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Investigation of Hydrogen Crossover Phenomena during Operation of Proton Exchange Membrane Fuel Cell Systems

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Abstract

Investigation of hydrogen crossover phenomena during operation of proton exchange membrane fuel cell systems

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In this study, the crossover phenomenon according to various parameters that have not been covered yet and during operation of proton exchange membrane fuel cell system were investigated to provide practical information and better understanding on thereof. Furthermore, the effect of the pinhole formation and the location of pinhole on hydrogen crossover were analyzed. For successful landing of proton exchange membrane fuel cell system on markets, durability is imperative issue to be improved. Since the crossover phenomenon is strongly related to degradation process of materials, in this

sense, conducting the researches for more practical parameters and conditions where the real system operates are needed. However, the most of previous researches were limited because it just had concentrated on the relationship between operating parameters and gas crossover that difficult to know even reflect on system operation.

Therefore, in this study, we are focused on the useful parameters and conditions to apply its results on real proton exchange membrane fuel cell system. Firstly, effects of the bipolar plate designs, relative humidity condition difference between anode and cathode and flow direction (co-flow, counter-flow) on hydrogen crossover rate under unloaded condition are experimentally investigated to complements previous researches by dealing with new topics. Through this research, it was found that the bipolar plate design can have an influence both on performance and crossover rate due to the pressure in channel. To identify the effect of the relative humidity condition precisely, not only effect of the relative humidity condition difference between anode and cathode but also the behavior under flooding is analyzed. The relative humidity of air has more effect on hydrogen crossover because the amount of supplied air is higher than that of hydrogen, and higher relative humidity accelerates more crossover rate. However, too much water contributes to blocking the porous of gas diffusion layer and leads to prevent

gas crossover. Also, the influence of the flow direction on crossover rate is studied. From the result, even if the performance under the fully humidified condition has little difference between the co and counter-flows, the hydrogen crossover rate greatly differs between both cases due to the gas distribution in the cell. Furthermore, the effect of the clamping pressure, relative humidity condition, flow direction and stoichiometric ratio on hydrogen crossover rate are analyzed under the real system operation condition. The effect of the relative humidity condition, flow direction and stoichiometric ratio with specific condition is totally changed as the current density is increased. Through this research, the importance of measuring crossover rate under loaded condition will give an insight to the further research on crossover phenomenon.

Lastly, effect of the pinhole formation on crossover rate is studied. It was found that even if the size of a pinhole is too small to detect its existence by the performance change, it can be confirmed by detecting hydrogen crossover rate under various current densities. In addition, the location of the damage of MEA can be analyzed through the hydrogen crossover rate pattern for loaded and unloaded condition. Greatly scattered hydrogen crossover pattern was measured for blemish at inlet and higher hydrogen crossover rate was detected for pinhole at outlet. Based on this result, it is determined that the membrane

of anode inlet and outlet side have an important role in performance and hydrogen crossover. This can suggest the guideline for manufacturing process of MEA that which part should be made carefully and strongly. Furthermore, judgement method for pinhole existence with four different parameters was proposed to provide detecting technique for MEA and stack manufacturers.

Keywords: Proton Exchange Membrane Fuel Cell, Gas Crossover, Membrane Swelling, Open Circuit Voltage, Current Density, Pinhole, Relative Humidity

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Nomenclature

C	Concentration (%)
D	Gas diffusivity
J	Gas crossover rate
l	Thickness (μm)
S	Solubility (mol/m^3)
P	Partial pressure (Pa)
Ψ	Permeability (mol/m s Pa)

Superscript

AN	anode
CA	cathode

Subscript

H_2	Hydrogen
MEA	membrane electrode assembly

Chapter 1. Introduction

1.1 Background of the study

Environmental issue such as global warming and the shortage of oil problems leads to consider about eco-friendly and renewable energy resource based new system for the future. With this reasons, millions of researches have been released and suggested to alternate present system to newly developed system. Specially, these efforts have been done for vehicles because many harmful gases are emitted and main fuel of the system is oil in transportation field [1, 2]. Among various systems such as hybrid electric system, Li-ion battery system, etc., fuel cell system has been greatly highlighted for next generation vehicles [3]. There are some reasons for fuel cell system is treated as latest system: the fuels of this system is hydrogen and oxygen which are acquired from abundant water and air, no emission except for water, high efficiency, potential possibility to apply to diverse systems [4].

There are five different types classifying fuel cells into its electrolyte and proton exchange membrane fuel cell (PEMFC) whose electrolyte is polymer membrane is considered as the most suitable type for vehicles [5]. Therefore, proton exchange membrane fuel cell system based car has attracted numerous

attentions to realize its commercialization in industry. With these efforts, there has been a huge leap in technology of fuel cell for hundred years. However, there still remain unresolved problems which should be solved. The durability issue of the membrane electrode assembly (MEA) is one of the most important problems for successful landing of fuel cell vehicles on markets [6-8].

In this sense, many researches have been conducted for durability of MEA. Researches had performed from different points of view such as the sources and operating conditions for causing degradation, characteristic of material that related to degradation process, etc. [6-9]. Among many reasons accelerate membrane degradation, crossover is important for not only the durability of the membrane but also the safety of the system. Therefore, research on crossover phenomenon which is strongly related to the durability of the membrane is imperative to study.

Gas crossover occurs inevitably because of the porosity of membrane [10, 11]. In fuel cell system, there is membrane which plays a role as a medium of proton transfer from hydrogen. This membrane should allow proton transfer from anode to cathode while it has to prevent mix of hydrogen and air. However, membrane is porous material that makes gas transfer possible. This gas crossover phenomenon is realized by porous of membrane and it is

accelerated by difference between pressure and concentration of anode and those of cathode [10, 11]. Thus, the research to avoid this phenomenon, such as changing membrane material and finding certain conditions where it is likely to happen has been conducted. However, it is not that successful to provide useful alternatives.

In this study, therefore, more practical parameters and conditions where the practical system operates are considered to analyze crossover phenomenon in system operating condition. Therefore, effects of the land/channel width ratio of bipolar plates, the relative humidity condition difference between anode and cathode and the flow direction (co-flow, counter-flow) on gas crossover are investigated. Effects of the relative humidity condition difference between anode and cathode and the flow direction (co-flow, counter-flow) and the stoichiometric ratio on gas crossover are also analyzed under loaded condition. Furthermore, effect of the pinhole formation on crossover rate is measured to explain the relation between pinholes and crossover phenomenon and suggest the new method to detect existence of pinholes.

1.2 Literature survey

Since the durability of membrane is being influenced by gas crossover phenomenon, the study on crossover phenomenon has received much attention in recent researches. Researches have been conducted not only for the exact gas crossover rate, but also for the permeability, diffusivity, solubility of the gas in membrane that fundamentally related to the gas crossover phenomenon.

Generally, gas crossover phenomenon in proton exchange membrane fuel cells includes hydrogen, oxygen and nitrogen crossovers. In case of parameters affecting crossover phenomenon, their influence on the crossover has similar trends. But, because they can have different result from the same phenomenon, detailed research about each parameter should be conducted. With this reason, the effect of various operating parameters, materials have conducted with the hydrogen crossover and the caused problems through the crossover phenomenon have analyzed each crossover. Inaba et al. discovered the effect of the temperature and relative humidity [10]. Nam et al. expanded the research numerically, then investigated the effect of the membrane thickness, relative humidity on hydrogen crossover [12]. Furthermore, Baik et al. studied the effect of the operating parameters on the hydrogen crossover and suggested the quantitative influence of each parameter to the crossover

rate [13]. Zhang et al. analyzed the influence of the variable side chains of perfluorosulfonic acid membrane on hydrogen crossover [14]. According to the research about crossover of each gas, hydrogen and oxygen crossover have attracted lots of attention since they are reactant gas in fuel cell system. Bessarabov et al. emphasized the lowered performance due to the hydrogen crossover [15]. Furthermore, as oxygen crossover has been proven to have an influence on membrane deterioration, much research about oxygen crossover has begun. Endoh et al. suggested degradation mechanism due to the oxygen crossover [16]. Inaba et al. investigated the factor accelerating production of H_2O_2, focusing on it is made from degradation process [17]. In addition, new technique for accurate detection of oxygen crossover rate was developed by Baik et al [18]. For nitrogen crossover, lots of research has been done on the view of whole fuel cell system because it has more impact on the fuel cell when hydrogen recirculation technique is applied to the system. Therefore, Promislow et al. suggested the analytic model of fuel cell anode recirculation including nitrogen crossover [19]. In addition, Baik et al. and Rabbani et al. analyzed the characterization of nitrogen crossover to give an insight about the purging strategy the system adopting hydrogen recirculation [20, 21].

Because the detecting the small amount of gas is very sensitive, the detecting technique also have been developed along with the researches on

crossover phenomenon. Firstly, it was measured by the volumetric method and time-lag method by Sakai et al. to find the gas permeation rate [22, 23]. The volumetric method and time-lag method apply the pressure difference between the membrane and measure the flow rate, the time to reach the steady-state in the downside, respectively. These detecting methods which have limitation on confirming the effect of various factors are replaced with more direct gas detection methods using gas chromatography (GC) and mass spectrometer (MS). The electrochemical method is using gas and acid solution to detect the current which occurs from gas crossover. However, this method is also limited because it needs acid solution in opposite side unlike with real situation. The direct detection method using GC or MS is used popularly since it can apply many other operating parameters of real fuel cell systems. With this reason, Baik et al. analyzed the effect of operating parameters on hydrogen crossover rate and developed new technique for accurate detection of oxygen crossover rate [13, 18]. Furthermore, Baik et al. also considered the effect of thin membrane and increased clamping pressure on hydrogen crossover according to the gas diffusion layer (GDL) structure [24].

Lately, developed from fundamental analysis of the crossover phenomenon, the research about membrane degradation process which is closely related with gas crossover has been studied [25, 26]. Furthermore,

the crossover phenomenon in various type of proton exchange membrane fuel cell system has been conducted actively. Cheng et al. and Chippar et al. investigated the numerical modeling for the gas crossover effect in newly developed high temperature proton exchange membrane fuel cell system [27]. Ito et al. analyzed the influence of gas crossover in solid polymer water electrolyzer which uses fuel cells reversely for water electrolysis [28].

In addition, the necessity of durability research for fuel cell systems regarding crossover has been emphasized as commercialization of fuel cell vehicles approaches.

1.3 Objectives and scopes

Numerous analytical and experimental researches on gas crossover have been conducted, however, the most researches have been performed at open circuit voltage. It means that results from these researches are limited to estimate the tendency of crossover rate occurs under real system operation condition. Therefore, the object of present study is to analyze the crossover phenomenon for more practical parameters and conditions where the practical system operates then suggest guidelines to reduce the crossover rate in system operation. Moreover, analyzing the case of pinhole created by manufacturing process or harsh crossover phenomenon, the investigation of gas crossover is made more practical.

In chapter two, effects of the land/channel width ratio of bipolar plates, the relative humidity condition difference between anode and cathode and the flow direction (co-flow, counter-flow) on hydrogen crossover rate under unloaded condition are experimentally investigated. Basic theory for crossover phenomenon is also summarized with short description about experimental apparatus and test procedure to detect crossover rate.

In chapter three, effects of the clamping pressure, relative humidity condition difference between anode and cathode, flow direction (co-flow, counter-flow) and stoichiometric ratio on hydrogen crossover rate are

analyzed under loaded condition. Furthermore, the hydrogen crossover rate under various current densities is confirmed based on simple analytical model.

In chapter four, effect of the pinhole formation on crossover rate is studied through experiments to explain the relation between pinholes. In addition, hydrogen crossover pattern according to the location of the pinhole is also analyzed to suggest the new detecting method for existence of pinholes.

Finally, concluding remarks is given along with the brief summarization of results from this study.

Chapter 2. Measurement of crossover rate under unloaded condition

2.1 Introduction

The most important issue for successful soft landing of fuel cell cars is the durability of the system and MEA is the main target to be considered to solve this problem [29]. In this sense, investigation on the crossover phenomenon which is strongly related to the durability of the proton exchange membrane fuel cell system, is important.

In order to perform the experiments for detecting hydrogen crossover rate, the simply explanation about crossover theory is needed along with experimental setup for this research. How the system is composed, the method to conduct experiments and how we can get the exact amount of hydrogen gas from raw data are described. Then, in this chapter, effects of the land/channel width ratio of bipolar plates, the relative humidity condition difference between anode and cathode and the flow direction (co-flow, counter-flow) on hydrogen crossover rate under unloaded condition are experimentally investigated to make up for the research on crossover phenomenon by dealing with new topics which have not been covered yet.

2.2 Gas crossover mechanism

In a proton exchange membrane fuel cell, the proton exchange membrane plays important roles as a barrier for gases and medium for protons. However, its porosity enables gas molecules to transfer from side to side as shown in Fig. 2.1. Furthermore, the difference concentration and pressure conditions between anode and cathode accelerate the crossover phenomenon occurrence. This means that the crossover phenomenon is estimated by the diffusion mechanism. Therefore, the gas crossover rate is expressed by the Fick's first law with two assumptions. First, the fuel cell system is in a steady state. Second, the concentration at membrane surface remains constant. Then, the hydrogen crossover rate is expressed as below

$$J_{H_2}^{crossover} = D_{H_2} \frac{C_{H_2}^{AN} - C_{H_2}^{CA}}{l_{MEA}} \tag{2.1}$$

where D_{H_2} is the overall hydrogen diffusion coefficient, l is the thickness of the membrane and $C_{H_2}^{AN}$, $C_{H_2}^{CA}$ are the concentration of hydrogen at the interface between the GDL surface and anode, cathode gas phase, respectively [30]. In this equation, $C_{H_2}^{CA}$, the hydrogen concentration at the cathode side could be assumed as zero. Then, from the Henry's law, which calculates solubility and the amount of gas absorbed by water, the hydrogen

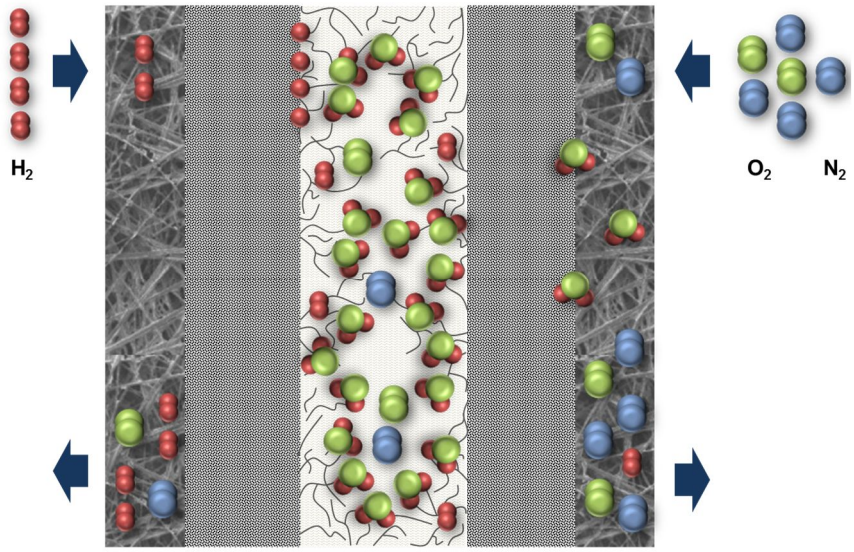


Fig. 2.1 Schematic diagram of crossover phenomenon through the membrane

concentration at the GDL surface and anode is expressed as

$$C_{H_2}{}^{AN} = S_{H_2} \times P_{H_2}{}^{AN} \tag{2.2}$$

where S_{H_2} is the hydrogen solubility of the membrane and P_{H_2} the hydrogen partial pressure at the anode.

Combining Eqs. (2.1) and (2.2), the hydrogen crossover rate can be represented as below

$$J_{H_2}{}^{crossover} = D_{H_2} \frac{C_{H_2}{}^{AN}}{l_{MEA}} = D_{H_2} \frac{S_{H_2} \times P_{H_2}{}^{AN}}{l_{MEA}} \tag{2.3}$$

From the definition of the permeability, the gas flux membrane is expressed as

$$\Psi_{H_2} = S_{H_2} \times D_{H_2} \tag{2.4}$$

From Eq. (2.4), the hydrogen crossover rate is arranged by the permeability of the membrane as below

$$J_{H_2}{}^{crossover} = \frac{\Psi_{H_2}{}^{AN}}{l_{MEA}} P_{H_2}{}^{AN} \tag{2.5}$$

Based on Eq. (2.5), the parameters that related to the hydrogen crossover rate can be estimated. From this equation, we can expect that diffusivity, solubility, thickness of membrane and partial pressure of hydrogen are dominant factor for gas crossover phenomenon. In addition, these are includes temperature, concentration, relative humidity, etc. that can have an influence on thereof.

2.3 Experimental apparatus and test

2.3.1 Single cell preparation

In this study, the single fuel cell with an active area of 9, 25 cm^2 were used. This single fuel cells consist of a membrane electrode assembly (MEA), gas diffusion layers (GDLs), bipolar plates and end plates. The membrane electrode assemblies (MEAs) used in this experiment were the Nafion® 212 membrane, which has Pt loading of 0.4 mg Pt cm^{-2} at both the anode and cathode sides or the Gore™ PRIMEA® series 57 (W. L. Gore & Associates, Elkton, MD, USA). The 35BC gas diffusion layer (SGL Carbon Weisbaden, Germany), which is made of a micro-porous layer and macro-porous layer substrate, was used. To prevent gas leakage, Teflon® gaskets between two bipolar plates and the rubber O-rings between the each side of bipolar and end plates were used. Lastly, all prepared parts were uniformly assembled by a torque wrench [31].

2.3.2 Experimental apparatus

The experimental setup for this experiment is presented in Fig. 2.2. As shown in Fig. 2.2, the flow rate, temperature and relative humidity were

controlled and pressure was monitored. Mass flow controllers (HI-TEC MFC, Bronkhorst, Netherlands) were used to manage the flow rate with a fixed stoichiometric ratio of gases. The temperature controller (UT 550, Yokogawa, Japan) was used to control heaters for the fuel cell and gas lines and was connected between the humidifier and the fuel cell. To control the temperature, T-type thermocouples (TCs) were inserted in the both bipolar plates, humidifiers and gas lines. For setting relative humidity, bubble-type humidifiers were used for each gas line. Pressure transmitters (PA-21SR, Keller, Switzerland) were attached at each inlet of the anode and cathode. For conducting the activation process and measuring an electrochemical performance, the electric loader (PLZ 664WA, Kikusui Electronics, Japan) was equipped for the single fuel cell system setup. To detect the hydrogen crossover rate, the on-line quardrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK) was used and installed at the cathode outlet [31].

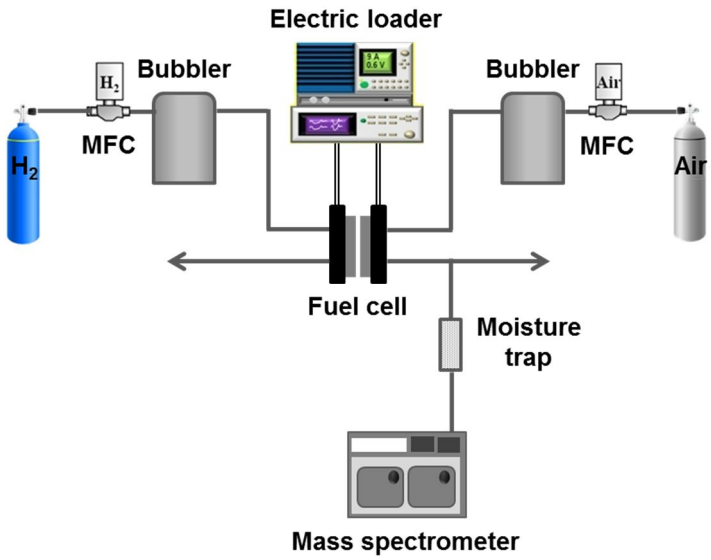


Fig. 2.2 Schematic diagram of the experimental setup

2.3.3 Mass spectrometer

The main purpose of this experiment is to detect the hydrogen crossover rate. As shown in Fig. 2.2, the on-line quardrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK) whose detection capability from 100% to less than 5 ppb, was connected to the cathode outlet. It analyzes and detects by electron impact ionization via thermionic emission from a hot filament. For the accurate detection of hydrogen concentration, a flush line where only a small amount of a nitrogen flow was added with the three-way valve. To detect hydrogen gas more accurately, a calibration process for the mass spectrometer was conducted with a nitrogen-based standard gas mixture containing specific amount of hydrogen before the main experiment [31].

2.3.4 Test procedure

At first, the activation process was conducted with a fresh membrane at a steady state where the temperature was 65℃, the relative humidity condition was 100%, and stoichiometric ratio was 1.5 for hydrogen and 2.0 for air. After nearly 8 hours of the activation process, the electrochemical performance of fuel cells was measured when the temperature and the

relative humidity were 65℃ and 100% for both gases and the stoichiometric ratio was 1.5 for hydrogen and 2.0 for air. At the same time, the calibration process as mentioned above was carried out for quantitative measurement.

After all ground work was done, the port from the mass spectrometer was connected to the cathode outlet to measure the hydrogen crossover rates. Then the concentration of transferred hydrogen was measured through the mass spectrometer at each condition and this value for the hydrogen concentration was estimated as the average value from the specific time interval. The original value from this experiment was concentration in the unit of ppm, so it was needed to be converted into the real hydrogen crossover rate in the unit of $mol/s \cdot cm^2$. Therefore, the hydrogen crossover rate was acquired through considering the amount of supplied and used air at the cathode outlet [31, 32].

The water content in MEA is very important for experiments in crossover. Therefore, apart from activation process, the same conditioning process to preparing constant condition of materials was performed before each experiments.

2.4 Effect of the land/channel width ratio of bipolar plates

2.4.1 Bipolar plates

Among the diverse materials which comprise the fuel cell stack, a bipolar plate is a key component that influences the total weight and manufacturing cost thereof [31, 33-34]. Therefore, a lot of researches about bipolar plates, such as their material, manufacturing process, and their geometry, have been done [35-38]. They usually aim to reduce the price of plates and to improve plates' performance. In this experiment, it is considered that the design of plates' channel is related to gas crossover.

In order to show the effect of the land/channel ratio of bipolar plate on gas crossover, three different types of bipolar plates were designed. Every bipolar plate is made of 316L stainless steel (SS) without a gold layer coating as shown in Fig. 2.3. All bipolar plates have four multi-channel flow fields with serpentine flow. The shape of the cross-section of each bipolar plate is rectangular. The cross-sectional view of three different bipolar plates is shown in Fig. 2.4.

The land width of each bipolar plate varies from 0.38 to 1.12 mm and

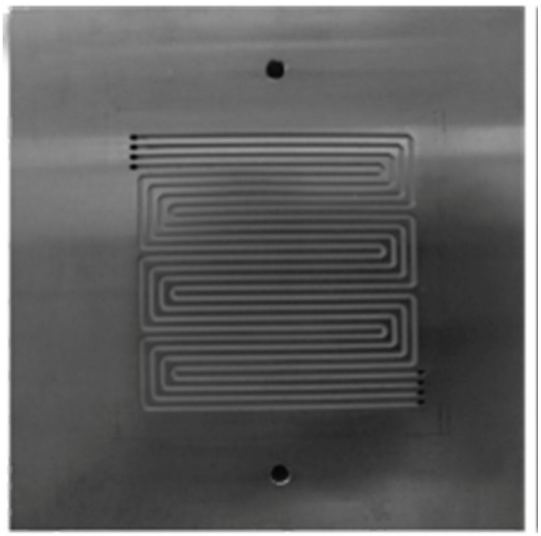


Fig. 2.3 Pictures of anode side of bipolar plates

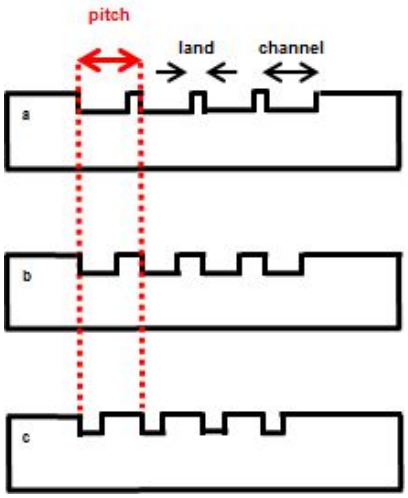


Fig. 2.4 The cross-sectional view of each bipolar plate: (a) BP1, (b) BP2, (c) BP3

Table 2.1 Geometrical characteristics of the bipolar plates

Types	Land width [mm]	Channel width [mm]	Land/channel width ratio
BP1	0.38	1.42	0.27
BP2	0.75	1.05	0.71
BP3	1.12	0.68	1.65

the channel width of each bipolar plate varies from 0.68 to 1.42 mm. All geometrical characteristics of these bipolar plates are shown in Table 2.1. To isolate the effects of land/channel width ratio, the pitch which is the sum of the land and channel width is kept the same as 1.8 mm for all cases. Because of the mass flow rate between anode and cathode, the channel depths are different from each other. The channel depth of the anode side is 0.4 mm and that of the cathode side is 0.6 mm [31].

2.4.2 The electrochemical performance of PEMFCs

Depending on the geometrical characteristics of bipolar plates, not only the crossover rates but also the electrochemical performances are affected. Therefore, the electrochemical performance for every bipolar plate is measured. The performance is recorded with various stoichiometric ratios of hydrogen which is changed from 1.5 to 2.5 when the stoichiometric ratio of air is fixed as 2.0. The results are shown in Fig. 2.5. The BP2 case has the best performance at the overall current range. This indicates BP2 has a suitable land/channel width ratio for fuel and air supply due to complicated reasons. However, when the stoichiometric ratio of hydrogen is 2.5, BP3 performs the best as shown in Fig. 2.6. Furthermore, the difference of the

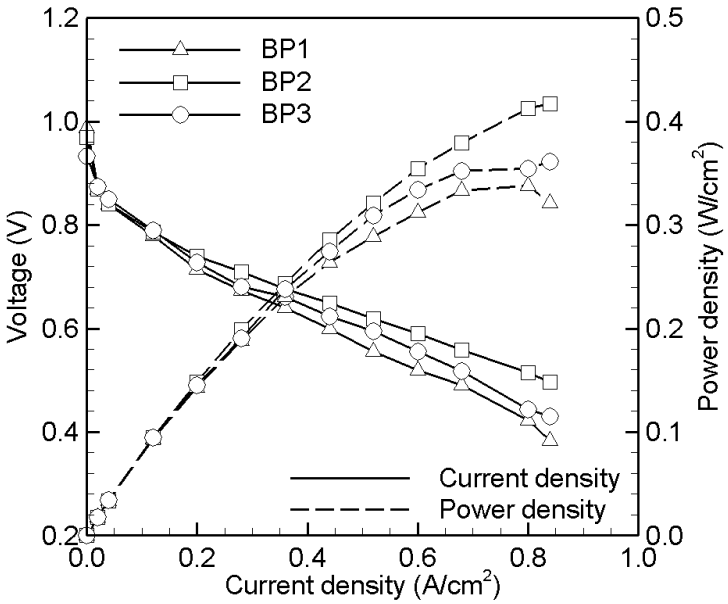


Fig. 2.5 Electrochemical performance of each case when the stoichiometric ratio of hydrogen is 1.5

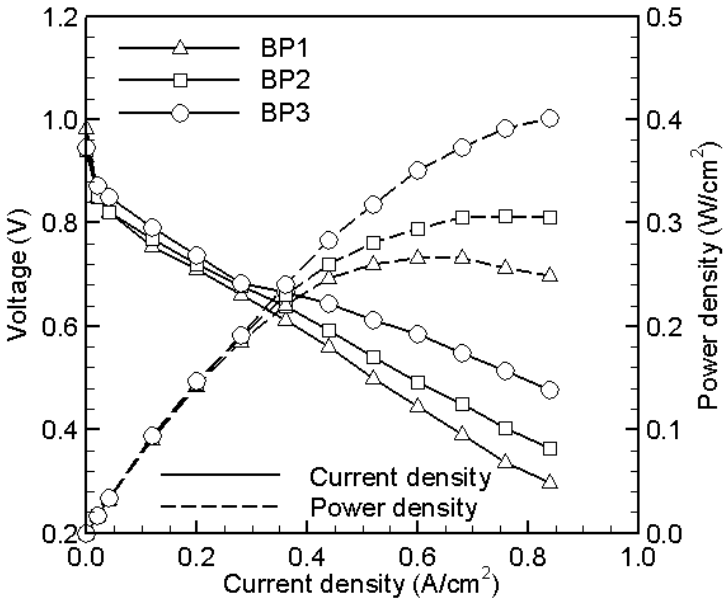


Fig. 2.6 Electrochemical performances of each case when the stoichiometric rate of hydrogen is 2.5

performances between BP3 and the other two bipolar plates in the region where the current density is between 0.4 and 0.8 A/cm^2 is greater when the stoichiometric ratio is 2.5 than when it is 1.5. For example, where the current density was 0.6 A/cm^2, for the 1.5 hydrogen stoichiometric ratio case, the voltage of BP2 was 0.59 V while the voltage of BP1 and BP3 was 0.51 and 0.56 V, respectively. However, for the 2.0 hydrogen stoichiometric ratio case, the voltage of BP3 was 0.58 V while the voltage of BP1 and BP2 was 0.44 and 0.49 V. This kind of phenomenon is probably explained by the pressure at the cathode channel.

The high pressure in the flow channel has a positive effect of fuel cell performance, especially from the 0.4 to 0.8 A/cm^2 current density regions. At medium and high current ranges, more water is produced than at a low current range because the reaction is more active to draw a lot of electrical power. Therefore, flooding frequently happens and this range requires purging, which is the technique for removing water from the channel. Since the water is originally produced at the cathode side, the purging process is carried out at the cathode channel with sufficient air [11, 39]. But, if the gas pressure of gas at the channel is high enough to push the water away, this complex process is not needed.

In Fig. 2.7, the pressure of the cathode channel is described with respect

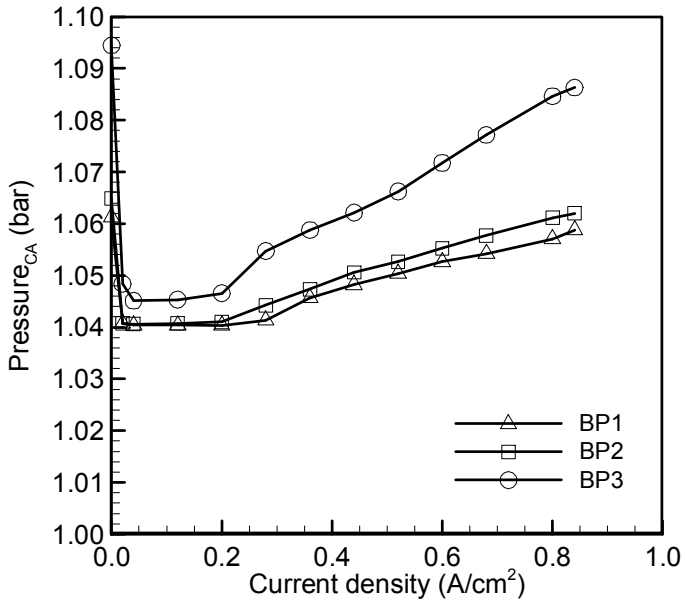


Fig. 2.7 Cathode inlet pressure when the stoichiometric ratio of hydrogen is 1.5

to different bipolar plates and current density when the stoichiometric ratio of hydrogen is 1.5. In every range of current density, BP3 has the highest pressure because it has the narrowest flow channel among the bipolar plates used in this experiment as shown in Fig. 2.3 and 2.4. Moreover, the pressure difference between BP3 and other cases increases when current density increases and the water produced in BP3 is removed successfully from the channel when the pressure difference is great. Therefore, BP3 has particularly high electrochemical performance when the current density is between 0.4 and 0.8 A/cm^2.

2.4.3 Hydrogen crossover rate of PEMFCs

The hydrogen crossover rate from the anode to cathode side is presented in Fig. 2.8. Hydrogen concentration was measured from three different bipolar plates, BP1, BP2, and BP3, according to temperature change from 45 to 65℃. Crossover rates are increasing for all cases along with the operating temperature, which is a well-known phenomenon in the crossover [10, 13].

BP3, which is designed with the narrowest channel, has the highest hydrogen concentration at the cathode side when the temperature varies from

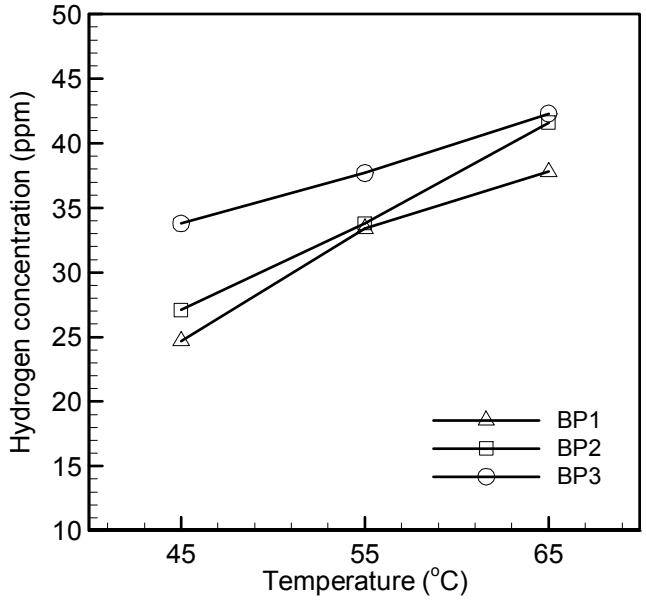


Fig. 2.8 Hydrogen concentration for all bipolar plates according to increasing temperatures

45 to 65℃. The reason for this can be understood by the explanation about the anode inlet pressure.

Even though the order of the amount of the transferred hydrogen is very small, open circuit voltage is powerful indirect evidence to support this result among the different bipolar plates. Fernandes et al. and Vilekar et al. insisted that crossover has a strong effect on the open circuit voltage state [40, 41]. Therefore many researchers have been particularly interested in the change in crossover rate in the open circuit voltage state. From their accumulated knowledge, it is verified that open circuit voltage decreases if there are a lot of transferred gases in a fuel cell. This means that the case which has the highest hydrogen concentration must have the lowest open circuit voltage. The open circuit voltage is shown in Fig. 2.9 when the stoichiometric ratio of hydrogen is 1.5 and it is observed that BP3 has the lowest open circuit voltage. This phenomenon of low open circuit voltage due to hydrogen crossover depicted in Fig. 2.8 coincides well with both the observed hydrogen crossover rate and other researchers' assertions.

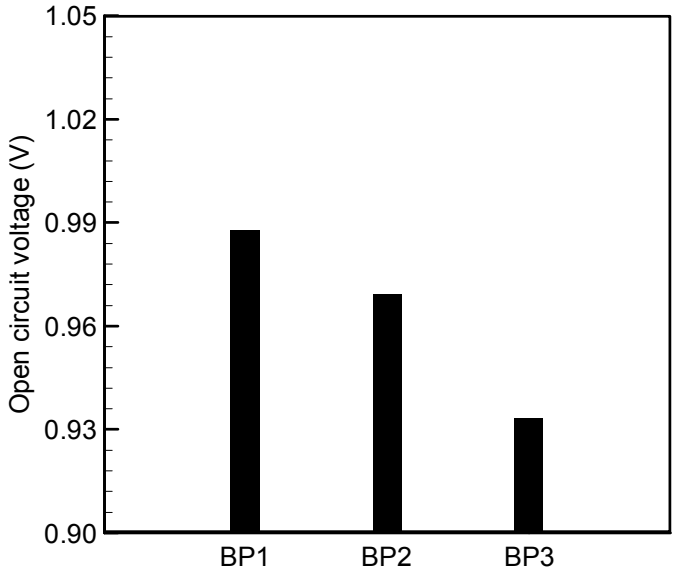


Fig. 2.9 Open circuit voltage when the stoichiometric ratio of hydrogen is 1.5

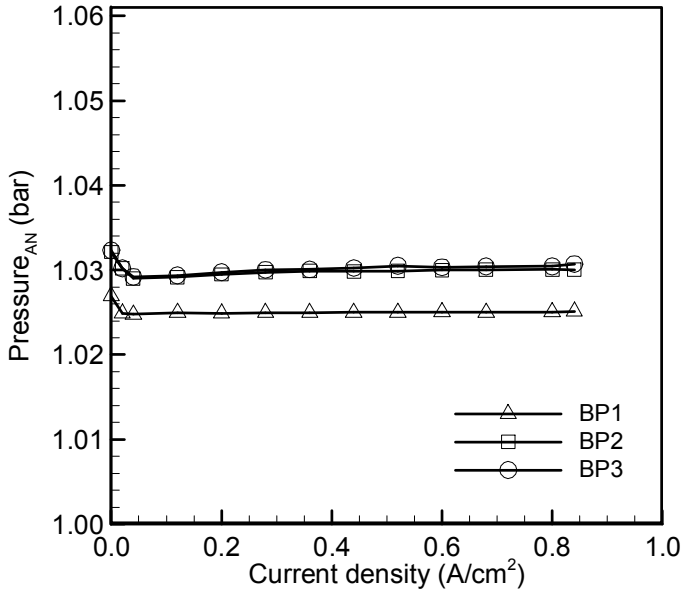


Fig. 2.10 Anode inlet pressure when the stoichiometric ratio of hydrogen is 1.5

2.4.4 Anode inlet pressure of PEMFCs

The pressure at the anode inlet side can also affectively explain the hydrogen crossover rate as well as the open circuit voltage. It was already reported that pressure is the most dominant parameter among the fuel cell operating conditions [13]. Although the same amount of hydrogen is injected into the bipolar plates, the inlet pressure at the anode is different due to the differences in the land and channel width ratios of each bipolar plate. Inlet pressure of each bipolar plate is represented in Fig. 2.10.

Similarly to the inlet pressure at cathode side as shown in Fig. 2.7, BP3 has the highest anode inlet pressure when the stoichiometric ratio of hydrogen is 1.5. That is caused by the fact that the same flow rate of hydrogen enters every bipolar plate. Because the same amount of hydrogen flows in different volumes of flow channels, pressure is increased in the bipolar plate channel which has a smaller volume, such as BP3. Compared with the cases of cathode pressure differences for three bipolar plates expressed in Fig. 2.7, the anode pressure differences between BP3 and other cases are quite small. This is because the stoichiometric ratio of nitrogen was 2.0 instead of 1.5.

2.5 Effect of the relative humidity condition

2.5.1 Hydrogen crossover rate under different relative humidity conditions

It was already known that the relative humidity condition has an effect on crossover [10-11, 13]. However, before examining the effect of the relative humidity condition difference between anode and cathode, it might be useful to briefly consider the general effect of relative humidity conditions on hydrogen crossover. First, the effect of the relative humidity conditions on performance of the fuel cell system is represented in Fig. 2.11. As shown in Fig. 2.11, the performance is elevated as the relative humidity is increased, so the relative humidity of 50% case shows a lower performance than that of 100% case. However, the open circuit voltage for the relative humidity of 50% case is 1.03 V and it is higher than that of 100% case. It is because the elevation of the amount of vapor for higher relative humidity condition causes the lowering of relative concentration of fuels. Therefore, the open circuit voltage is decreased as the relative humidity condition is increased. And the effect of the relative humidity conditions on hydrogen crossover is shown in Fig. 2.12. As it has been ascertained already, the more

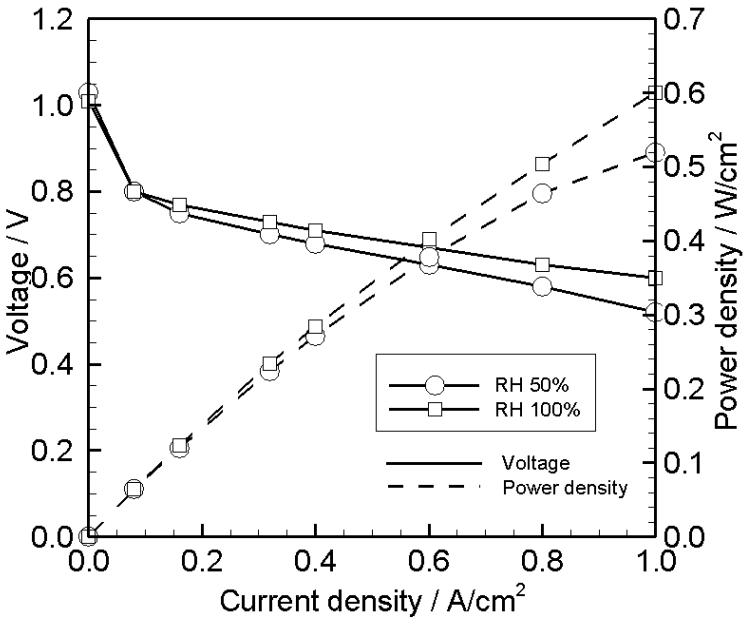


Fig. 2.11 Effect of the relative humidity on the performance

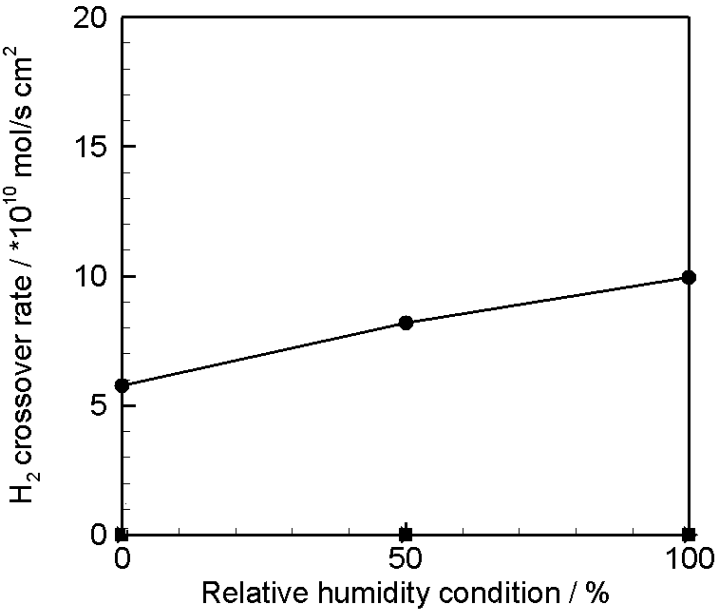


Fig. 2.12 Effect of the relative humidity condition on hydrogen crossover rate

hydrogen crossover rate is measured for the higher relative humidity condition case. This tendency of the effect of the relative humidity conditions on the hydrogen crossover from this figure coincides well with other previous researches [10-11, 13]. The reason for this could be explained by the degree of hydration of membranes. A proton electrolyte membrane is sensitive to the water contents in it. Therefore, the degree of hydration of membranes is improved due to the increased water contents and these change of the internal characteristics of membrane leads to the swelling of the membrane. As a result, membrane swelling caused by increased relative humidity conditions accelerates the growth in hydrogen crossover rate.

2.5.2 Effect of the relative humidity condition difference between anode and cathode

As mentioned above, the research on the effect of the relative humidity is one of the basic themes that have studied actively. Many researches have conducted according to the conditions where relative humidity of both anode and cathode changes at the same time and amount. However, each relative humidity condition for anode and cathode is usually varied in different ways to each other. Therefore, studies on the effect of the relative humidity

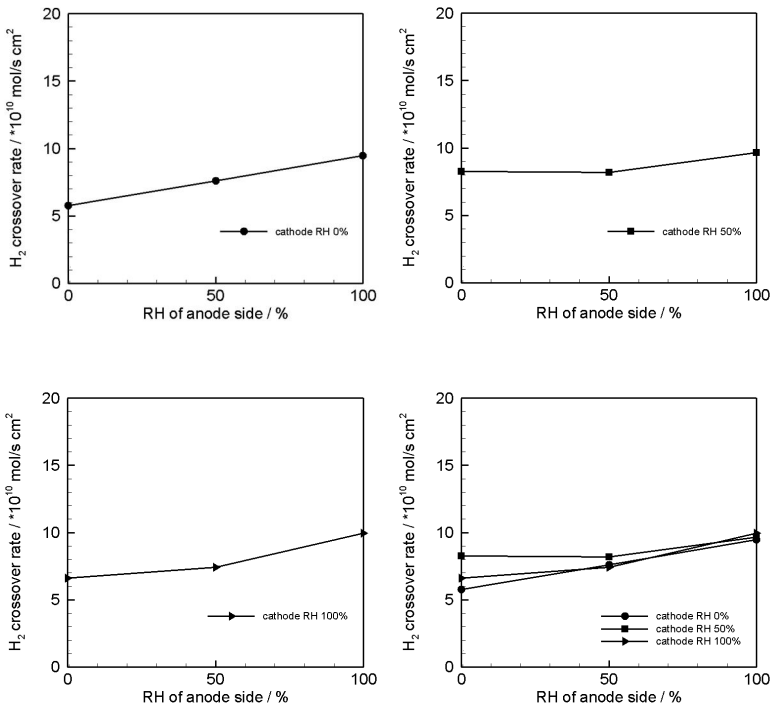


Fig. 2.13 Effect of the relative humidity condition difference between anode and cathode on hydrogen crossover rate: when cathode relative humidity is (a) 0, (b) 50, (c) 100% and (d) for all cases

Table 2.2 Experimental condition for various relative humidity

Relative humidity AN / CA [%]	**AN 0**	**AN 50**	**AN 100**
CA 0	0 / 0	50 / 0	100 / 0
CA 50	0 / 50	50 / 50	100 / 50
CA 100	0 / 100	50 / 100	100 / 100

condition on hydrogen crossover is expanded to conditions which are likely to happen in real situations and the experiment is performed under this condition as shown in Table 2.2. The result of the amount of transferred gas is shown in Fig. 2.13, which is based on the condition in Table 2.2. As shown in Fig. 2.13, the hydrogen concentration is increased as the relative humidity and its difference between anode and cathode gets higher. These results are predictable from the previous researches. However, the interesting point is that relative humidity for air has more impact on crossover than that for hydrogen. This point which is observed from experiments with different relative humidity condition, can be clearly described if Fig. 2.13 is converted to Fig. 2.14. As shown in Fig. 2.14, the reason for more influence of condition of the air on hydrogen crossover is considered because of the higher amount of supplied air. Based on these results, it is revealed that the condition for air should be controlled with hydrogen when investigating hydrogen crossover.

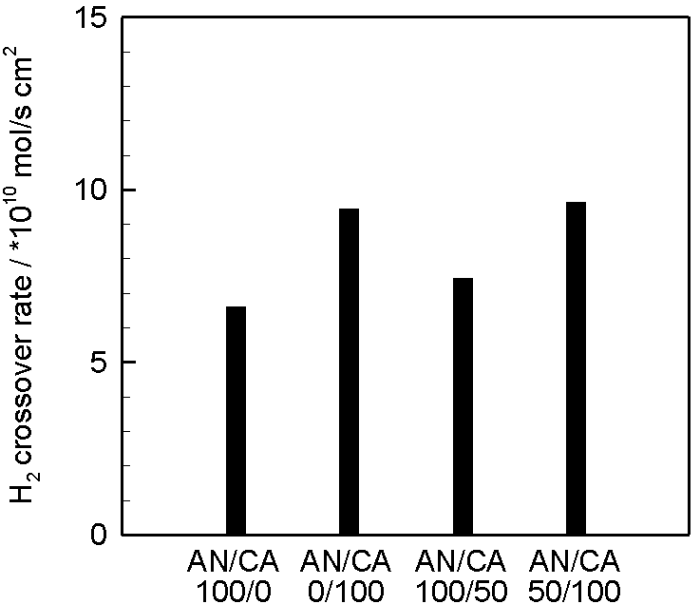


Fig. 2.14 Effect of the anode and cathode relative humidity conditions on hydrogen crossover rate

2.5.3 Analysis on behavior of crossover rate under flooding

From the previous experiments, it is clearly investigated that the crossover phenomenon is related to the hydration degree or water contents of membrane. It means that water serves as important role in crossover mechanism. To identify the relationship between the crossover phenomenon and water contents, the artificial flooding condition is prepared. Flooding is realized by increasing temperature of gas supplied, which makes the gas condensed. Detailed information is arranged in Table 2.3. The hydrogen crossover rate is detected according to the increased water contents conditions and the result is represented in Fig. 2.15. As shown in Fig. 2.15, the hydrogen crossover rate is increased as the elevation of water contents, however, it starts to decrease when too much water is supplied to the membrane. This can be explained by the trade-off relation between the hydration degree of the membrane and gas diffusion layer blocking. Basically, the membrane needs enough water for the hydration. However, the amount of water filled in membranes is limited. Therefore, excessive water can not be absorbed in membranes and create water film which covers the surface of membranes. It make porous of GDL filled with water, which prevent GDL transferring gas. When flooding occurs, the amount of crossover is decreased along with the fuel cell performance.

Table 2.3 Experimental condition for artificial flooding state

Temperature [℃]	**Amount of vapor [g/min]**	**Amount of condensed water [g/min]**
65	0.07883	-
70	0.07883	0.02802
71.6	0.07883	0.03936
75	0.07883	0.06888
75.9	0.07883	0.07822

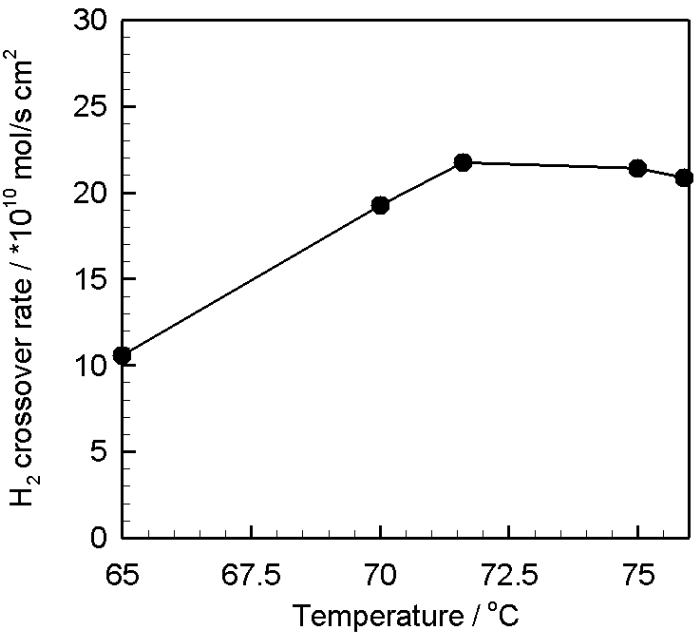


Fig. 2.15 Hydrogen crossover rate under flooding condition

2.6 Effect of the flow direction

To improve the performance of the fuel cell system, the research into the flow channel design and its flow direction have been studied actively. Specially, the research on the effect of flow change on the condition in fuel cell has been conducted to create better environment for fuel cell by understanding the characteristics of various flow channel design. Previous research has found that the change of the fuel cell performance by different flow direction originates from the change of distribution of pressure, gas concentration, and water inside fuel cell [42, 43]. Since gas crossover is closely related to those distributions, it can be influenced by flow direction. Therefore, in this experiment, the amount of transferred gas is studied with different flow direction, which is expressed in Fig. 2.16. As shown in Fig. 2.16, the hydrogen crossover rate of the counter-flow shows higher than the hydrogen crossover rate of the co-flow. Even if the performance under this standard condition has little difference between the counter and co-flows, the hydrogen crossover rate differs between both cases. This can be explained the gas distribution in the fuel cell. For counter-flow case, fully humidified gases are supplied to the upper and lower inlet for hydrogen and air, respectively. When the hydrogen goes into the inlet, there is lowered amount of air because it is started from the opposite site. In counter flow channel,

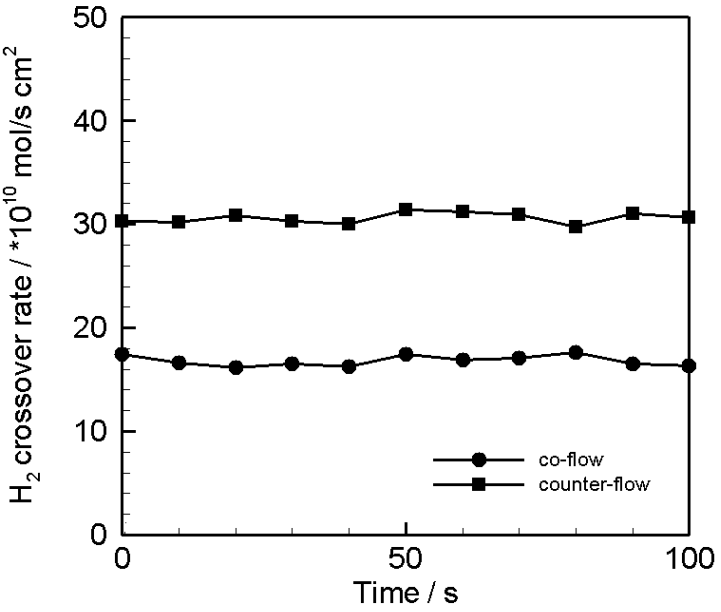


Fig. 2.16 Effect of the flow direction on hydrogen crossover rate

since two gases are injected from different directions, the distribution of pressure and gas concentration becomes more uneven than that of co-flow channel case. This uneven distribution in counter-flow direction makes the difference of pressure and gas concentration between both cathode and anode side bigger, which promotes gas crossover phenomenon as described in the graph. It can be altered if the water is condensed inside the fuel cell and this is covered in detail in later chapter.

2.7 Summary

The effect of land/channel width ratio of bipolar plates, relative humidity condition difference between anode and cathode and flow direction are experimentally analyzed in this study. It was found that the design of bipolar plates have an effect not only on the performance but also on the crossover rate because of the pressure change in channels. Furthermore, the effect of diverse relative humidity condition is analyzed in this experiment. The relative humidity condition difference between anode and cathode is considered and also the behavior of crossover rate under much higher relative humidity condition where water is condensed is studied. Through this research, the trade-off relation between the hydration degree of the

membrane and gas diffusion layer blocking is confirmed. In addition, the hydrogen crossover rate according to the different flow direction such as co and counter-flow are investigated. Based on the result, it is confirmed that the hydrogen crossover rate differs for both flows due to the gas distribution difference in the cell.

Chapter 3. Analysis on crossover phenomenon for various current densities

3.1 Introduction

The crossover phenomenon at open circuit voltage has been conducted actively. However, the gas crossover under system operating condition has never been applied to study. In this sense, the limited previous research area on crossover should be expanded to conditions which are likely to happen in real situations.

Therefore, in this chapter, effects of the clamping pressure, relative humidity condition difference between anode and cathode, flow direction (co-flow, counter-flow) and stoichiometric ratio on hydrogen crossover rate are analyzed under loaded condition. Furthermore, the hydrogen crossover rate under various current densities is confirmed based on simple analytical model.

3.2 Effect of the clamping pressure

From the previous studies, it is known that clamping pressure has

primary effect on the performance of the proton exchange membrane fuel cell system [44, 45]. This parameter can change the degree of contacts between each material, so it might have an influence on gas crossover. In this sense, the relation between the clamping pressure and hydrogen crossover rate should be analyzed specially under the real operating condition when water is generated. The hydrogen crossover rate and the performance of the single fuel cell is measured simultaneously under the test conditions in Table 3.1. The effect of the clamping pressure on performance and hydrogen crossover rate for whole current densities is presented in Fig. 3.1, 2, respectively.

As shown in Fig. 3.2 (a), the hydrogen concentration according to different current densities is almost constant. However, the hydrogen crossover rate is increased as the current density is increased, which means that the absolute amount of transferred hydrogen is increased for higher current density as represented in Fig. 3.3 (b). This result can be described easily as the pressure in flow channel and concentration difference between anode and cathode side. Firstly, the pressure in flow channel is increased because of the increased generated water according to the increased current density. Second, stoichiometric ratio is constant for all current density region, so the remained gas is increased for higher current. It means that the

Table 3.1 Experimental condition for measuring performance and hydrogen crossover rate

Operating parameters	Values
Stoichiometric ratio of hydrogen	1.5
Stoichiometric ratio of air	2.0
Temperature [℃]	65
Relative humidity [%]	50 / 100
Clamping pressure [N.m (lbf.in)]	7.91 / 9.04 (70 / 80)
Current density [A/cm^2]	0 ~ 1.0

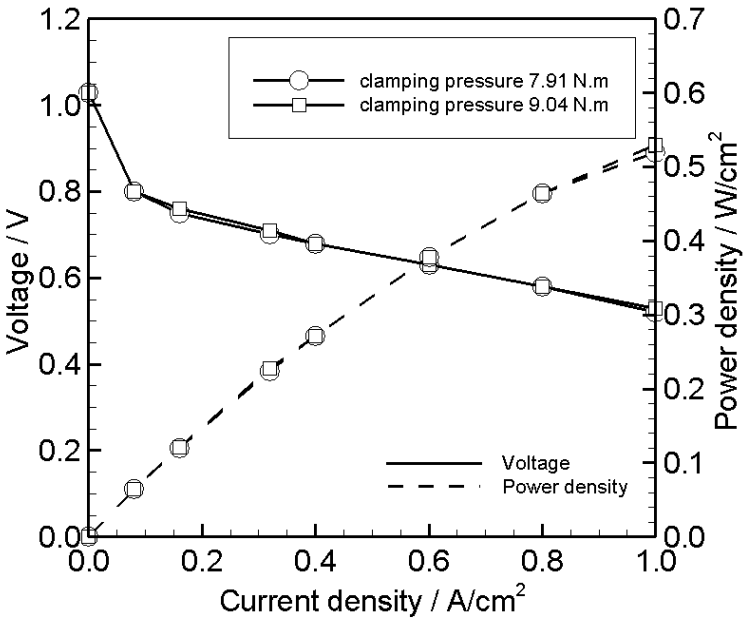
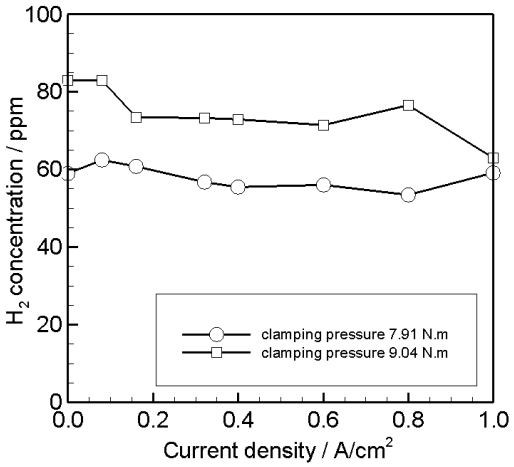
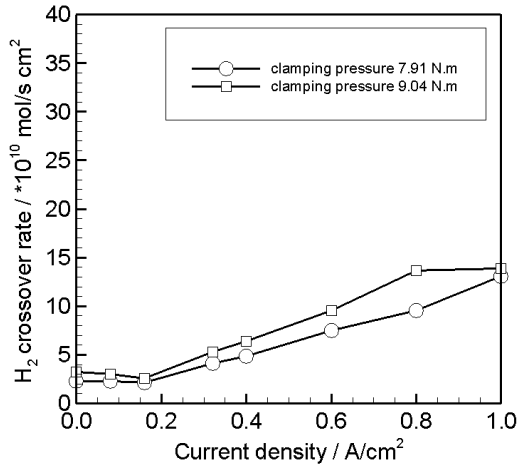


Fig. 3.1 Effect of the clamping pressure on the performance at 50% relative humidity condition



(a) Hydrogen concentration



(b) Hydrogen crossover rate

Fig. 3.2 Effect of the clamping pressure at the 50% relative humidity condition for various current densities

concentration different between anode and cathode becomes larger as current is increased. Moreover, this phenomenon would be encouraged because of the flexibility of the membrane [11, 22]. This concept has been discussed for many years since it was firstly suggested, and it has been used to explain the reason for the crossover rate. In the same way, the tendency of the increased hydrogen crossover rate according to the increased current density is analyzed by this concept. The primary reason for the increase in crossover could be understood as an increase in flexibility of the membrane. When the fuel cell is operated at higher current density, water is produced more in the system. This produced water makes the flexibility of the membrane enhanced due to the increased water contents. These change of the internal structure of MEAs depending on the water contents is shown in Fig. 3.3. This which is called as membrane swelling, is the main reason why the hydrogen crossover is increased as the current density is increased. This will be explained precisely with the explanation about effects of the relative humidity on crossover.

3.3 Effect of the relative humidity condition

In this chapter, as previous chapter, the effect of the relative

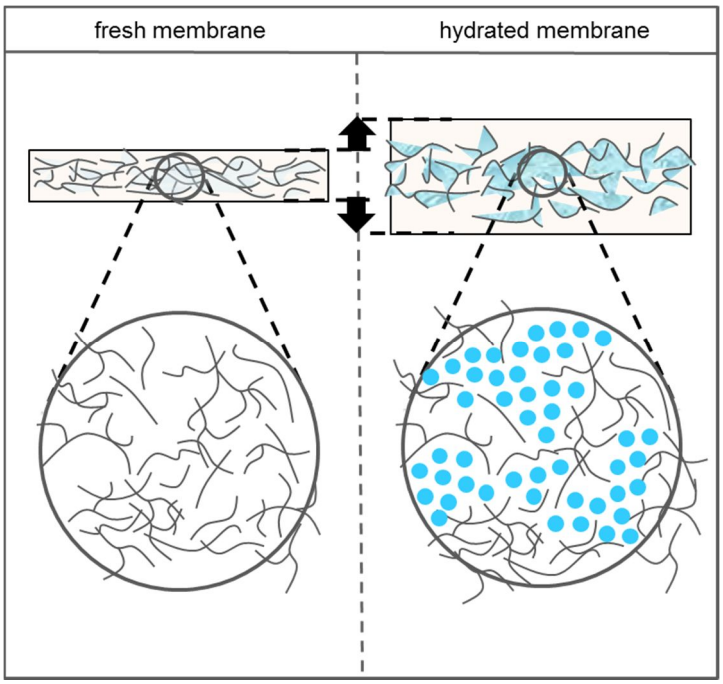
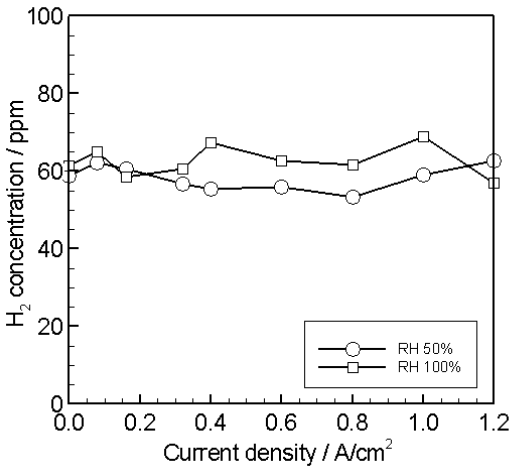
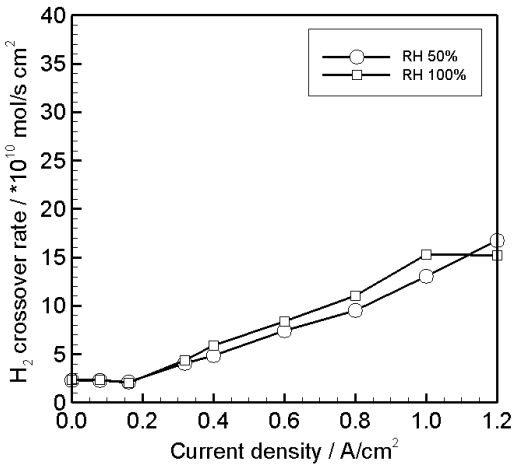


Fig. 3.3 Schematic of fresh and hydrated MEAs

humidity condition on hydrogen crossover rate under the loaded condition is studied and it is represented in Fig. 3.4. As it has been ascertained already, the more hydrogen crossover rate is measured for the higher relative humidity condition case. So the tendency of the effect of the relative humidity on the hydrogen crossover from these figures coincides well with other previous researches [10-11, 13]. However, when current density is higher than 1.0 A/cm^2, the gas crossover rate gets smaller with higher relative humidity condition. This phenomenon can be understood from the previous result through the analysis on behavior of crossover rate under flooding. The trade-off relation between the hydration degree of the membrane and gas diffusion layer blocking cause this as similar to the result on Fig. 2.15. Also, like the earlier case of the clamping pressure, the hydrogen concentration according to the different current densities is almost constant as shown in Fig. 3.4 (a), while the hydrogen crossover rate is increased as the current density is increased as shown in Fig. 3.4 (b). The reason for this pattern also could be explained by the pressure in flow channel, the amount of the remained gas and the flexibility of membrane. The flexibility of membrane is related to the amount water in membrane. As the water content is increased, the flexibility of membrane is also increased and then it finally caused more hydrogen crossover rate as shown in this



(a) Hydrogen concentration



(b) Hydrogen crossover rate

Fig. 3.4 Effect of the relative humidity condition for various current densities

figure. This phenomenon, that membrane flexibility is increased by water content, is called membrane swelling [46-51]. As shown in Fig. 3.3, the porous space is increased as the produced water is increased [32]. This is because the produced water takes the vacant space then it is expanded to make unfilled space wider. In this process, widen gap plays a door to gas crossover. Therefore, larger door by increased water helps to increase gas crossover rate. Based on this, for higher current density, which means that the generated water is increased, crossover rate is increased because the path for gas in expanded for more remained gas. This tendency of the crossover rate according to different current densities is rearranged to understand lucidly as shown Table 3.2.

3.4 Effect of the flow direction

From the previous chapter, the effect of the flow direction on hydrogen crossover at open circuit voltage condition is analyzed. In this chapter, the effect of the flow direction on hydrogen crossover under the system operation condition is studied. Hydrogen crossover rate for co-flow and counter-flow type fuel cells are measured for two different relative humidity

Table 3.2 Effect of the current density on crossover rate for different relative humidity conditions

Current densities [A/cm^2]	**Crossover rate at RH 50% [*10^{10} mol/s cm^2]**	**Crossover rate at RH 100% [*10^{10} mol/s cm^2]**
OCV	2.27	2.37
0.6	7.46	8.36
1.0	13.07	15.26

conditions and the result is shown in Fig. 3.5. As shown in Fig. 3.5, hydrogen crossover rate for clearly higher for counter-flow type at OCV conditions. However, as the reaction is proceeded to produce electrical power, hydrogen crossover rate is slightly higher for co-flow type. This result can be explained as the water distribution in the fuel cell. As mentioned previously, the amount of water content and the water distribution is very important for understanding the crossover phenomenon and water distribution can explain the reason why this happens. Many researchers have been performed the research on the characteristics of various flow directions [42, 42]. Kim et al. analyzed the water distribution and behavior for different flow directions through the visualization method [52]. The water distribution in co-flow and couter-flow type of fuel cells is explained in this paper precisely. It mentioned that the counter-flow makes the distribution of water and pressure more uniform then the co-flow when electricity generates. Especially, this research proves it with experiments and it helps to understand the result of Fig. 3.5.

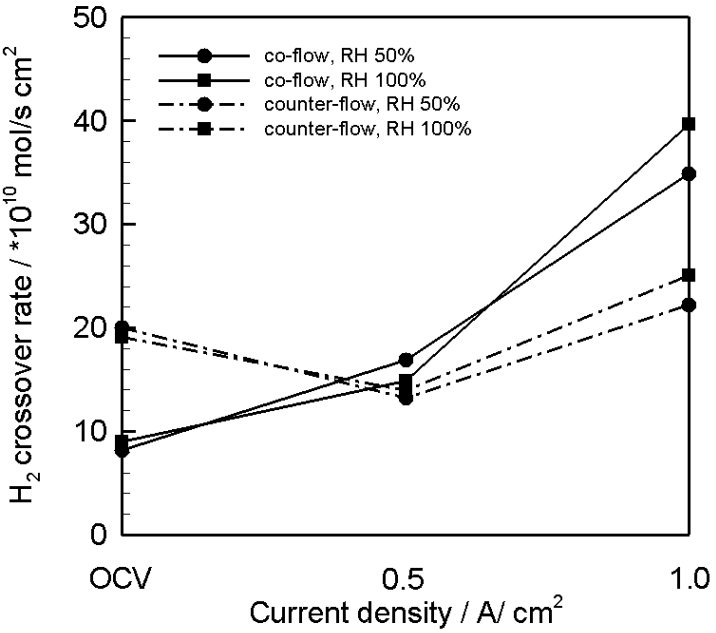


Fig. 3.5 Effect of the flow direction on hydrogen crossover rate

If the unit cell is in OCV conditions, loss of transferred gas occurs by the difference of concentration and pressure at inlet. If the cell operates with actual reaction, on the other hand, the gas crossover rate becomes lower due to more uniform distribution of pressure and water throughout whole active area. Until now, the crossover phenomenon when fuel cell generates electricity is expected to follow the result of that when it is in OCV conditions. However, this result shows that it is not true and the research about gas crossover should be conducted under loaded condition.

3.5 Effect of the stoichiometric ratio

Recently, to improve the performance of the fuel cell system, the fuel cell which can operates under high current density region is investigated. In this case, the operating area of current density is expanded from 1.2 ~ 1.4 A/cm^2 to 1.8 ~ 2.0 A/cm^2 or even more higher value. To make it possible, a lot of researches about not only inner materials but also systematic arrangements have been studied. The most important topic for the operation of higher current density is the flooding and oxygen transportation in cathode. With this reason, technology for supplying larger amount of

pressurized gas has been applied. This method is good for performance, but it has a possibility to deteriorate the crossover phenomenon which is strongly related to the durability of the membrane. Therefore, in this experiment, the hydrogen crossover rate is measured according to increasing stoichiometric ratio of air. Generally, hydrogen and air is supplied with stoichiometric ratio of 1.5 and 2.0, respectively. So the experiments for cases when the stoichiometric ratio of air is 2.5 and 3.0 are performed under the experimental condition as shown in Table 3.3. In Fig. 3.6 and 7, hydrogen crossover rate according to the three different stoichiometric ratios of air is represented under current densities. Fig. 3.6 and 7 is detected under the relative humidity of 50, 100%. As shown in these figures, the trend about stoichiometric ratio becomes different when relative humidity is 50 and 100% and it should be analyzed carefully. At first when relative humidity is 100% in Fig. 3.7, the amount of gas crossover increases a lot as stoichiometric ratio changes from 2.0 to 2.5. However, it slightly decreases when stoichiometric ratio changes from 2.5 to 3.0. This can be explained by the fact that increased amount of air with the relative humidity of 100% helps the membrane humidified and it promotes gas crossover. However, if the amount of air becomes too high, increased air pressure prevents hydrogen to be transferred. In this way the crossover rate does not elevated with much

Table 3.3 Experimental condition measuring hydrogen crossover rate

Operating parameters	Values
Stoichiometric ratio of hydrogen	1.5
Stoichiometric ratio of air	2.0 / 2.5 / 3.0
Temperature [℃]	65
Relative humidity [%]	50 / 100
Current density [A/cm^2]	0 / 0.5 / 1.0

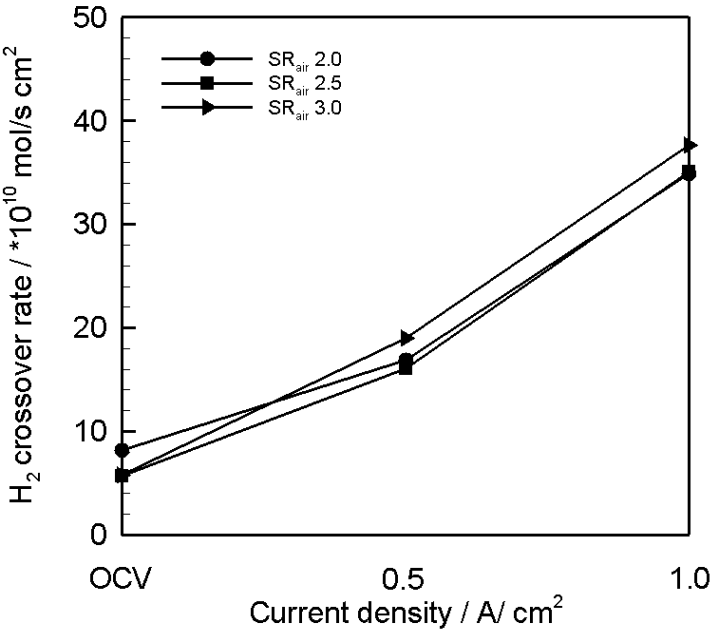


Fig. 3.6 Effect of the stoichiometric ratio at the 50% relative humidity condition

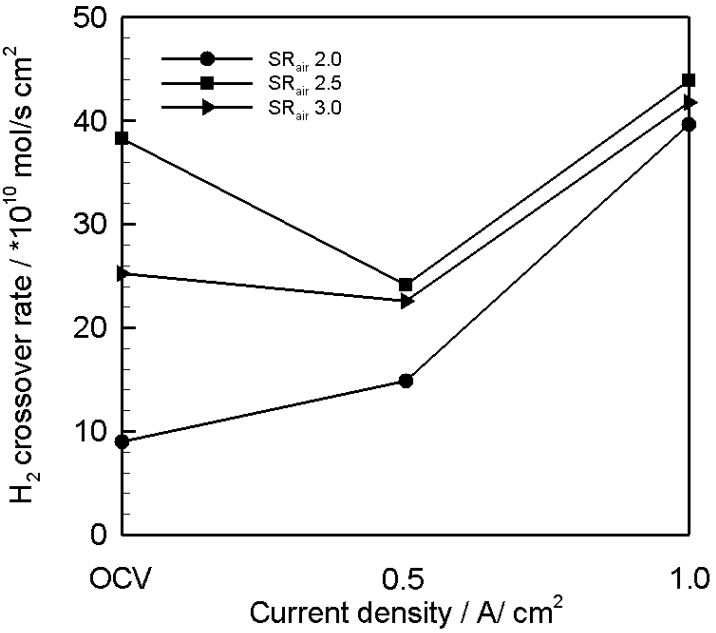


Fig. 3.7 Effect of the stoichiometric ratio at the 100% relative humidity condition

higher flow rate of air. When the relative humidity is 50%, the different phenomenon occurs. Generally, the gas crossover is expected to be accelerated by higher stoichiometric ratio. However, if the flow rate of supplied air is increased with the relative humidity of 50%, it make the membrane dehydrated easily. This can be confirmed by the data of the crossover rate and cell performance measured at the same time. As shown in Fig. 3.6, the fuel cell performance with the current density of 0.5, 1.0 A/cm^2 and the relative humidity of 50% becomes lower when the stoichiometric ratio of air increases. It proves that increment of air which is not fully hydrated does not have positive influence on the performance, which corresponds to gas crossover result. Thus, when the relative humidity is quite high, the difference of crossover rate regarding to various stoichiometric ratio is hard to find under system operation. Also, when the relative humidity is not sufficient, the amount of transferred gas is decreased with higher stoichiometric ratio.

3.6 Numerical analysis of crossover phenomenon under various current densities

In this chapter, the crossover phenomenon under various current densities has been hardly studied. The crossover phenomenon is usually analyzed at OCV condition, so the tendency through this research is needed to be confirmed by the numerical approach. To verify the crossover rate under the loaded condition, comparison between the simple modeling and experimental data is performed by using the Mathworks MATLAB/Simulink.

From the research by Kim et al., modeling was prepared with reference to the stack part in this paper [53]. The mass flow rates of the gases at inlet and outlet, the water vapor and liquid water follow the mass conservation equation as below

$$\frac{dm_{channel}}{dt} = \dot{m}_{gas,in} - \dot{m}_{gas,out} - \dot{m}_{gas,GDL}$$

$$\frac{dm_{vapor,channel}}{dt} = \dot{m}_{vapor,in} - \dot{m}_{vapor,out} + \dot{m}_{vapor,GDL} + \dot{m}_{evap} \quad (3.1)$$

$$\frac{dm_{liquid,channel}}{dt} = \dot{m}_{liquid,in} - \dot{m}_{liquid,out} + \dot{m}_{liquid,GDL} - \dot{m}_{evap}$$

The gas crossover rate is given by the following

$$J_{H_2}^{crossover} = -D\frac{dC_{H_2}^{AN}}{dl_{MEA}} + \Psi_{H_2}^{AN}\frac{dP_{H_2}^{AN}}{dl_{MEA}} \quad (3.2)$$

From the experimentally gained crossover rate, diffusivity of the

membrane is calculated through this modeling. As a result, diffusivity of the membrane is averagely $7.20 \times 10^{-11}\, m^2/\,\mathrm{s}$, this value is very similar to the scope of diffusivity from other researches. The estimated hydrogen crossover rate under various current densities through this model and experimental data are represented in Fig. 3.8. As shown in Fig. 3.8, the hydrogen crossover rate is also increased as the current density is increased. Because the one of major mechanisms for gas crossover is diffusion, the elevation of the amount of transferred gas along with the current density is reasonable.

3.7 Summary

In this chapter, the performance and the hydrogen crossover rate are measured simultaneously according to the different clamping pressure, relative humidity condition, flow direction and stoichiometric ratio at each current density. The effect of all parameters on the system performance and hydrogen crossover rate at OCV condition coincides well with previous researches. However, these tendency is changed as current is loaded to the system. The hydrogen concentration is almost constant, but the hydrogen crossover rate is increased as the elevation of current. This is also validated

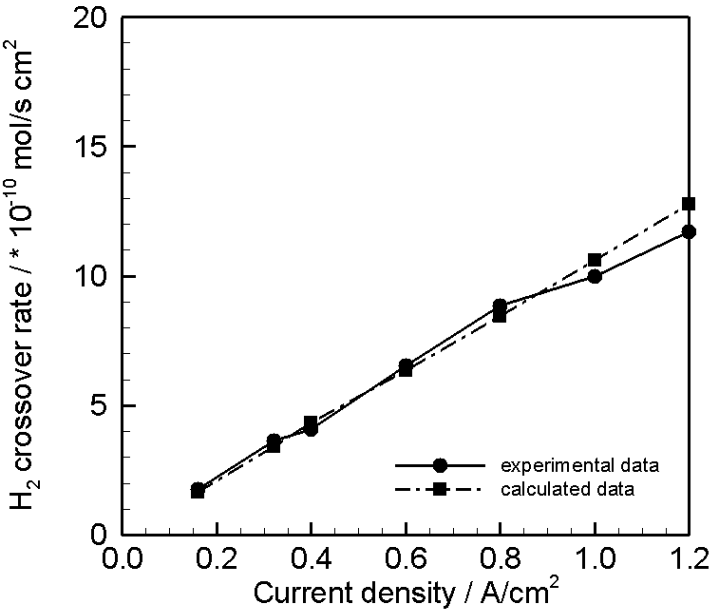


Fig. 3.8 Estimated hydrogen crossover rate by modeling

through the simple modeling. Furthermore, normally higher case at OCV condition is switched according to the current is loaded due to water generation in the cell. Based on these results, it is confirmed that the crossover phenomenon should be analyzed under the real system operation condition. This will contribute to give an insight to set the direction of further researches on crossover phenomenon.

Chapter 4. Effect of pinhole on the crossover at the membrane

4.1 Introduction

As gas crossover phenomenon occurs, simultaneously, local hot spot appears and chemical radicals which have an effect on catalyst are formed with the direct reaction between hydrogen and oxygen. Then, membrane thinning or pinhole formation is proceeded, which is the process of membrane degradation that has an interaction with crossover [12, 54-55]. In particular, pinholes, which can be formed physically during manufacturing process or chemically by membrane degradation process, damage MEA physically and chemically by increasing crossover rate [25-26, 56-58]. However, it is difficult to determine the existence of pinholes even if pinholes have a potential for making compulsory shut-down. Therefore, in this chapter, effect of the pinhole formation on crossover rate is studied through experiments to explain the relation between pinholes. In addition, to suggest the hydrogen crossover rate as the new detection method for pinholes, the hydrogen crossover pattern according to the existence and location of pinholes is also analyzed.

4.2 Pinhole formation processes

Cracks, pinholes or other blemishes can be formed mechanically and chemically in MEA. For mechanical damages, membranes can tear easily because of its papery thickness, so these damages can occur during manufacturing process. Furthermore, this problem can be worsened by performance enhancing techniques such as decreasing membrane thickness, assembling fuel cells with higher pressure and supplying pressurized gas [24]. With these technologies, Mittelsteadt et al. mentioned membrane puncturing process due to the GDL penetration and Baik et al. confirmed the effect of the diffusion media type on membrane puncturing process [24, 59]. For chemical damage, localized hot spot due to the system operation under harsh conditions, membrane thinning through the formation of hydroxyl and hydroperoxy radicals and many other degradation scenarios have been suggested. Since this spot can be produced from the direct reaction realized by crossover, the relation between gas crossover and membrane degradation is proposed as a new research topic [17]. Specially, the damage from cracks and pinholes created by mechanical and chemical process becomes more considerable when gas and water flows through them repeatedly. Therefore, it is very significant to understand this mechanism and develop preventive

measure for it.

4.3 Preparation of materials

4.3.1 Preparation of the perforated MEA

In this experiment, as mentioned previous chapter, the Gore™ PRIMEA® series 57 (W. L. Gore & Associates, Elkton, MD, USA) was used. This MEA was selected for this experiment because it has great durability among many commercialized MEAs. To suggest the new parameters to notice the existence of damage in MEAs clearly, the MEA who has resistant durability was adopted for this experiment.

Before conducting the activation process with raw materials, a pinhole was made artificially with micro-needles in MEA. The outside diameter of a needle is 470 μm and the SEM image of a pinhole is represented in Fig. 4.1. The range of measured diameter for a formed pinhole is approximately from 400 μm to 540 μm as shown in Fig. 4.2. After preparing the artificially perforated MEA, activation process is performed with perforated and unblemished MEAs. Activation process is carried out under the same

condition as previous experiments.

4.3.2 Test procedure

After the preparation of the pinhole in MEA and activation processes, the settled performances of cells for unblemished and perforated MEAs are measured at the temperature was 65℃, the relative humidity condition was 100%, and stoichiometric ratio was 1.5 for hydrogen and 2.0 for air. By the way hydrogen crossover rate is detected much longer under three specific current densities as shown in Table 4.1. Since the pinhole causes an unstable status for hydrogen crossover rate detecting in MEA, the crossover rate needs to be measured much longer than the performance to analyze the aspect of the change of it [60].

4.4 Effect of formed pinhole on the membrane

4.4.1 The electrochemical performance of the perforated MEA

As explained above, an artificial pinhole is made at the middle of MEA by micro-needle as represented in Fig. 4.3. With this perforated MEA, the

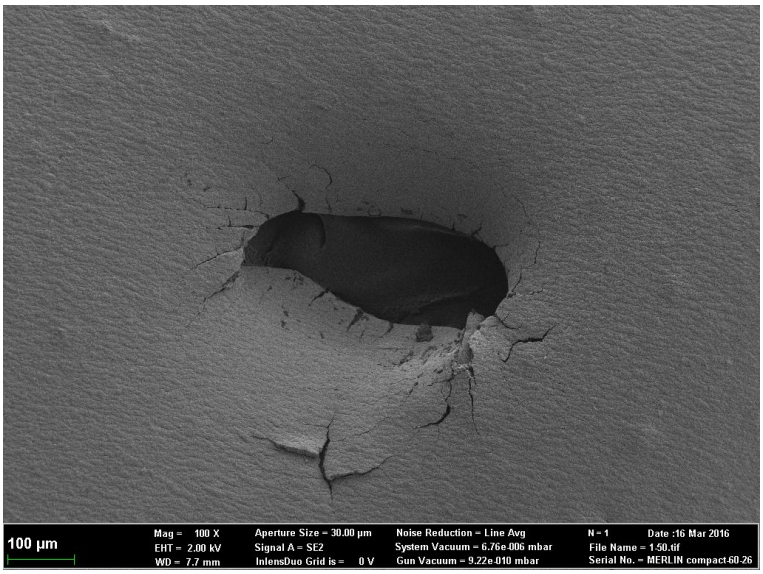


Fig. 4.1 SEM image of the pinhole

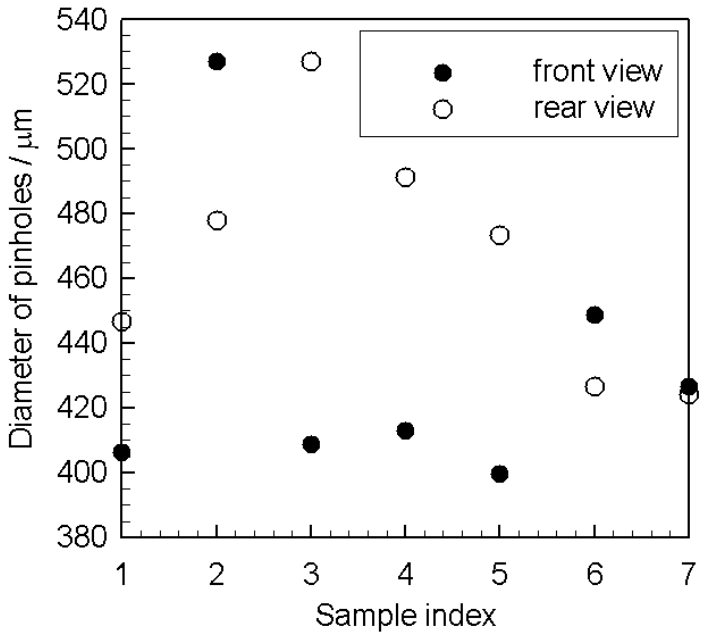


Fig. 4.2 The range of measured diameter for a formed pinhole

Table 4.1 Operating conditions during the performance test

Operating parameters	Values
Stoichiometric ratio of hydrogen	1.5
Stoichiometric ratio of air	2.0
Temperature [℃]	65
Relative humidity [%]	100 for both sides
Current density [A/cm^2]	0 ~ 1.0
Detection time [min]	3

electrochemical performance is measured and it is shown in Fig. 4.4. As shown in Fig. 4.4, even if the pinhole is formed in normal MEA, perforated MEA has a slightly higher performance than unblemished MEA. These results mean that the small sized hole contributes to effective hydration of membrane rather than accelerates consumption of fuel by direct combustion. In other words, if the size of pinhole takes up the only small part of the overall MEA active area, the pinhole just functions as a water container to improve the hydration degree of membranes which is related to performance. It has been said that performance deterioration by pinholes is very hard to be noticed if the number of pinhole or their area is not enough [58]. Therefore, another parameter which can decide whether a pinhole is created or not before its adverse effect become enormous needs to be investigated. Also, since the pinhole in this study does not affect the fuel cell performance significantly, its size is designed appropriately for such intention.

4.4.2 Hydrogen crossover rate of the perforated MEA

The hydrogen concentration at cathode and the crossover rate for unblemished MEA are shown in Fig. 4.5. Fig. 4.5 (a) is raw data from mass spectrometer and Fig. 4.5 (b) is the conversion data from concentration to

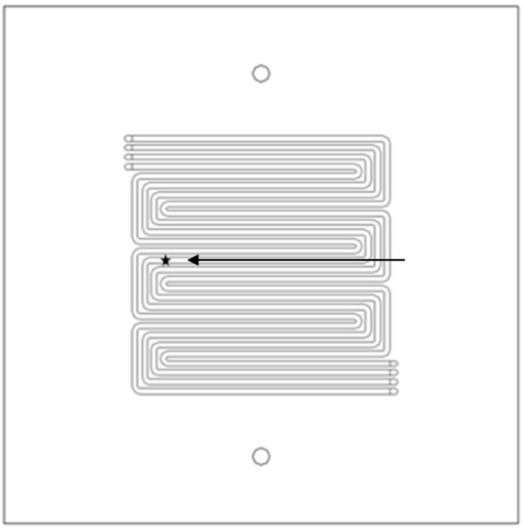


Fig. 4.3 Schematic of the position of the pinhole in the middle

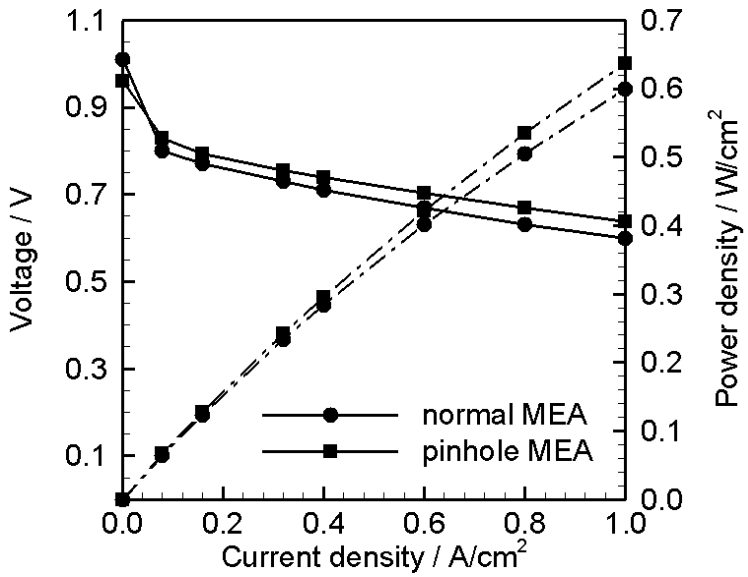
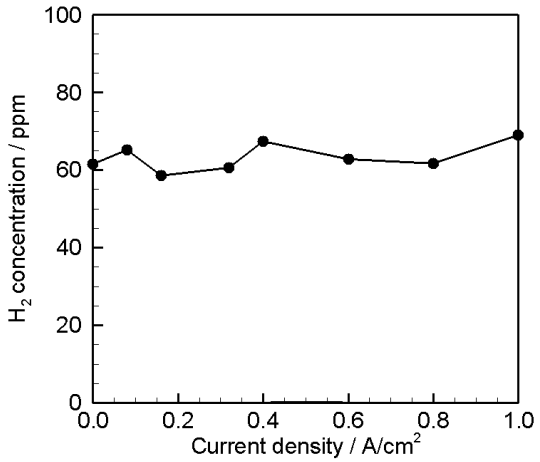
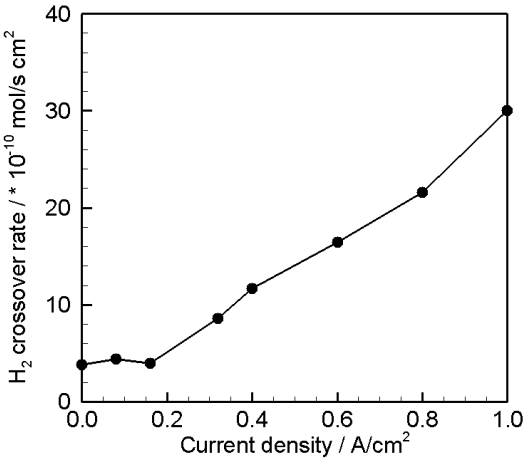


Fig. 4.4 Electrochemical performance of unblemished and perforated MEAs

crossover rate of which unit is mol/s cm^2. As shown in Fig. 4.5 (a), the hydrogen concentration is approximately 60 ppm under whole current density region. However, in Fig. 4.5 (b), the exact hydrogen crossover rate is increased as current density is increased. This is explained by increase of the pressure in flow channel and concentration difference between anode and cathode for higher current density. Because the mass flow rate of gases is also increased as current density is increased to maintain the constant stoichiometric ratio for various current densities. The hydrogen concentration at cathode and the crossover rate for perforated MEA is shown in Fig. 4.6 and 7. For damaged MEA, the detecting duration is enlarged as shown in Table 4.2 because it would be hard to reach the steady state than normal MEA. In Fig. 4.6, the overall hydrogen concentration value of pinhole MEA is higher than that of normal MEA and it is almost constant for whole current densities. However, specific pattern occurs in blemished MEA case at OCV. As shown in Fig. 4.6, the hydrogen concentration is dramatically increased from its average value to steady value. This rapid increment is caused by the flow of transferred gas through pinholes during OCV conditions. This growth would be caused because the water contained in the pinhole is removed as gas is supplied continuously. This concentration



(a) Hydrogen concentration



(b) Hydrogen crossover rate

Fig. 4.5 Hydrogen concentration and crossover rate for normal MEA

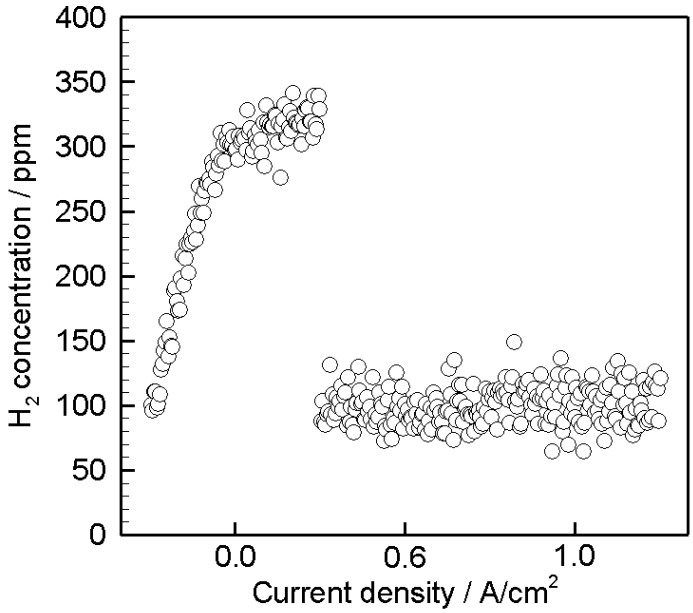


Fig. 4.6 Hydrogen concentration for perforated MEA (pinhole in the middle)

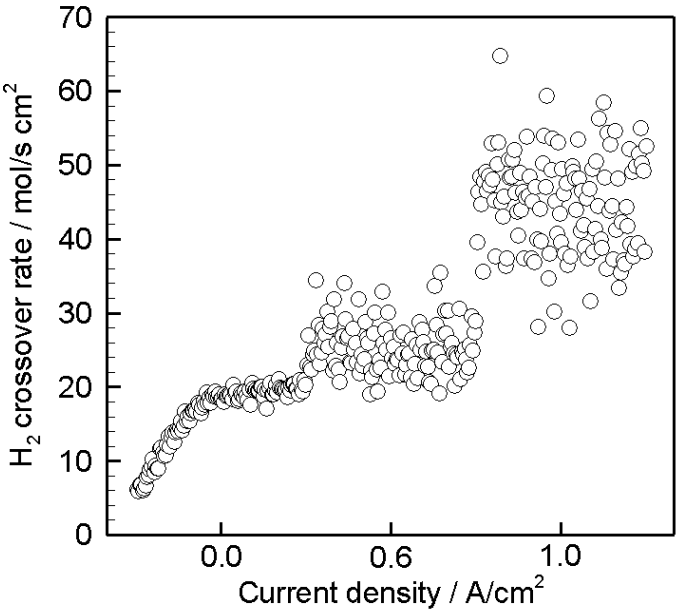


Fig. 4.7 Hydrogen crossover rate for perforated MEA (pinhole in the middle)

Table 4.2 Operating conditions during the crossover test

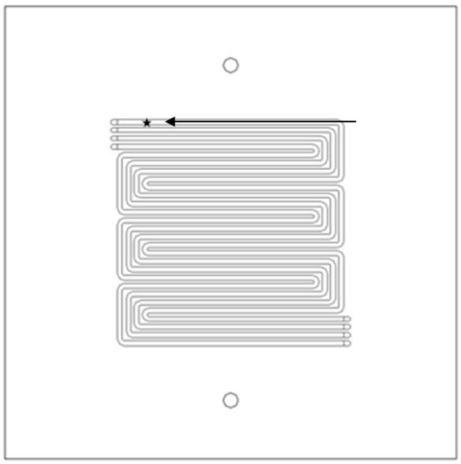
Operating parameters	Values
Stoichiometric ratio of hydrogen	1.5
Stoichiometric ratio of air	2.0
Temperature [℃]	65
Relative humidity [%]	100 for both sides
Current density [A/cm^2]	0 / 0.6 / 1.0
Detection time [min]	20

data is also converted to crossover rate as represented in Fig. 4.7. Similarly to the previous result from Fig. 4.5 (b), the exact amount of transferred hydrogen gas is also increased in pinhole MEA when the current density is increased.

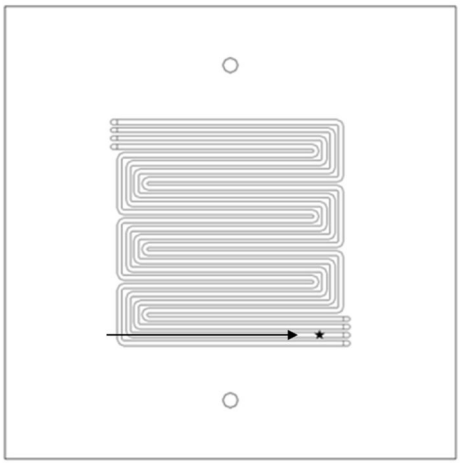
4.5 Effect of the location of pinhole on gas crossover

4.5.1 The electrochemical performance according to the location of pinhole

Based on the previous results, it is interpreted that the specific pattern of crossover rate which occurs at OCV is related to the location of the pinhole. To analyze the effect of position of pinhole, another perforated MEA samples which has pinhole at anode side inlet and outlet are prepared as shown in Fig. 4.8. The electrochemical performance of the perforated MEAs is represented in Fig. 4.9. As shown in Fig. 4.9, the MEA which has a pinhole at the middle shows a better performance than other perforated MEAs which has a pinhole at inlet or outlet. This result is caused by the local performance difference for active area [43]. The local performance difference means that even if the gas of the same condition is supplied to the fuel cell, the performance variation occurs partially. The reason for the importance of inlet and outlet side on local current distribution is explained



(a) At inlet



(b) At outlet

Fig. 4.8 Schematic of the location of the pinholes

by the supplied gas and the generated water. First, the gas for whole area is supplied at inlet so the concentration and the amount of the gas is the highest at inlet. Therefore, the performance of a fuel cell with the pinhole at inlet becomes lower than that at the middle because the pinhole is not filled with water by continuously supplied gas. Second, the generated water is normally gathered to the outlet side, because of the gravity and the consistently supplied gas. Therefore, the water contents and the relative humidity condition is the highest at outlet [43, 61]. So the flooding occurs at outlet, and the pinhole formed at outlet accelerates this situation getting worse. With these reasons, it is known that the pinhole at inlet or outlet has more effect on performance than the one at the middle. This difference in performance is shown clearly for OCV condition. In Fig. 4.10, the OCV for unblemished and perforated MEAs is shown. It is hard to figure out the formation of pinhole through Fig. 4.9, but normal MEA shows the highest OCV. This means that the small blemish which is hard to catch has an effect on OCV.

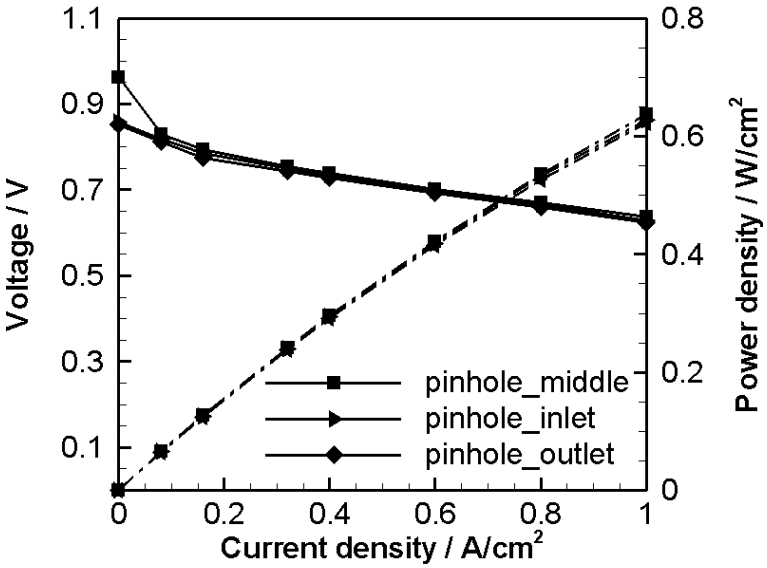


Fig. 4.9 Electrochemical performance of perforated MEAs

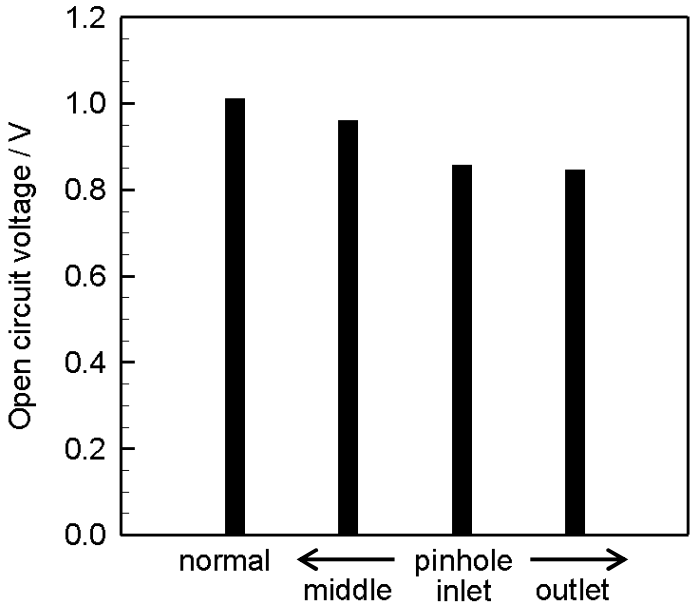
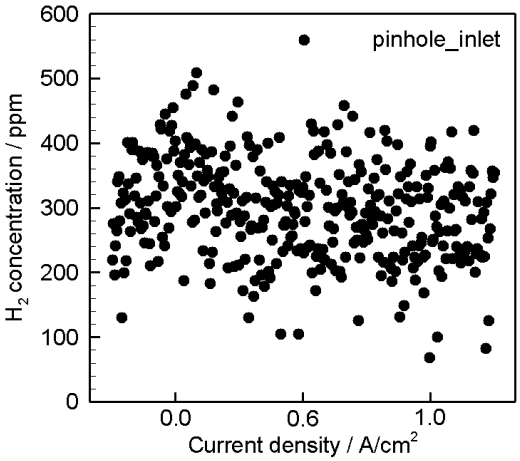


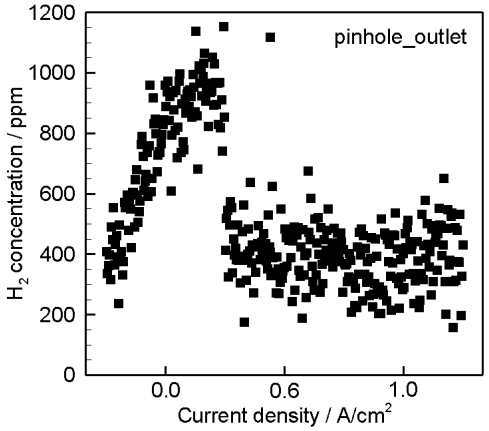
Fig. 4.10 Open circuit voltage of normal and perforated MEAs

4.5.2 Hydrogen crossover rate according to the location of pinhole

To confirm the difference due to the pinhole location in MEAs, the hydrogen concentration is also measured for different location of pinholes and they are shown in Fig. 4.11. As shown in Fig. 4.11 (a), the hydrogen concentration for MEA which has pinhole at inlet scatters greatly under different current densities. This figure shows that the water fastly fills and moves through a pinhole because the pinhole is close to inlet where lots of gases are supplied. On the other hands, the hydrogen concentration for pinhole at outlet is similar to that for the pinhole in the middle as represented in Fig. 4.11 (b). To compare the pattern in hydrogen concentration for different pinhole locations, the hydrogen concentration of inlet, outlet and middle pinhole is represented in Fig. 4.12. As shown in this figure, the case whose blemish is located in inlet represents very dispersed hydrogen concentration under whole the current densities. Specially, the overall hydrogen concentration is the highest when the pinhole is at outlet, because a lot of water helps hydrogen to crossover through the membrane swelling. Based on those results, it is clear that the damage near anode inlet and outlet has more severe effect not only on performance but also on hydrogen crossover rate which is related to durability for long term usage. And this could give an effective guideline to manufacturers to improve the durability of MEA.



(a) At inlet



(b) At outlet

Fig. 4.11 Hydrogen for perforated MEAs (pinhole at inlet and outlet)

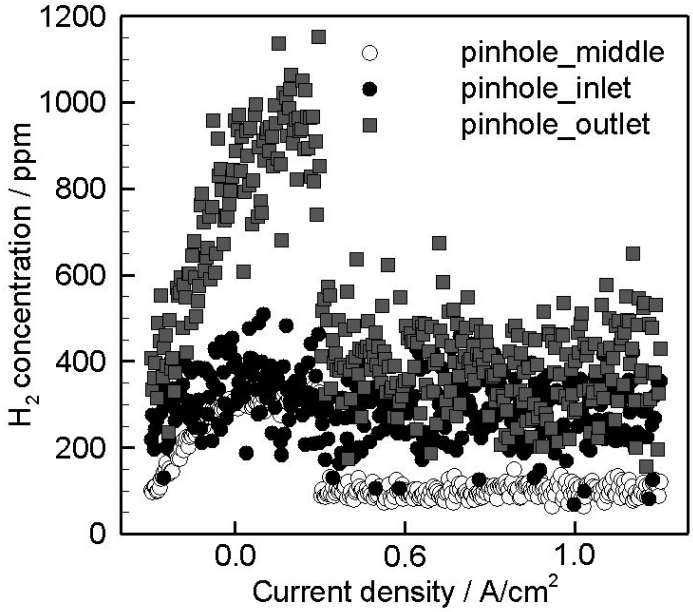


Fig. 4.12 Hydrogen concentration for all perforated MEAs

4.6 Development for judgement method of pinhole existence

4.6.1 Open circuit voltage

As explained above, small cracks or pinholes are hard to check because their size takes up the only little part of the overall area of MEA. Therefore, as shown in Fig. 4.9, damage of MEA is not represented through the electrochemical performance. However, as shown in Fig. 4.10, even small size of damage that hard to figure out through the performance change effects on OCV. In this regard, the open circuit voltage of cell or stack can be considered as one of the detecting parameter for the damage of MEA. On the other hand, it is the parameter that easily affected by other experimental conditions. Therefore, OCV needs to be considered in combination with other detecting parameters for correct judgement.

4.6.2 Crossover rate

Based on the previous results, it is clearly confirmed that specific pattern of crossover rate at OCV appears when the damage occurs in MEA. This is proved for different position of pinholes as represented in Fig. 4.6 and 11. As shown in these figures, the exact amount of crossover rate is increased and unique pattern at OCV is seemed for perforated MEA. Through this result, the crossover rate is definitely considered as one of the

judgement parameter for blemished MEA.

4.6.3 Overshooting under loaded conditions

Under the activation and conditioning process for perforated MEA, specific phenomenon appears when current is represented as shown in Fig. 4.13. As shown in this figure, during the process, undershooting of voltage is revealed occasionally. Furthermore, the detected current is very unstable even if the voltage is controlled constantly. The unstable current is usually measured when flooding occurs. However, several overshooting or undershooting is uncommon. Therefore, this phenomenon under loaded conditions is also regarded as one of detecting parameter for the damage of MEA.

4.6.4 High frequency ratio

Generally, it has been known that the high frequency ratio (HFR) is related to the ion conductivity of the membrane. So water contents of MEA have an effect on the ion conductivity of it. Therefore, if the result from the previous experiment is true, the HFR of MEA will be different when water fills and moves through the pinhole. For this reason, HFR can be thought as the detecting parameter for blemished MEA.

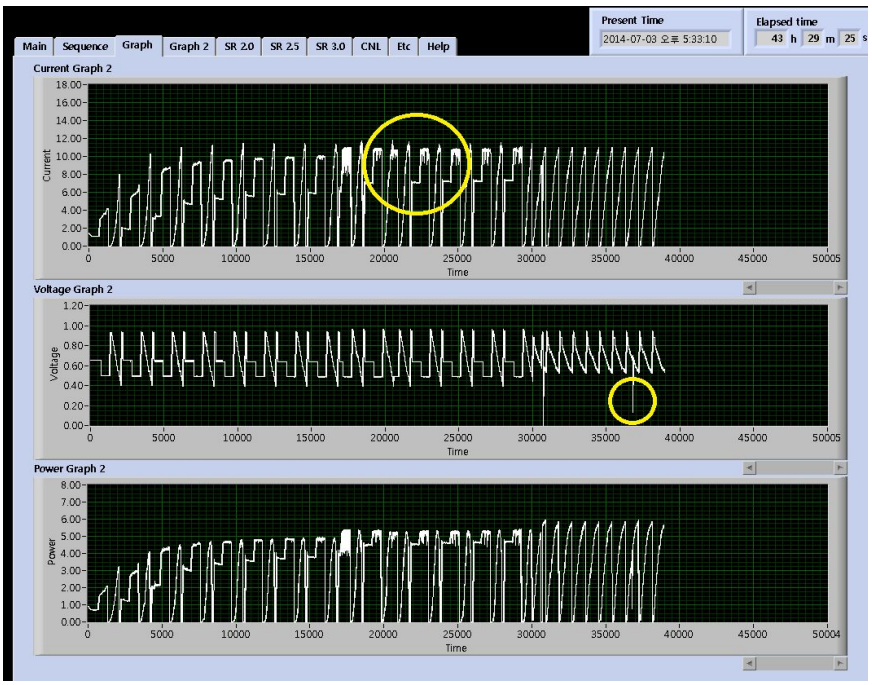


Fig. 4.13 Overshooting of current under the activation and conditioning process for perforated MEA

4.7 Summary

A pinhole is artificially formed by micro-needle and performance changed and transferred hydrogen concentration under various current densities are measured in this experiment. Moreover, to analyze the effect of the position of pinhole formation, performance and hydrogen concentration at cathode are measured differently located pinhole cases. As a result, it is confirmed that such a small size of pinhole can be identified through measuring crossover rate under loaded conditions. Furthermore, the location of pinhole can be approximately predicted with the specific hydrogen concentration pattern which is caused by pinhole formation. Lastly, detecting parameters for damage existence in MEA are arranged. In fuel cell systems, identifying a blemish such as crack or pinhole by only one of the factor may have an uncertainty because the reaction and generation of electricity and water is proceeded at the same time. Therefore, although the necessity of the judgement technique for perforated MEA, it has been difficult to suggest the definite detecting method. In this sense, it can be said that the significance of this research is providing useful and practical guidelines to actual industry applications.

Chapter 5. Concluding remarks

In a proton exchange membrane fuel cell (PEMFC), durability is one of the most important issue for successful commercialization of this system in industries. In this sense, the crossover phenomenon which occurs inevitably due to the porosity of membrane is imperative to study. In this study, to provide useful information and help for better understanding, the effect of practical parameters is considered and measuring under the real system operating condition is applied.

Firstly, effects of the land/channel width ratio of bipolar plates on gas crossover are analyzed with three different channel size of bipolar plates. In the narrowest type of channel of a bipolar plate, more hydrogen crossover occurred, and this was verified by the anode inlet pressure. Because of the reduced channel volume in narrowest case, the inlet pressure at anode was increased and caused the increased hydrogen crossover. To conduct the improved research on relationship between relative humidity and gas crossover, different relative humidity condition between anode and cathode is considered. Furthermore, to identify the effect of water content on gas crossover, artificially flooding situation is prepared and the effect of the condensed water on it is studied. With these results, the trade-off relation

between the membrane swelling and gas diffusion layer blocking is confirmed. And also, the influence of the co and counter-flow type of channels on crossover is analyzed. Even if the performance under fully humidified condition has little difference between two flows, however, the hydrogen crossover rate greatly differs for both cases due to the distribution of gas in channels.

In additions, the effect of the clamping pressure and relative humidity condition on the hydrogen crossover is studied under different current densities. The crossover phenomenon could be affected by the concentration gradient, water production, etc. that changed by the electrical load. In this sense, the hydrogen crossover rate is measured for not only the open circuit voltage but also the other voltages. In contrast to the predicted result from the previous numerical researches, the hydrogen concentration is almost constant for both loaded and unloaded conditions. However, the gas crossover is greatly increased according to the elevation of current density. Moreover, the effect of the relative humidity condition, flow direction and stoichiometric ratio is totally turned over as the current density is increased. Based on these result, the importance of analyzing crossover phenomenon under the real system operating condition is emphasized for further researches.

Lastly, the effect of the pinhole formation on the hydrogen crossover is studied. Although the size of a pinhole is too small to detect its existence by the performance change, it is confirmed by detecting hydrogen crossover rate under various current densities. The crossover rate of perforated MEA under all current densities is higher than that for normal MEA. Furthermore, the crossover rate of perforated MEA at OCV is greatly increased from average hydrogen concentration at other current densities because the gas can be directly transported through the pinhole when water does not exist in it. From this pattern of crossover rate under various current densities, the position of a pinhole can be estimated. The lower performance and higher crossover rate is shown for the case whose pinhole is formed at hydrogen inlet and outlet side. It means that the blemish near gas inlet and outlet have more influence over performance and durability because of increased hydrogen crossover rate. Therefore, to improve the durability of membrane, the inlet and outlet part of membrane should be manufactured more strongly and treated more carefully. In addition, detecting parameters for perforated MEA are suggested through this research. This result will contribute to give useful technique for MEA and stack manufacturers.

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국 문 초 록

고분자 전해질막 연료전지에서 발생하는 기체 크로스오버 현상은 전해질막의 내구성과 밀접한 연관을 갖는 중요한 현상이며, 전해질막의 내구성은 고분자 전해질막 연료전지 시스템이 성공적인 상용화를 통해 다양한 분야로 응용될 수 있게 하기 위해 반드시 해결되어야 하는 중요한 문제이다. 특히, 연료전지 시스템의 성능 향상을 위해 막의 두께가 얇아지고, 스택이 체결되는 압력은 높아지고, 기체들은 높은 압력으로 공급되는 등 기체 크로스오버가 악화될 수 있는 기술들이 개발되고 적용되고 있다. 그러나 상용화가 가능한 시스템 내 재료의 내구성에 대한 규제와 안전성 측면에서 기체 크로스오버가 언급되며, 기체 크로스오버 현상에 대한 연구는 보다 많은 주목을 받고 있다. 기존에 수행된 많은 연구들은 기체 크로스오버에 영향을 끼치는 인자들에 대해 연구되어왔는데, 이는 성능을 우선시하여 시스템의 운전 환경이 정해짐으로 인해 연구 결과들이 충분히 활용되지 못하였다. 이와 같은 기존 연구들의 한계성에서 나아가, 본 연구에서는 실질적인 시스템 운전 상황에서 고려될 수 있는 운전 환경에 대해 분석하고자 하였다. 따라서 본 연구에서는 분리판의 형상, 양 극간의 상대 습도 차 및 기체의 유동 방향과 같이 기존 연구에서 다뤄지지 않은 인자들에 따른 기체 크로스오버 현상을 분석하였고, 더 나아가 양 극간의 상대 습도 차 및 기체의 유동 방향, 그리고 기체의 당량비와 같은 실제 운전 상황에서 조절 가능한 인자들이 시스템에 부하가 걸리는 상황일 때 기체 크로스오버에 어떠한 영향을 끼치는 지를 분석하였다. 이를 바탕으로, 분리판의 설계 형상이 기체 크로스오버 현상에 영향을 끼치는 내부 압력 분포를 변화시키기 때문에 이 역시 기체 크로스오버량 변화의 원인이 되며, 공기로 주입되어 수소측보다 다량의 기체가 공급되는 공기측의 상대 습도가 수소 크로스오버에

더 큰 영향을 끼치는 것을 확인하였다. 또한 상대 습도가 충분하여 성능의 차이가 크게 나지 않는 평행류와 대향류에서의 기체 크로스오버량이 내부 물 분포 차이로 인해 대향류의 경우에서 더 많이 발생하는 것을 밝혔다. 또한 이와 같은 인자들이 기체 크로스오버 현상에 미치는 영향에 대해 실제 시스템이 운전되는 상황인 부하가 걸리는 환경에서도 분석을 하였다. 그 결과, 체결 압력과 같은 인자의 경우, 부하가 걸린 상태와 걸리지 않은 상태에 대해 같은 경향성을 가지는 것을 확인하였다. 그러나 상대 습도, 기체의 유동 방향, 기체의 당량비와 같은 인자들은 부하가 걸리고 내부에서 물이 생성되면서 그 경향성이 부하가 걸리지 않은 개회로 상태 때와는 달라지는 것을 확인하였다. 이를 통해, 내구성 및 안전성 측면에서 중요한 기체 크로스오버 현상이 반드시 실제 시스템이 운전되고 있는 상황에서 연구되어야 할 필요성이 있다는 것을 밝혔고, 이는 향후 수행될 기체 크로스오버 현상과 관련된 많은 연구들의 연구 방향에 기여할 수 있을 것으로 생각된다.

마지막으로, 막 손상에 따른 기체 크로스오버량의 변화와 시스템 운전 시 발생하는 기체 크로스오버량의 양상을 통한 막 손상의 위치에 대해 분석하였다. 이를 통해 부하가 걸린 상태에서의 기체 크로스오버량 측정을 통해, 성능 측정으로는 어려운 크기의 손상도 확인이 가능하며, 더 나아가 손상의 위치도 짐작이 가능함을 확인하였다. 손상의 위치에 따라 성능 및 기체 크로스오버에 영향을 끼치는 정도가 다르다는 것을 밝혔고, 이러한 결과는 막의 손상을 확인할 수 있는 실용적인 기법을 제공하여, 막의 생산 및 스택의 양산 업체에서 활용도가 높을 것으로 기대된다.

주요어: 고분자 전해질막 연료전지, 기체 크로스오버, 막 팽윤, 개회로 전압, 전류 밀도, 핀 홀 (pinhole), 상대 습도

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