flooding was examined.

2. EXPERIMENTAL

2.1. Experimental Apparatus

The unit cell used in an experiment has an effective area of 5 cm × 5 cm and a modified serpentine type flow channel shape, as shown in Figure 1. A channel design of equal configuration was applied on both cathode and anode sides. Inlet air and hydrogen gas feeds form semi-counter flow with each other. There are seven points and each point is the gas extraction port. The positions have same fractional distance each other. The membrane electrode assembly (MEA) adopted in this study was based on Nafion®112.

Schematic diagram of the experimental set-up for GC measurement is presented in Figure 2. Dry air and dry hydrogen of ultra high purity were used as oxidant and fuel respectively and were controlled by a mass flow controller (MFC). The bubbling type humidifiers for the humidification of air and hydrogen gases were used. A backpressure regulator was adopted to control the operating pressure of the fuel cell. The water trap for protecting the backpressure regulator was used at the outlet of the unit fuel cell. A 1 kW capacity electronic loader was used. A loader program and data acquisition program based on Labview were used for data processing.

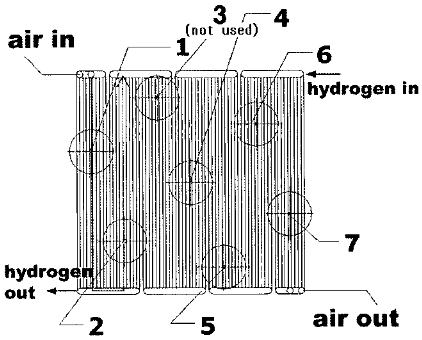


Figure 1. Channel configuration and gas extraction positions.

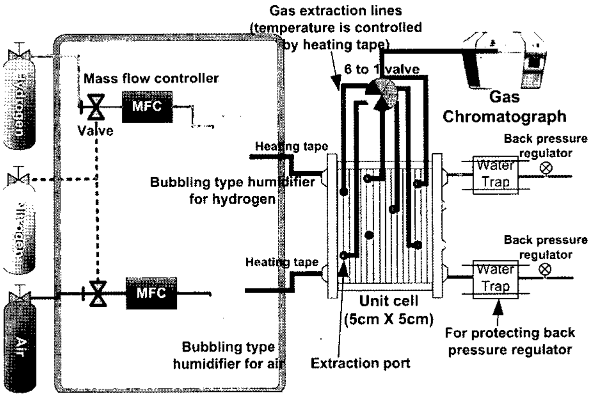


Figure 2. Schematic of experimental apparatus for species measurement using GC.

To analyze the ingredients, HP 5890 series II gas chromatograph was applied. Dry helium of ultra high purity (99.999%) was adopted as main carrier gas for the GC measurement. Molecular Sieve 5A packed column was applied to measure the oxygen and nitrogen concentrations along the cathode flow channels.

Figure 3 shows the unit cell used and the gas extraction ports with heating lines. As presented in Figure 1, six measurement holes were drilled along the cathode flow channels. The reactant gases along the cathode channels were extracted from each sampling port and their ingredients were analyzed using the GC.

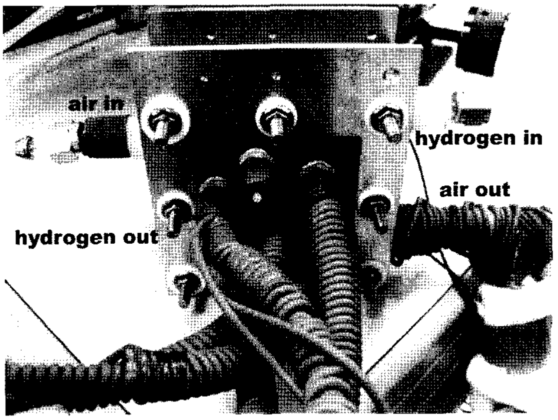


Figure 3. Unit cell and gas extraction ports.

2.2. Gas Chromatograph

Gas chromatography was filled with bonded phase within column, and gas was divided into bonded phase gas and carrier gas (mobile phase) by different distribution processes. Bonded phase is classified into Gas Solid Chromatography (GSC) and Gas Liquid Chromatography (GLC). GSC uses a porous solid type carrier as the bonded phase, and division process occurs through gas-solid adsorption equilibrium. On the other hand, GLC uses liquid as bonded phase, and division process occurs through gas-liquid adsorption equilibrium.

Basically, gas chromatograph consists of an injection port, a detector that detects detached ingredients, and a Chemstation that quantifies the recorded signal from the detector. In this study, thermal conductivity detector (TCD) which can be suitable for measuring the oxygen and nitrogen gases was applied.

2.3. Experimental Conditions

The operating temperature, operating voltage and inlet humidity of unit cell were chosen as independent variables of this study.

In the GC experiment, air and hydrogen were supplied at the constant volume flow rate of 1 l/min and 0.2 l/min, respectively. Since the stoichiometric ratio is an important factor for fuel cell performance, it is desirable to perform experiment with setting the stoichiometric ratio as constant. However, to fix the stoichiometric ratio, air flow rate should be adjusted with operating current density.

Consequently, the change in air flow rate affects the flooding phenomena because the air velocity in the flow channel and GDL interface changes. In this study, to investigate the correlation between flooding and oxygen consumption with operating temperature and current density, the gas flow rate was set as a constant for each test condition. The supplied pressure of gas was kept at ambient pressure. The change of oxygen concentration for each extraction port was investigated at the operating temperatures of 40°C and 70°C conditions.

Table 1. Details of experimental conditions.

Flow rate (Air) (l/min)	1
Flow rate (Hydrogen) (l/min)	0.2
Absolute pressure (bar)	1
Operating temperature (°C)	40, 70
Relative humidity (%)	99, 84
Cell operating voltage (V)	0.7, 0.3

During the experiment, the relative humidities of air and hydrogen were maintained equal to 99% (fully humidified condition) and 84%, respectively. The operating voltages of the unit cell were set as 0.3 V and 0.7 V. These are specified as the standard conditions of the GC experiment. The details of experimental conditions are summarized in Table 1.

3. RESULTS AND DISCUSSION

We investigated the change of oxygen consumption according to various operating conditions of the unit fuel cell presented in Table 1. The effect of these conditions on oxygen distributions was examined. And the oxygen consumption was investigated with the level of flooding in cathode flow channel combined with visualization study of flooding phenomena.

Figure 4 represents a typical chromatogram of oxygen and nitrogen by gas chromatograph. In GC measurement, it is found that the oxygen gas was firstly detected and then the nitrogen gas was sampled.

3.1. Oxygen Concentration Distribution with Operating Voltage

In this section, the change of oxygen concentration along the cathode flow channels for two different operating cell

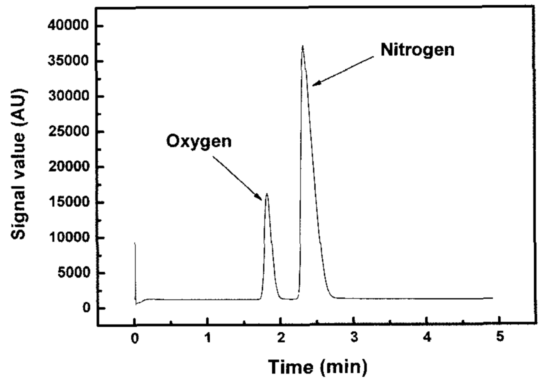


Figure 4. Oxygen and nitrogen chromatograms from gas chromatography.

Table 2. Average current density with operating temperature and voltage conditions.

Temperature (°C)	70		40	
Voltage (V)	0.3	0.7	0.3	0.7
Average current density (A/cm^2)	1.16	0.48	0.96	0.4

voltages (0.3 and 0.7 V) was investigated. In fuel cell, operating cell voltage of 0.3 or 0.7 V actually represents the corresponding electric current density.

In fuel cell, operating cell voltage of 0.3 V or 0.7 V actually represents the corresponding electric current density. Average current densities for GC measurement conditions are summarized in Table 2.

Figures 5 and 6 show the plot of oxygen concentrations along the cathode channels at the operating temperatures of 70°C and 40°C, respectively. The sampling port next to sampling port 2 is named sampling port 4 because the distance between sampling port 2 and sampling port 4 was twice of the intervals as those of other sampling ports. In this study, although linearity in oxygen concentration between two ports cannot be assured, the oxygen concentrations between two adjacent ports are connected by dotted line for visual comparison.

These two graphs show that oxygen mole fraction gets lower at a lower operating cell voltage (i.e. higher current density). Specially, sudden decrease in oxygen mole fraction between holes 4 and 5 for a higher current density (0.3 V) was observed in Figures 5 and 6.

This can be explained by combined effects of two factors. One is channel flooding by water accumulation that can lower the oxygen mole fraction in GC measurement. The other is the oxygen consumption by electrochemical reaction. Since, air and hydrogen flow in counter flow mode (i.e. opposite side of the air outlet corresponds to the hydrogen inlet as shown in Figure 3), it is thought that reaction occurs more actively at the air exit than in the co-flow channel configuration.

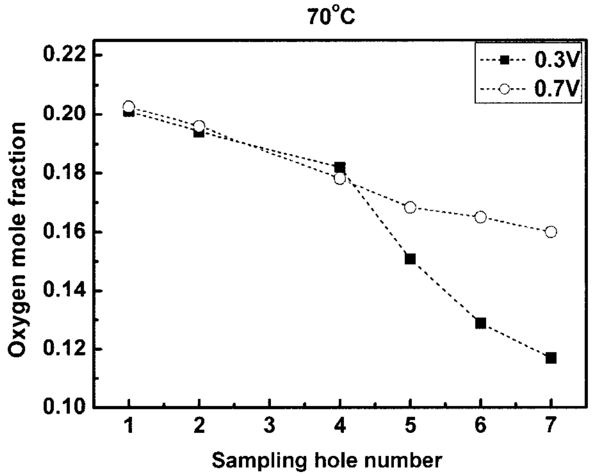


Figure 5. Oxygen concentrations for two cell operating voltages at operating temperature of 70°C and inlet relative humidity of 99%.

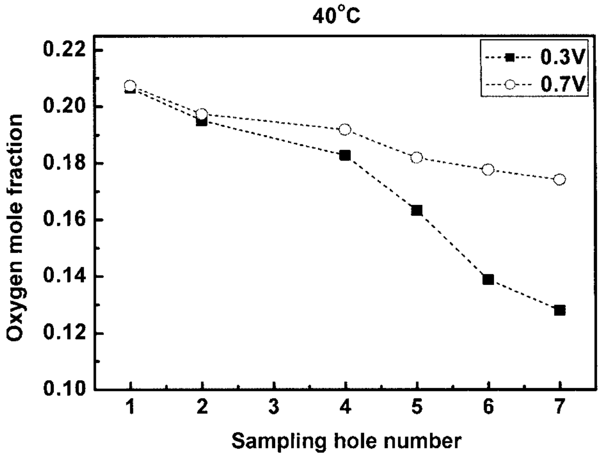


Figure 6. Oxygen concentrations for two cell operating voltages at operating temperature of 40°C and inlet relative humidity of 99%.

3.2. Oxygen Concentration Distribution with Inlet Relative Humidity

Furthermore, the oxygen concentration distribution with inlet relative humidity conditions was examined. Simultaneously, a visualization experiment is carried out to obtain more relevant results. In the case of PEM fuel cell, due to low temperature (< 90°C), water produced by electrochemical reaction in the catalyst layer was not exhausted properly and remained in the gas channel. When this phenomenon occurs, accumulated liquid water causes mass transfer limitation, which leads to the decline of PEM fuel cell performance; this phenomenon is called flooding (Pasaogullari *et al.*, 2004). Since flooding affects the reactant distributions by the electrochemical reactions of gases inside the PEM fuel cell, a visualization experiment was carried out to understand the reactant distributions along the flow channels combined with the flooding phenomenon in detail (Kim *et al.*, 2005).

3.2.1. Flooding visualization

Experimental conditions were almost the same as those of the GC experiment. With other conditions (pressure, air, and hydrogen flow rate) fixed, the temperature, operating voltage, and inlet relative humidity of the fuel cell were changed for visualization experiment.

The transparent unit cell with acryl window on cathode

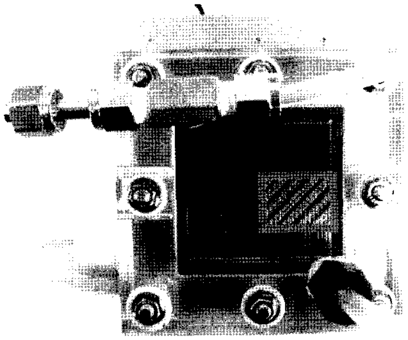
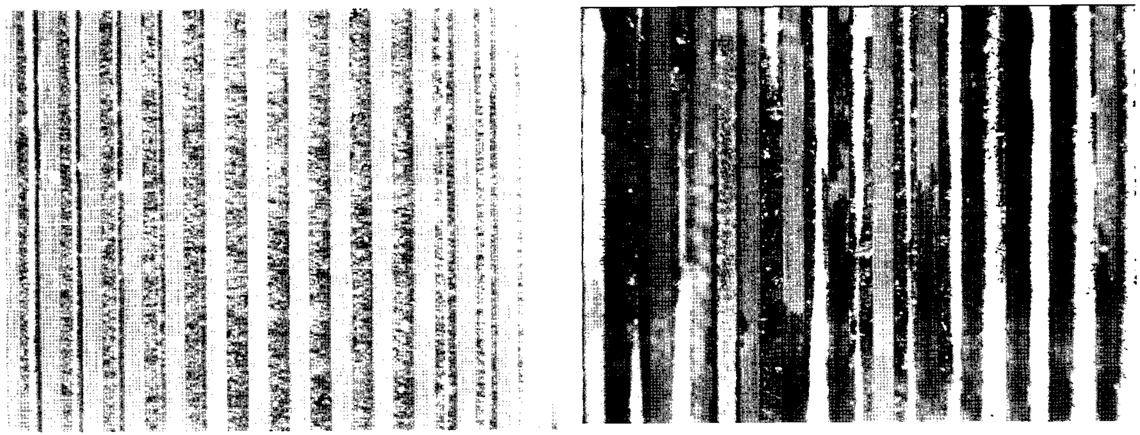


Figure 7. Visual unit cell used for this study.

side was fabricated. Acryl window is adopted because of compromise between the cost and good transparency. However, it has some limitations of precise control of the operating temperature due to low thermal conductivity of acryl. To control the cell operating temperature, the heating pad on anode side was adopted with a PID temperature controller. The temperatures inside the cathode and anode flow channels were monitored. Figure 7 shows the transparent unit cell used for this study. The marked area of red in cathode flow channels of Figure 7 was taken by a CCD camera. (The marked area in Figure 7 represents the major zone of cathode flooding.)

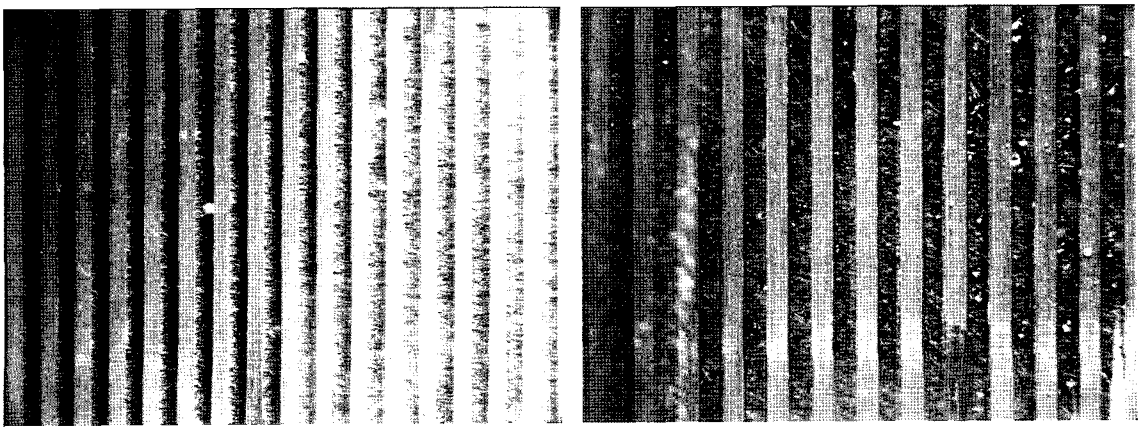
Figure 8 represents the difference of flooding according to cell working temperature and inlet humidity conditions. The flat part is the land, and the bumpy part is the channel that air flows through. The white part and liquid water droplets represent the flooding area. Flooding level becomes higher at high inlet humidity and low operating temperature, because high humidity prevents the evaporation of the product water. And if the operating temperature gets higher, more product water can effectively evaporate for the same 1% difference in inlet relative humidity.

Figure 9 shows the full shot image of flow field flooding at operating temperature of 40°C and inlet humidity of 99%. It shows the level of cathode flooding for more parts of the cathode flow channels than the area presented



(a) 70 °C operating temperature and 99% humidity

(b) 40 °C operating temperature and 99% humidity



(c) 70 °C operating temperature and 84% humidity

(d) 40 °C operating temperature and 84% humidity

Figure 8. Images of flow field flooding with operating temperature and inlet relative humidity.

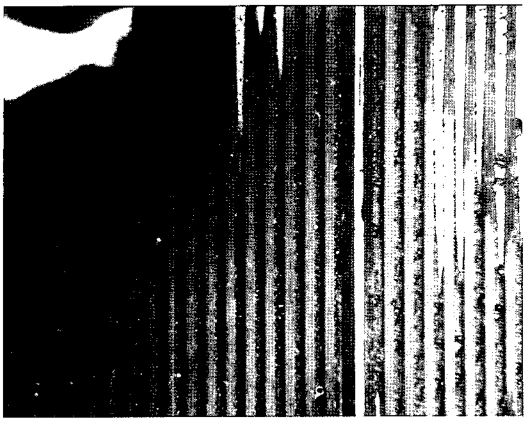


Figure 9. Full shot image of field flooding at 40°C of operating temperature and 99% of inlet humidity.

in Figure 7.

It is found that flooding mainly occurs at the air exit because a lot of water is accumulated at the exit of air flow channel by cathode stream. Since the vapor became nearly saturated as it passed through the channel, the produced water could not evaporate well and remained as the liquid phase. Hence, product liquid water disturbs the oxygen's contact with hydrogen, and this can lead to the decrease of oxygen consumption and fuel cell performance.

In this study, only the results of humidity conditions of 84% and 99% were presented, because the experiment carried out at various operating conditions showed similar trends. These two conditions were typically selected to compare the characteristics of the flooding with those of non-flooding.

It is highly desirable to carry out the experiment with MEA that can also provide good performance even at dry condition, but the MEA that has been developed gives the best performance at almost fully humidified condition. Therefore, an appropriate humidity condition that does not cause significant flooding phenomena and humidify the MEA sufficiently should be determined. An optimized flow channel design that can effectively remove the liquid water from the cathode channel and does not cause severe flooding under high humidity conditions are highly needed. To achieve this goal, we investigated the conditions that cause flooding and examined how the oxygen concentration changes according to the degree of flooding (Kim *et al.*, 2005; Tüber *et al.*, 2003).

3.2.2. Relations with inlet relative humidity, flooding, and oxygen mole fraction

The change of the flooding phenomena according to operating temperature and inlet relative humidity was investigated in the preceding section. In this section, the correlations between these characteristics and oxygen consumption are examined.

Table 3. Average current density with operating temperature and humidity conditions.

Temperature (°C)	70		40	
Relative humidity (%)	99	84	99	84
Average current density (A/cm^2)	1.16	1.16	0.96	0.99

Table 3 shows the average current density with operating temperature and inlet relative humidity. It is found that average current densities for two relative humidity conditions (99% and 84%) at 70°C are almost in the same level. Liquid water in the flow channel does not always cause performance degradation in PEM fuel cell. However, we could observe the small difference in average current density for two humidity conditions at the operating temperature of 40°C. Actually, it is found that the fluctuation in current density increases for the high humidity conditions. The increased fluctuation can be a big obstacle to control the cell performance of the fuel cell stack for automotive applications. Therefore, the techniques of preventing the flooding are highly required to make the fuel cell properly operate under various operating conditions.

Figure 10 shows the change of oxygen mole fraction with inlet relative humidity at 70°C cell operating condition. Although liquid water droplets cannot be observed in the channel at these conditions (Figure 8(a) and (c)), oxygen mole fractions examined at extraction ports 6 and 7 suddenly decrease. This is because flooding occurred in the GDL and electrode and this lowers the estimate of oxygen mole fraction level.

Figure 11 shows the oxygen mole fraction distribution

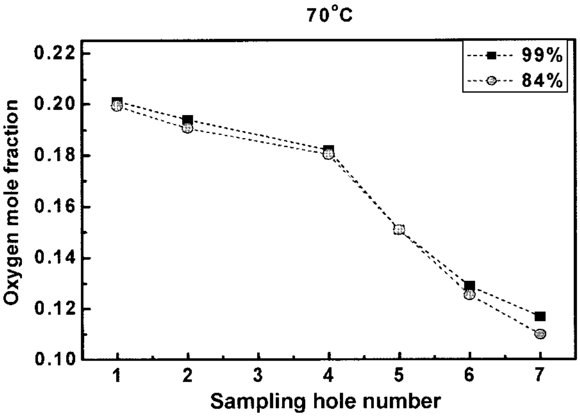


Figure 10. Oxygen concentrations along the cathode channels for two inlet relative humidity conditions at operating temperature of 70°C and operating voltage of 0.3 V.

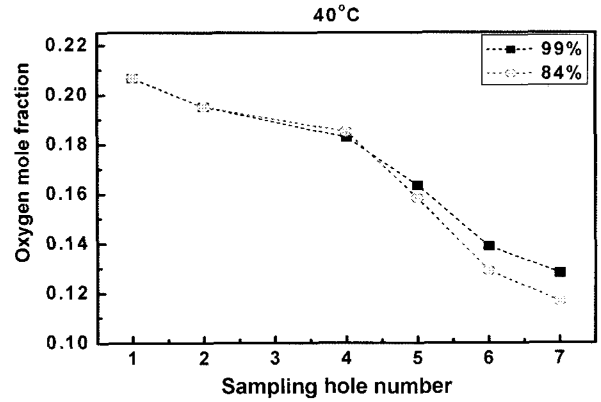


Figure 11. Oxygen concentrations along the cathode channels for two inlet relative humidity conditions at operating temperature of 40°C and operating voltage of 0.3 V.

at the operating temperature of 40°C. The difference in oxygen mole fractions between two inlet humidity conditions at ports 6 and 7 is found. It is seen that the oxygen mole fraction is little lower with lower inlet relative humidity condition (84%). This can be explained by combined effects of two main factors. One is high level of flooding which is lower than that of flooding for fully humidified condition (99%). It can be also confirmed that high level of flooding occurs near the exit of cathode channels as presented in Figures 7 and 8. Flooding lowers the estimate of oxygen mole fraction. The other is that from the current density data, more active electrochemical reactions occurred near the cathode exit compared with fully humidified conditions (flooding disturbs the reaction of oxygen and hydrogen). From this result, it is thought that the effect of relative humidity on cell performance is larger for the case of lower operating temperature (40°C).

The results above also show that the amount of oxygen consumption and flooding are not uniform along the cathode flow channels. Hence, appropriate and optimized flow path design and operating condition that can enable more uniform electrochemical reaction are highly required. Novel flow channel design and channel surface treatment that can effectively remove the product water are also needed for the improvement of fuel cell performance.

4. CONCLUSIONS

To better understand the reactant distributions in an operating PEM fuel cell, the GC technique was used. The effects of cell operating voltage and inlet relative humidity on the oxygen distributions along the cathode channels were investigated. We had drawn the following conclusions based on our experimental results.

- As the drawn current density becomes higher, more amount of oxygen is consumed. The decrease of oxygen mole fraction at the air outlet was higher than that at the air inlet because of high water content at this place.
- Through the visualization experiment of this study for the various operating conditions, the highest flooding level can be observed under the condition of operating temperature of 40°C and inlet humidity of 99%.
- It is found that oxygen mole fraction suddenly decreases near the outlet of cathode channel where flooding occurs. This is due to the combined results of water production by electrochemical reaction and the accumulation of liquid water in GDL and cathode flow channels. Liquid water in the channel does not always cause performance degradation. However, the instability of current density was observed under liquid water abundant conditions.

With these results, it can be said that the basic insight for an effective water management for PEM fuel cell and the importance of a suitable inlet humidification condition are presented. It is expected that the results obtained from this study can be effectively used as base data to verify the results of the CFD analysis to be conducted in the very near future. It is thought that this study can provide meaningful data for automotive applications with low temperature conditions such as vehicle cold start-up.

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