

Visualization of Liquid Water Distribution in Fuel Cell by Using Neutron Radiography

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ABSTRACT

The accumulation of liquid water in the cell is given as a major factor affecting the electric generation performance of fuel cells, and the visualization and quantification of this liquid water is a key technology for fuel cell water management.

This study used neutron radiography to visualize the liquid water distribution inside a fuel cell during electric generation, and quantified the liquid water.

The results showed that resistance overpotential, which is one factor that reduces electric generation performance, tends to drop as the quantity of liquid water in the CCM increases. However, the resistance overpotential becomes constant at a certain quantity of liquid water or more. In addition, it was also shown that the amount of voltage drop during constant-load electric generation is strongly correlated with the quantity of liquid water in the GDL, and that the amount of voltage drop increases as the quantity of liquid water in the GDL increases.

1. Introduction

Fuel cell electric vehicles are being developed as a vital technology capable of addressing current issues facing mobility, including environmental issues such as global warming and air pollution, and energy issues due to depleting petroleum resources.

Fuel cells generate electric power by reacting the hydrogen supplied as fuel from the anode side with the oxygen in the air supplied from the cathode side. The reaction formulae for each side are as follows:

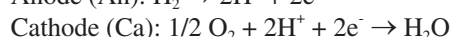


Figure 1 shows the sectional structure of a fuel cell. The fuel cell reaction is performed by a membrane electrode assembly (MEA) obtained by joining a catalyst-coated membrane (CCM) created by attaching catalyst layers to both sides of a polymer electrolyte membrane (PEM), with gas diffusion layers (GDL). Inside the MEA, the PEM is a proton conductor that manifests proton conduction functions in the water retaining state, which is thought to lower the resistance overpotential that is one factor reducing electric generation performance. Conversely, liquid water accumulation in the GDL would lower the gas diffusivity

of the GDL and reduce the oxygen level around the catalyst layers, which is thought to be one factor reducing electric generation performance.

However, the exact impact on cell performance of liquid water in the PEM, GDL and other parts of the MEA is not yet well known.

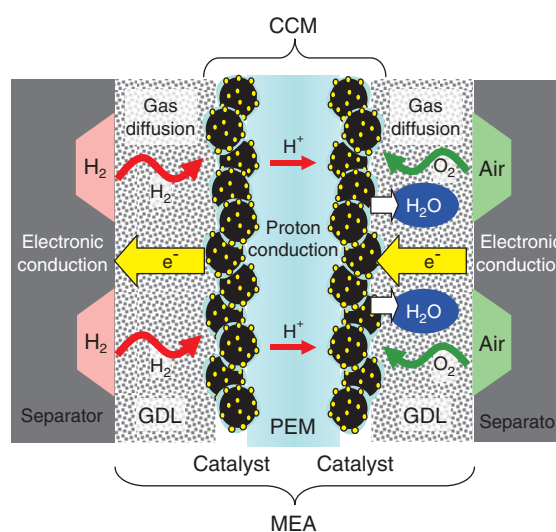


Fig. 1 Schematic of fuel cell

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2. Research Goals

The goal of this study was to use neutron radiography to visualize the liquid water in the MEA section during electric generation, and to understand the relationship between the quantity of liquid water in each part of the MEA obtained from these visualization results, and the resistance overpotential and voltage drop during constant-load electric generation.

3. What is Neutron Radiography?

Neutron radiography is a method enabling the quantification of materials using the neutron attenuation characteristics of the constituent atoms of the subject. Al, C, F and other elements often present in the component materials of fuel cells have small attenuation characteristics, but substances containing H atoms have large attenuation characteristics. These characteristics were used to measure the neutron attenuation of liquid water, which has a high concentration of H atoms, and to visualize and quantify the liquid water in the cell section.

Figure 2 shows the mass attenuation coefficients of typical atoms and molecules with respect to thermal neutrons⁽¹⁾. This shows that H₂O molecules, which include H atoms, have a larger mass attenuation coefficient compared to other atoms. (Note that H₂O is plotted according to the atomic number of H.) The Lambert-Beer law indicated by Eq. (1) is used to deduce the thickness t [cm] of the test piece from the neutron attenuation.

$$I_{out} = I_{in} \exp(-\alpha \cdot t) \quad (1)$$

Here, I_{in} is the incident neutron intensity, I_{out} is the transmitted neutron intensity, and α indicates the neutron mass attenuation coefficient (cm²/g) of the test piece. The thickness of the liquid water in the MEA was measured as described above under various electric generation conditions. The liquid water in the MEA was then quantified by dividing the liquid water thickness by

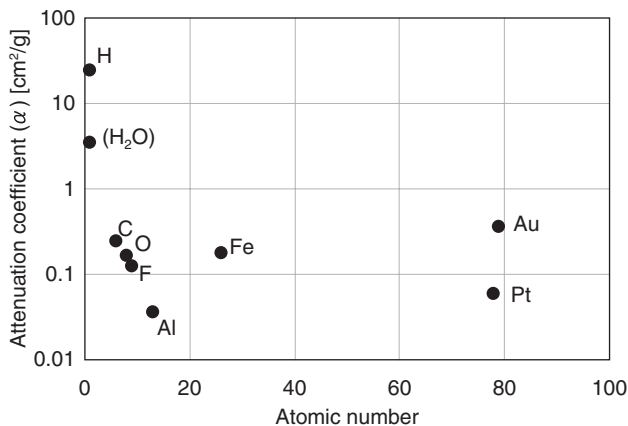


Fig. 2 Attenuation coefficient of elements

the thickness (5 mm) in the neutron ray direction of the effective electrode (described hereafter), and expressing the result as the liquid water occupancy (vol%) per unit volume.

Neutron radiography measurements were performed at the ICON beam line of the Paul Scherrer Institute (PSI) in Switzerland, in collaboration with the PSI Electrochemistry Laboratory (ECL) and Neutron Imaging and Activation Group (NIAG). These measurements were based on the recent advances in high resolution imaging of fuel cells realized at PSI^{(2), (3)}.

4. Test Method

Figure 3 shows the cell configuration. The cell for neutron radiography was created by clamping a MEA consisting of a CCM and GDL, together with gaskets to prevent gas leakage, between two separators.

The neutron transmission image was measured from the cell section direction as shown in Fig. 3. To increase the spatial resolution in the section direction in the observation region where the total of the flow field depths (An, Ca) and the MEA thickness is between 1 mm and 2 mm, measurement was performed by inclining the detector (CCD) relative to the section direction as shown in Fig. 4⁽²⁾.

By measuring with only one direction (in this study, the MEA thickness direction) of the neutron transmission image stretched in this manner, the resolution of the obtained image was increased from 13.5 μm/pixel to 2.3 μm/pixel.

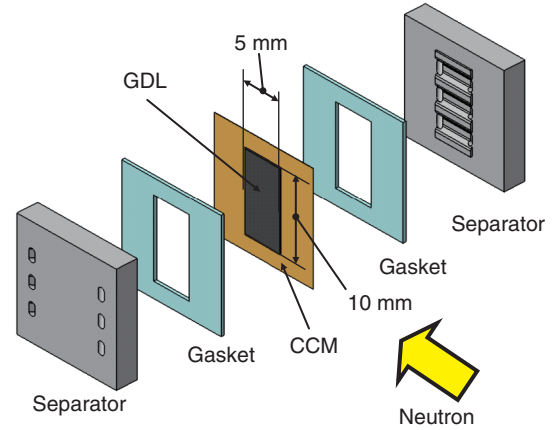


Fig. 3 Configuration of cell for neutron radiography

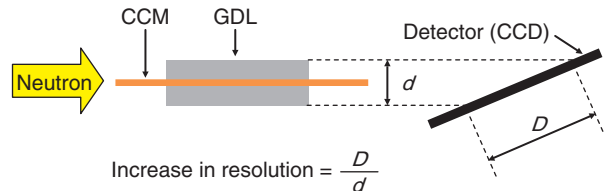


Fig. 4 Schematic of increase in resolution

Table 1 Cell configuration and test conditions

Cell configuration	Electrode area	0.5 cm ²
	Separator	3 channels
Test conditions	Current density	1.0 A/cm ²
	Cell temperature	50, 70, 85 °C
	An gas	H ₂
	Ca gas	Air
	An gas humidity	50, 100 %RH
	Ca gas humidity	40, 70, 100 %RH

However, due to the limited collimation of the neutron beam and the inherent blurring of the detector, the actual spatial resolution was approximately 20 μm .

Table 1 lists the cell specifications and the test conditions. Electric generation was performed while varying the three parameters of the cell temperature, Ca gas humidity, and An gas humidity. The terminal voltage and resistance overpotential during electric generation were measured, and the liquid water distribution in the MEA at that time was also visualized simultaneously.

5. Effects of Liquid Water Distribution on Electric Generation Performance

Figure 5 shows examples of images obtained by neutron radiography. The blue-colored portions indicate liquid water. Electric generation was performed with a fixed current density of 1.0 A/cm², so the quantity of water generated by the fuel cell reaction was the same for any

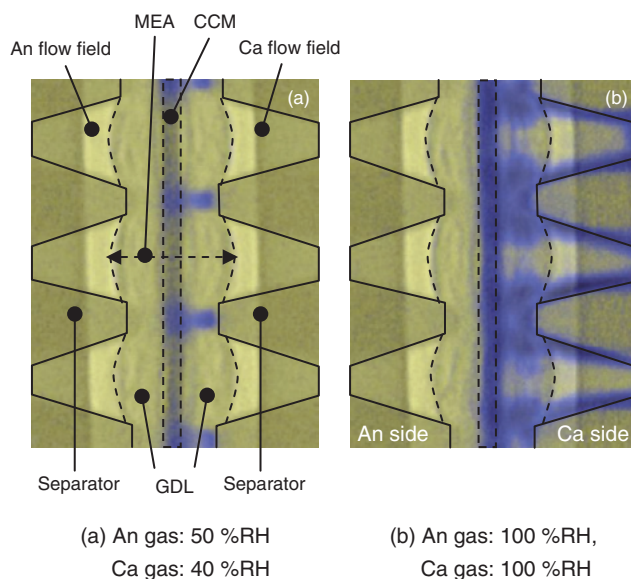


Fig. 5 Images of liquid water distribution during electric generation and regions of quantitative analysis

electric generation condition. However, when low-humidity gas was flowed to both electrodes as shown in Fig. 5(a), the inside of the MEA was drier and there was less liquid water compared to when high-humidity gas is flowed as shown in Fig. 5(b). (The cell temperature was 70°C in either case.)

Next, Fig. 6 shows the electric generation performance (terminal voltage) under each test condition listed in Table 1.

Under cell temperature conditions of 50°C at which the water saturation pressure is low and the MEA does not dry easily, the terminal voltage dropped as the Ca gas humidity increased. This is thought to be because the liquid water accumulated in the catalyst layers and GDL impeded the movement of the gas to the catalyst, which reduced the effective electrode area. On the other hand, at a cell temperature of 85°C that results in a high water saturation pressure, the terminal voltage was confirmed to drop as the relative humidity decreased. This is thought to result from a drop in PEM proton conduction functions (increased resistance overpotential) due to drying. At a cell temperature of 70°C, high performance was obtained under Ca gas humidity conditions of 70%RH, and the test conditions that yielded the highest terminal voltage were an An gas humidity of 100%RH and a Ca gas humidity of 70%RH.

To clarify the voltage behavior relative to the cell temperature and gas humidity, the liquid water in the CCM and GDL regions shown in Fig. 5 were quantified using neutron radiography. The correlation with the terminal voltage and resistance overpotential also obtained at the same time was then analyzed, and the effects of the liquid water distribution on electric generation performance were clarified.

5.1. Relationship between Quantity of Liquid Water in the CCM and Resistance Overpotential

Figure 7 shows the resistance overpotential measured under each electric generation condition listed in Table 1.

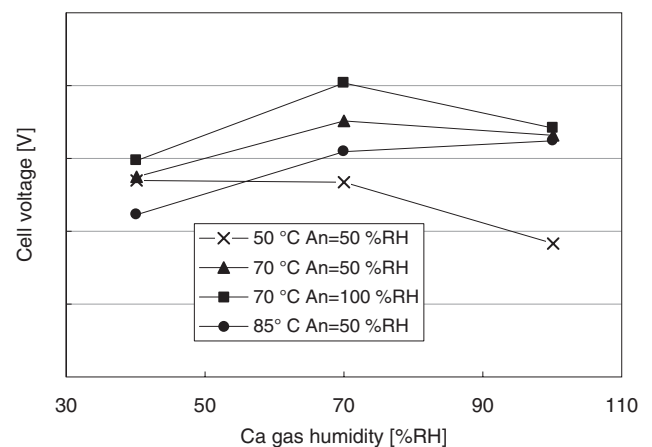


Fig. 6 Cell voltage of each test condition

At all cell temperatures, lowering the Ca gas humidity increased the resistance overpotential. In particular, at a cell temperature of 85°C that results in a high water saturation pressure, the increase in resistance overpotential as the Ca gas humidity decreased was larger than that at other cell temperatures. The behavior of the terminal voltage at 85°C shown in Fig. 6 can be explained by this resistance overpotential behavior. The quantity of liquid water measured using neutron radiography was compared to verify the relationship between the resistance overpotential and the quantity of liquid water in the MEA at this time. As described above, the quantity of water in the PEM greatly influences the change in resistance overpotential, so the ideal approach is to quantify only the liquid water in the PEM. However, the PEM thickness is relatively small given the neutron radiography resolution, and it is a challenge to clearly separate the quantities of liquid water in the PEM and the catalyst layers. Therefore, this study used the quantity of water in the CCM. Figure 8 shows the relationship between the resistance overpotential and the quantity of liquid water in the CCM.

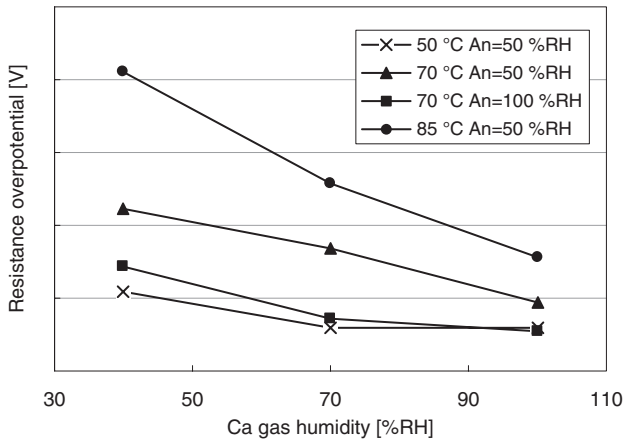


Fig. 7 Resistance overpotential of each test condition

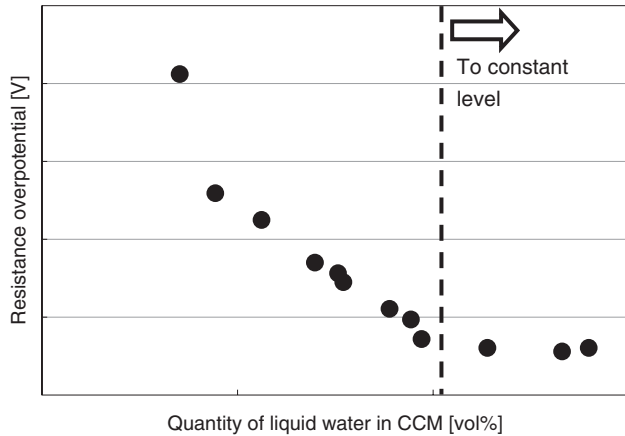


Fig. 8 Relation between resistance overpotential and liquid water in CCM

The resistance overpotential dropped as the quantity of liquid water in the CCM increased, but then became constant at a certain quantity of liquid water or more. This indicates that in order to increase electric generation performance, a certain quantity of liquid water or more should be maintained for the PEM to exhibit sufficient proton conduction functions.

5.2. Relationship between Quantity of Liquid Water in the GDL and Voltage Drop

There are two possible factors affecting the voltage drop during constant load electric generation due to accumulation of liquid water in the MEA. One is a drop in gas diffusivity within the catalyst layer due to liquid water accumulating in the catalyst layer, and the other is a drop in the amount of gas movement to the catalyst layer due to liquid water accumulating in the GDL. Accurate measurement of the quantity of liquid water in the catalyst layer is a challenge because the catalyst layer thickness is relatively small given the neutron radiography resolution. Therefore, the relationship between the liquid water accumulated in the GDL and the voltage drop was verified. The voltage drop behavior was quantified by measuring the amount of voltage drop from the start of constant-load electric generation at 1.0 A/cm². The terminal voltage includes the aforementioned change in resistance overpotential, so the drop in IR free (sum of the terminal voltage and the resistance overpotential) that cancels out this change was used as the amount of voltage drop. Figure 9 shows an example of the IR free behavior when electric generation is performed with a cell temperature of 50°C, An gas humidity of 50%RH and Ca gas humidity of 70%RH. Figure 10 shows the neutron visualization results measured at the same time (0 min and 10 min after the start of electric generation).

Figure 9 shows a high IR free level immediately after the start of electric generation, and Fig. 10(a) shows that almost no liquid water has accumulated in the MEA at that time. However, as constant-load electric generation

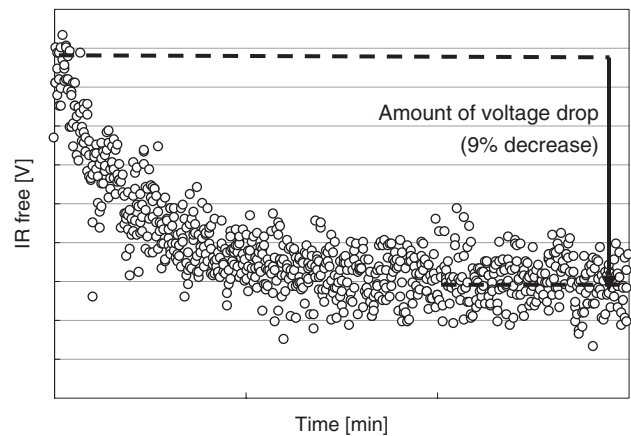


Fig. 9 Time evolution of IR free and voltage drop

continues, the IR free level drops to a constant value. Figure 10(b) shows that liquid water accumulates in the MEA by the time this IR free constant region is reached, and that most of this liquid water accumulates in the GDL near the separator ribs.

Next, Fig. 11 shows the amount of voltage drop during constant-load (1.0 A/cm^2) electric generation under each electric generation condition listed in Table 1.

The increase in the voltage drop amount due to changes in the Ca gas humidity is larger for a cell temperature of 50°C , at which there is low water saturation pressure, than at other cell temperatures. The terminal voltage behavior at 50°C shown in Fig. 6 can be explained by this voltage drop behavior. The quantities of liquid water in the GDL measured by neutron radiography were compared to verify the relationship between the amount of voltage drop and the quantity of liquid water in the GDL. As shown in Fig. 10(b), the quantity of liquid water in the GDL differs greatly near the gas flow fields and near the ribs (the convex portions of the separator that contact the GDL for

electric conduction), with more liquid water tending to be distributed near the ribs. This is thought to be because gas did not easily diffuse in the GDL near the ribs, so there was less drying of the generated water compared to the flow fields. Therefore, the quantity of liquid water in the GDL was measured for the three patterns of near the ribs, near the flow fields, and the average of the two (GDL average), and the correlation between each pattern and the amount of voltage drop was verified. The results for all patterns showed that when the quantity of liquid water in the GDL increases, the amount of voltage drop also tends to increase. This confirmed that in order to suppress the voltage drop during constant-load electric generation, it is necessary to reduce the quantity of liquid water in the GDL. Of the three patterns used to measure the quantity of liquid water, the GDL average was most strongly correlated with the amount of voltage drop. Figure 12 shows the relationship between the average quantity of liquid water in the GDL and the amount of voltage drop.

The reason for the strong correlation between the average quantity of liquid water in the GDL and the amount of voltage drop is thought to be that the accumulation of liquid water reduces the GDL diffusivity. This behavior, where the movement of gas to the catalyst layers is impeded, is most closely represented by the average quantity of liquid water in the GDL.

5.3. Observations Regarding the Ideal Water Distribution

Figure 13 shows the results of combining the relationship between the quantity of liquid water in the CCM and the resistance overpotential shown in Fig. 8, and the relationship between the quantity of liquid water in the GDL and the voltage drop shown in Fig. 12.

Of the various test conditions used in this study, the maximum terminal voltage was obtained at a cell temperature of 70°C , An gas humidity of 100%RH, and Ca gas humidity of 70%RH as shown in Fig. 6.

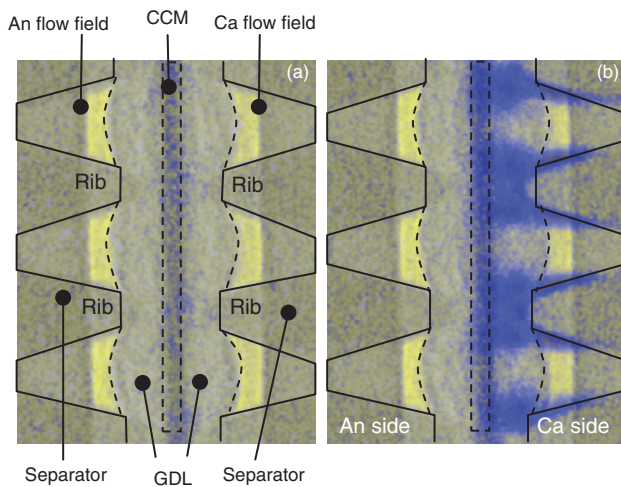


Fig. 10 Change in liquid water distribution during electric generation (a) $t = 0 \text{ min}$, (b) $t = 10 \text{ min}$

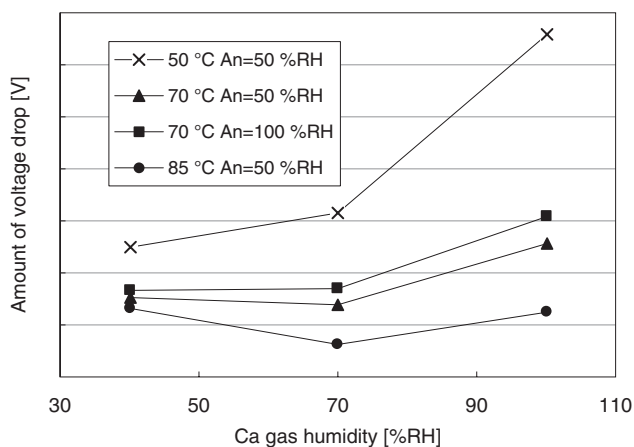


Fig. 11 Voltage drop of each test condition

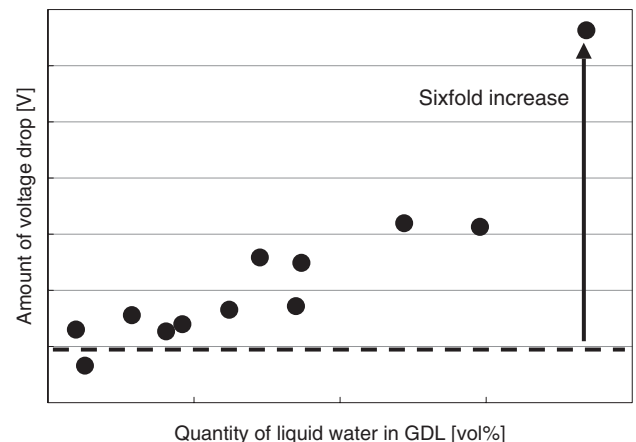


Fig. 12 Relation between voltage drop and liquid water in GDL

Figure 14 shows the neutron visualization image under these conditions, and indicates that these conditions result in the minimum quantity of liquid water in the CCM needed to reduce the resistance overpotential to a constant value as shown in Fig. 13. When drier conditions are used, the PEM cannot retain sufficient liquid water, which increases the resistance overpotential. When wetter conditions are used, the quantity of liquid water in the GDL increases, which reduces the effective electric generation area. Both of these cases are thought to result in lower performance.

When considering the ideal water distribution in the MEA, it is thought important to retain a sufficient quantity of liquid water in the CCM (PEM) to manifest proton conduction functions, while at the same time minimizing the quantity of liquid water in the GDL that reduces the effective electric generation area. However, when the cell temperature, gas humidity or other electric generation

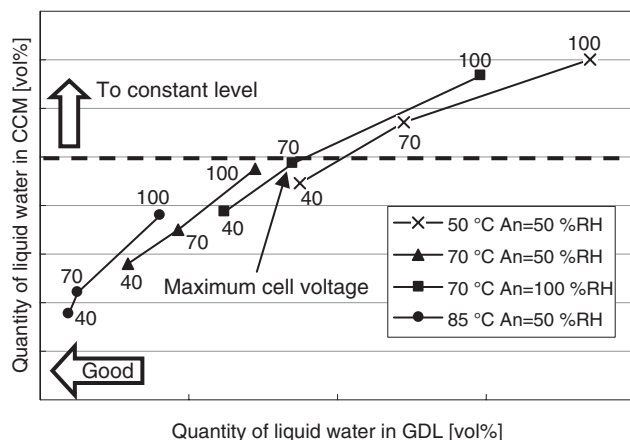


Fig. 13 Relation between liquid water in CCM and GDL (represented by cathode gas humidity)

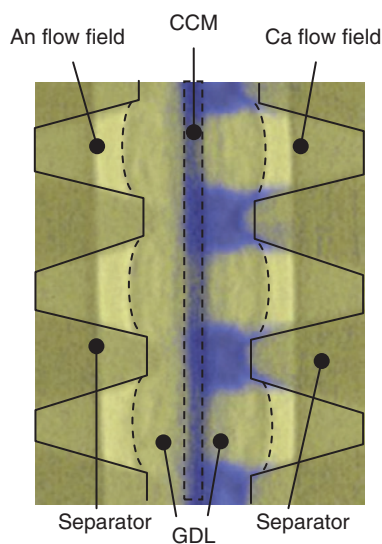


Fig. 14 Image of liquid water distribution under the best condition (An gas: 100 %RH, Ca gas: 70 %RH)

conditions are simply changed, the quantity of liquid water in the GDL increases together with that in the CCM. Therefore, to enhance electric generation performance, it is considered necessary to develop materials, optimize layer structures, and investigate flow field structures in order to approach the ideal water distribution in the MEA.

6. Conclusion

The water distribution during electric generation was visualized and quantified using neutron radiography to verify the relationship between the resistance overpotential and amount of voltage drop during constant-load electric generation, which affect the electric generation performance of fuel cells, and the quantity of liquid water in each part of the MEA. The results were as follows.

- (1) The resistance overpotential tends to drop as the quantity of liquid water in the CCM increases, but becomes constant at a certain quantity of liquid water or more.
- (2) The amount of voltage drop increases after the start of constant-load electric generation as the quantity of liquid water in the GDL increases.
- (3) The electric generation environment that can provide high electric generation performance is the environment in which the quantity of liquid water in the CCM (PEM) is the minimum required to manifest proton conductivity. However, further material development and flow field design are needed to realize the ideal water distribution.

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