

Development of in-situ X-ray Imaging Technologies for Measuring Water Distribution in Generating PEFC

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ABSTRACT

Water management in fuel cells is a key technology for enhancing the performance and durability of polymer electrolyte fuel cells (PEFC), and water transport phenomena in PEFC have to be clarified.

In-situ measurement techniques in generating PEFC using X-ray computed tomography (CT) and X-ray radiography were developed, and water transport phenomena in the Gas Diffusion Layer (GDL) and gas channels were analyzed.

The water inside the GDL was observed to increase in accordance with the current density, and it was also observed that water is discharged from the GDL to the channels along the hydrophilic channel wall surfaces. In addition, image processing was performed, and the water distribution inside the GDL during generation was quantitatively evaluated. The results confirmed that a large amount of water easily accumulates in the GDL under the rib.

1. Introduction

In recent years, fuel cells have been the focus of attention as a high-efficiency, zero-emission energy conversion system. Polymer electrolyte fuel cells (PEFCs), in particular, are the target of research and development as a next-generation automobile power source due to its low operating temperature and high output density. One advantage of PEFC is that only water is emitted. On the other hands, water management is an important issue. To further enhance PEFC generation performance and durability, it is necessary to prevent the condensed water in the catalyst layers, Gas Diffusion Layers (GDLs) and gas channels from impeding the diffusion and flow of oxygen, while at the same time maintaining an appropriate water content to prevent the proton exchange membrane from drying out. The water transport mechanism must be clarified to solve this type of water management issue, so active efforts are underway to develop measurement technologies that uses neutron imaging⁽¹⁾ and Magnetic Resonance Imaging (MRI)⁽²⁾, and prediction technology based on numeric simulations⁽³⁾. Though X-ray computed tomography (X-ray CT) is also used to measure water in PEFCs, most of the measurements are made after generation. However, since water distribution after generation is different from that during generation, measurement after generation is insufficient to clarify the water transport mechanism during

generation. In addition, the fibrous structure of the GDL and the water are not separated and water distribution in PEFC was not evaluated quantitatively^{(4), (5)}. Therefore, in this study, measuring technologies are developed for quantitative evaluation of the water distribution in the GDL and the gas channels. These include X-ray CT to measure the three-dimensional water distribution inside a generating fuel cell with high spatial resolution, X-ray radiography to measure the dynamic behavior of water with high temporal resolution, and image processing to evaluate the water distribution quantitatively.

2. Analysis of Water Transport Using X-ray CT

2.1. Overview of X-ray CT Imaging

X-ray CT is a technique for generating a three dimensional image by collecting attenuated transmitted X-ray signal data while rotating the X-ray source and detector or the observation sample by 180° or 360°⁽⁶⁾. Compared to MRI and neutron imaging, X-ray CT has the advantages of a high spatial resolution (in submicron-order), the ability to measure both the 3D object structure and the water distribution, low cost, and high safety. On the other hand, the X-ray absorption coefficient is proportional to the molecular mass, so X-ray CT has lower sensitivity for water molecules, which include hydrogen atoms that have a small molecular mass, compared to neutron imaging which

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has better sensitivity to substances with a small molecular mass. This issue, however, can be solved by reducing the X-ray energy and enhancing the S/N ratio of the carbon and the water and pores.

Figure 1 shows an overview of the X-ray CT measuring system. The X-ray tube used a reflective-type sealed tube with tungsten as both the filament material and the target material, and the detector used a 1.45 M-pixel CCD with an image intensifier. Measurement was performed at a tube voltage of 110 kV and a tube current of 80 μ A.

The spatial resolution of the image is determined by the relative positions of the X-ray source, observation sample and detector, and the detection element matrix as shown in Eq. (1).

$$S = D/(L/I)/A \quad (1)$$

Here, S is the spatial resolution, D is the effective photoreceptor size, L is the distance from the X-ray source to the detector, I is the distance from the X-ray source to the observation sample, and A is the detection element matrix. In addition, L/I is the projection magnification ratio, and the spatial resolution increases as the sample approaches the X-ray source. In this test, the cell was located at a distance of 2.5 mm from the X-ray source. In consideration of the balance between the degree of geometric shape detail, the contrast and the measurement time, the number of views was set at 1000, the average number of frames at 20, and the time per CT scan at 30 minutes, and measurement was performed with a spatial resolution of 2.5 μ m.

Figure 2 shows an exploded view of the fuel cell used for X-ray CT measurement. The electrode area was 10 mm x 10 mm, and consisted of a 15 mm x 15 mm carbon separator with 11 straight channels each having a groove width of 0.5 mm, peak width of 0.5 mm, and depth of 0.5 mm. The temperature was measured by a thermocouple and adjusted with a ceramic heater. To obtain high contrast CT images of the GDL and the channels, the cell was positioned horizontally relative to the X-ray source, so that only a small portion of the X-ray beam transmits through the catalyst layer containing platinum with a large X-ray attenuation coefficient (Fig. 1). In addition, a boltless surface pressure rotating mechanism was developed to

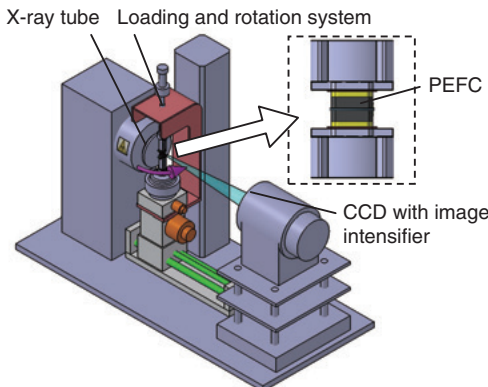


Fig. 1 X-ray CT imaging system

avoid X-ray attenuation due to the metal parts used in the cell surface pressure supporting bolts. The fuel cell was rotated while performing control to maintain a constant load using a surface pressure cylinder. When generation was performed at a constant current, there was no cell position offset or gas leaks, and measurement could be performed at a constant cell voltage.

2.2. Experimental Procedure

The proton exchange membrane used a DuPont NR212, and the catalyst layer was composed of a platinum content of 0.5 mg/cm², carbon content of 0.5 mg/cm², and an electrolyte content of 0.38 mg/cm². In addition, the GDL used Toray TGP-H-060 carbon paper, and constant current aging tests were performed at 0.6 A/cm² with the GDL assembled into the fuel cell. Following the aging tests, the Membrane Electrode Assembly (MEA) and GDL were removed from the cell and vacuum degassing was performed to completely saturate the insides of the MEA and GDL with water. The MEA and GDL were then reassembled into the fuel cell in the completely water-saturated condition and X-ray CT measurement was performed to obtain reference images in the completely water-saturated condition. After that, N₂ purge was performed and X-ray radiography was used to confirm the internal drying process to the dry condition, and then the interior condition of the fuel cell was measured using X-ray CT to obtain reference images in the dry condition.

After that, generation was performed at a constant current density, and X-ray radiography and CT measurement were performed while maintaining a stable voltage. Image processing was performed on the results to visualize the water distribution and quantify the saturation distribution inside the GDL.

2.3. X-ray CT Measurement Results

Hydrogen moisturized at a dew point temperature of 300 K was supplied to the anode side at a rate of 50 ml/min, oxygen moisturized at a dew point temperature of 300 K was supplied to the cathode side at a rate of 150 ml/min, and the test was performed at a cell temperature of 300 K.

Figure 3 shows a fuel cell image reconstructed in three dimensions by X-ray CT. This image is the result of observing the 2.5 mm diameter area around the center axis of the fuel cell shown in Fig. 2. The top side of Fig. 3 is the

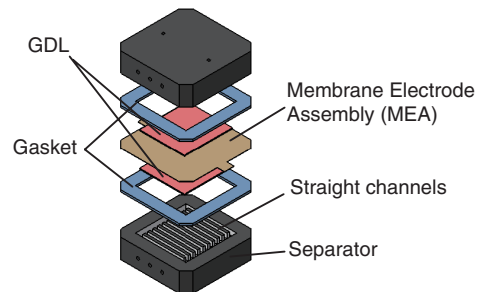


Fig. 2 Fuel cell for X-ray CT imaging

anode, the bottom side is the cathode, the green rectangular areas indicate the gas channels, and the orange rectangular areas indicate the separator ribs. In addition, the red areas indicate the GDLs, and the blue area indicates the MEA (catalyst layers and proton exchange membrane). Figure 4

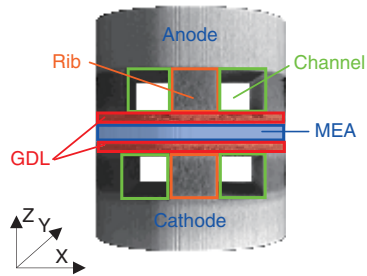


Fig. 3 Three dimensional X-ray CT image of PEFC

shows the I-V performance curve of this fuel cell, and Fig. 5 shows CT slice images obtained under some generating conditions. The respective images in Fig. 5 show (1) the reference images (dry condition), (2) the images at a current density of 0.30 A/cm², (3) the images at a current density

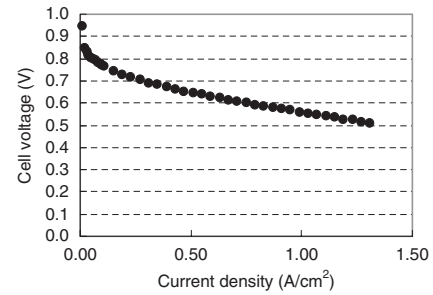


Fig. 4 I-V performance curve of PEFC

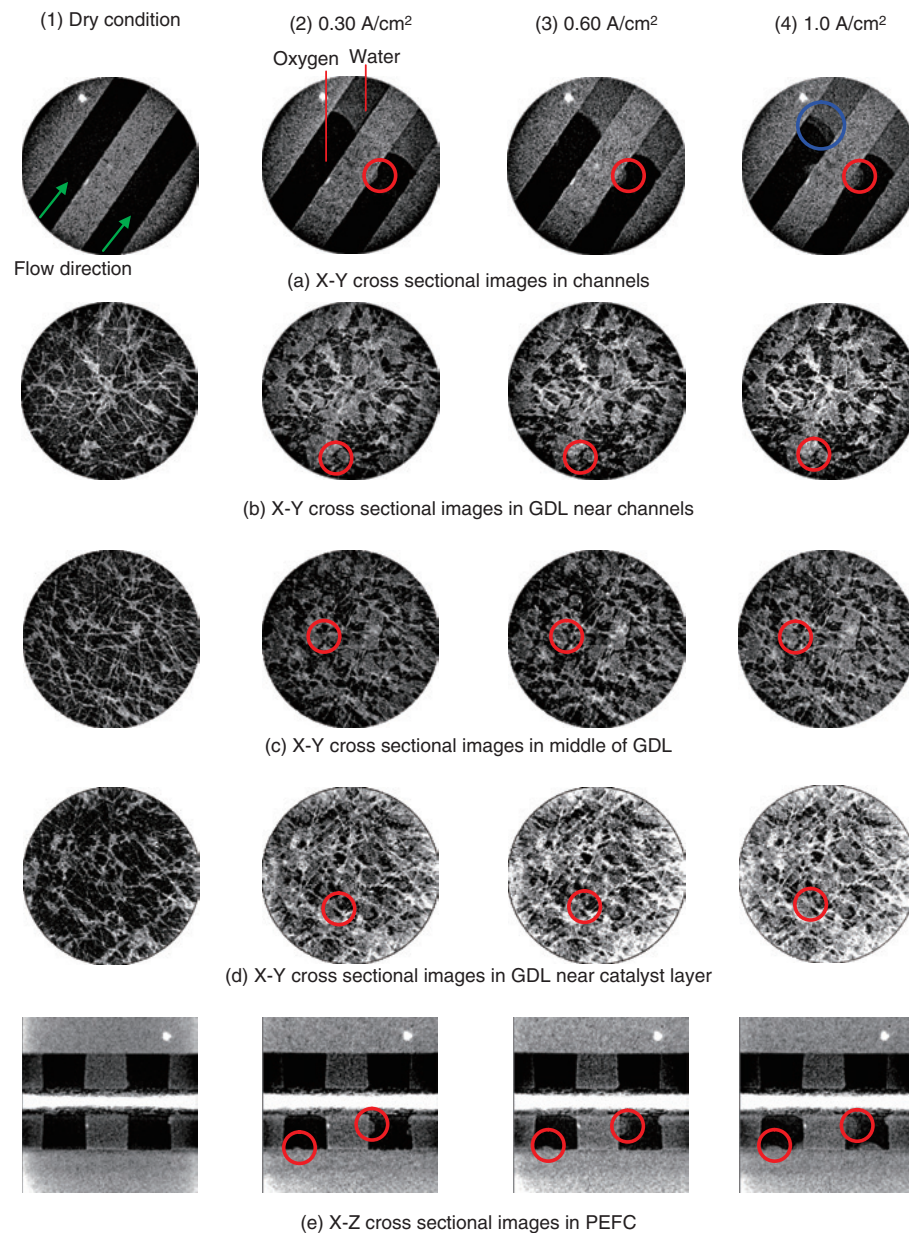


Fig. 5 Cross sectional images in generating PEFC

of 0.60 A/cm^2 , and (4) the images at a current density of 1.0 A/cm^2 . In addition, (a) to (e) show the images at the cathode, and are respectively (a) the (X-Y) cross-sections in the center of the channels, (b) the (X-Y) cross-sections of the GDL near the channels, (c) the (X-Y) cross-sections in the center of the GDL, (d) the (X-Y) cross-sections of the GDL near the catalyst layer, and (e) the (X-Z) cross-sections of the cell. The areas enclosed by the red circles show examples of the generated water.

Figure 5(a) shows the plugging phenomenon whereby liquid water is discharged to the channels at a current density of 0.30 A/cm^2 or more, with the result that the water blocks the channels. In addition, this water in the channels does not move much, so the contact boundary between the separator and the water can be observed, and the change in wettability can be measured. Figure 5(b) through Fig. 5(d) show that the water inside the GDL increases in both quantity and droplet size as the current density increases, and that the quantity of water tends to increase from the gas channel side towards the catalyst layer side. In addition, Fig. 5(e) shows that size of the water droplets in the channels increase as the current density increases. Traces of the water boundary inside a channel having moved during one rotation (30 min) of the cell can be confirmed in the area enclosed by the blue circle in Fig. 5(a)-(4). In this manner, the water distribution inside a generating fuel cell could be measured by using X-ray CT. Next, image processing technique was applied to quantify the water.

2.4. Image Processing Procedure

Image processing was performed on the data obtained by X-ray CT to identify and quantify the water distribution inside a generating fuel cell. Water stays statically under

the test conditions used in this study, so images with good contrast could be obtained. Therefore, the water distribution was extracted by the procedure shown in Fig. 6.

- (1) The dry condition images were converted to binary images and divided into fiber parts and pore (oxygen mixed with water vapor) parts, while taking into account the histogram of each cross-section and the diameter of the GDL carbon fibers.
- (2) The generating condition images were converted to binary images and divided into pore parts and fiber with water parts in the same manner as in step (1).
- (3) 3D position alignment was performed for the images obtained in steps (1) and (2) to eliminate the effects of expansion of the proton exchange membrane and thermal expansion of the materials due to generation.
- (4) The difference between the images aligned in step (3) was obtained, and the distribution of the water that increased during generation was extracted.
- (5) 3D ternary voxel data of the pores, fibers and water was created using the water data separated in step (4) and the data in step (1).

2.5. Image Processing Results

Figure 7 shows the water distribution extraction results. The respective images in Fig. 7 show (1) the images in the dry condition after N_2 purging, (2) the images at a current density of 0.30 A/cm^2 , (3) the images at a current density of 0.60 A/cm^2 , and (4) the images at a current density of 1.0 A/cm^2 . In addition, (a) to (d) show the images at the cathode, and are respectively (a) the (X-Y) cross-sections in the center of the channels, (b) the (X-Y) cross-sections of the GDL near the channels, (c) the (X-Y) cross-sections of the GDL near the catalyst layer, and (d) the (X-Z) cross-

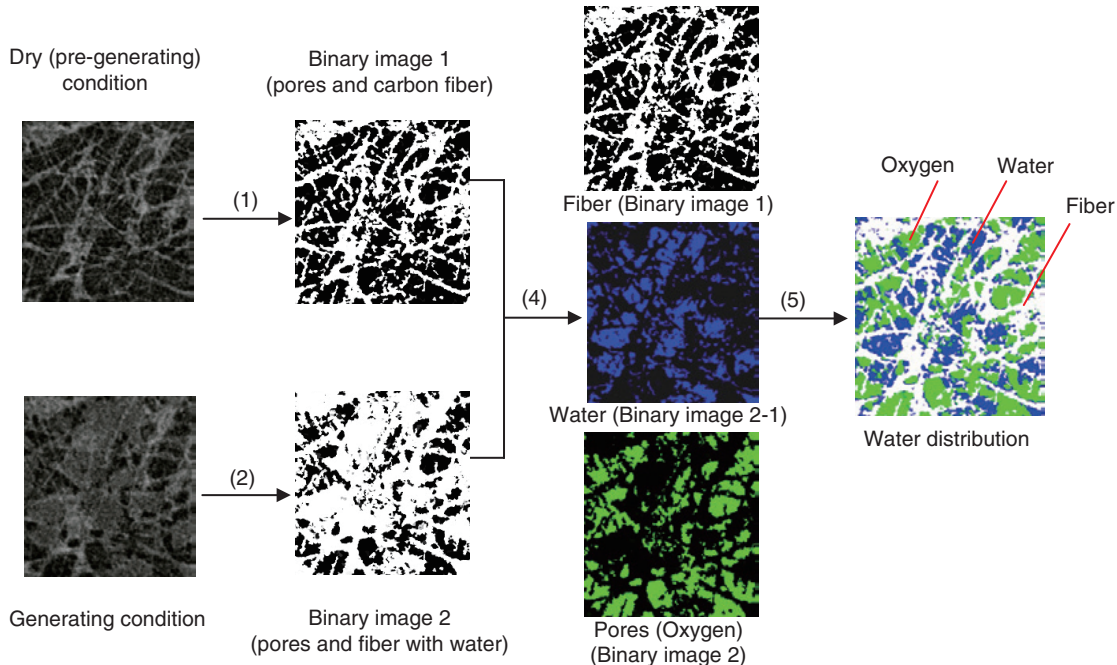


Fig. 6 Image processing procedure

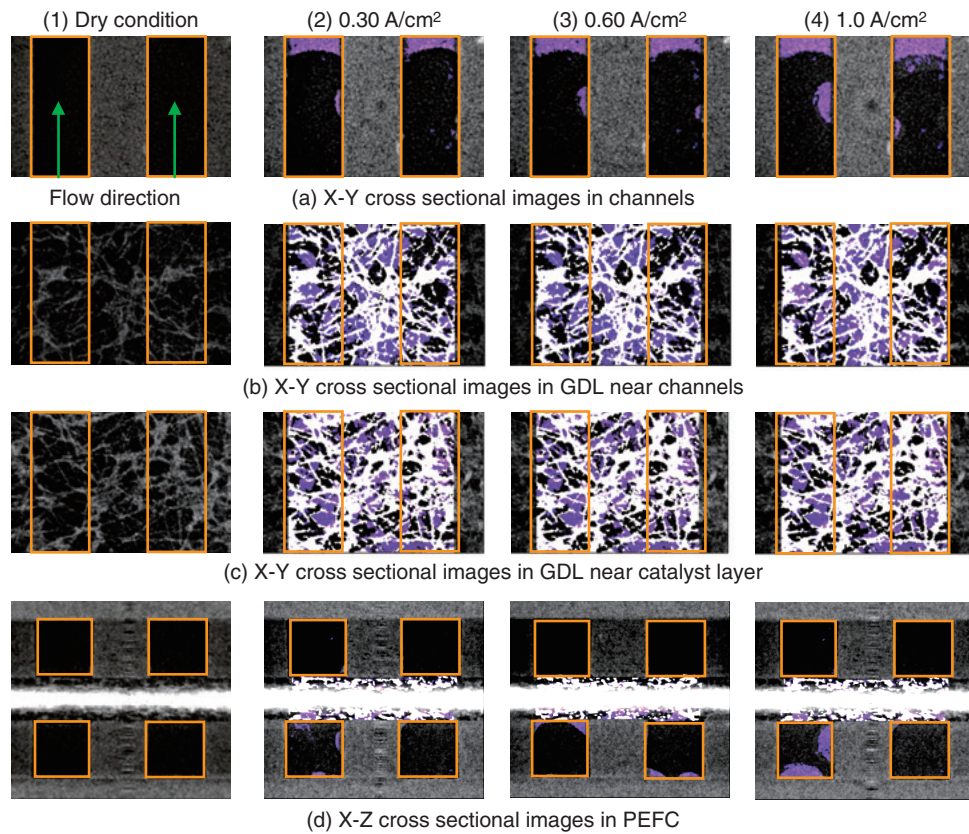


Fig. 7 Cross sectional images in generating PEFC

sections of the cell. As shown by the purple color in Fig. 7, the water distribution inside the generating fuel cell could be extracted by the image processing procedure described above.

Figure 8 shows a 3D representation of the water distribution inside the cathode gas channel and GDL at 1 A/

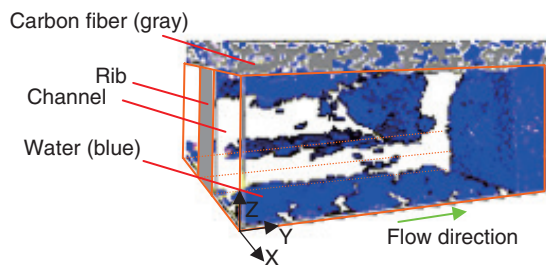


Fig. 8 Three dimensional water distribution in GDL and gas channels obtained by X-ray CT imaging

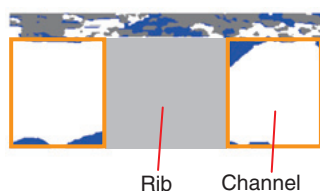


Fig. 9 X-Z cross sectional image

cm^2 . The condensed water adhering to the gas channel wall surface opposite the GDL, water being discharged along the channel wall surface, and the plugging phenomenon can all be confirmed from Fig. 8.

In addition, Fig. 9 shows the X-Z cross-sectional image and Fig. 10 shows the X-Y cross-sectional image of the water inside the GDL directly under the channels and rib. Figures 9 and 10 confirm that a large quantity of water accumulates in the GDL under the rib, and that there is less water in the GDL directly under the channels than directly under the rib.

Next, Figs. 11(a) and 11(b) show the results of analyzing the water saturation distribution at positions from the catalyst layer side to the channel side of the cathode GDL, based on the water distribution extracted by the 3D

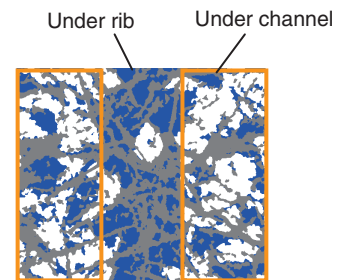


Fig. 10 X-Y cross sectional image directly under rib and channels

processing described above. Here, the water saturation is defined as the percentage of the pore area inside the GDL occupied by water. Figure 11(a) shows the water saturation distribution in the area under the channel, and Fig. 11(b) shows the water saturation distribution in the area under the rib. Overall, the area under the rib exhibits a higher water saturation than the area under the channel, and the water saturation in the area under the channel tends to decrease from the catalyst layer side towards the channel. Conversely, the water saturation in the area under the rib tends to be higher directly under the rib compared to the catalyst layer side.

The factors for water accumulating under the rib are thought to be as follows.

- (1) The separator that forms the rib is hydrophilic; that is to say, contact angle of the water becomes smaller so the water moves less easily.
- (2) The discharge distance under the rib to the channels is long, and the GDL pores also become crushed, so gas does not flow easily and the gas flow cannot easily remove the water.
- (3) The rib is a part of the separator that is cooled by the outside air, so water condenses easily.

A large quantity of water accumulates under the rib even in tests at room temperature such as the tests in this study. This indicates that wettability and pore crushing under the rib have a large effect on the water discharge behavior from the GDL to the gas channels.

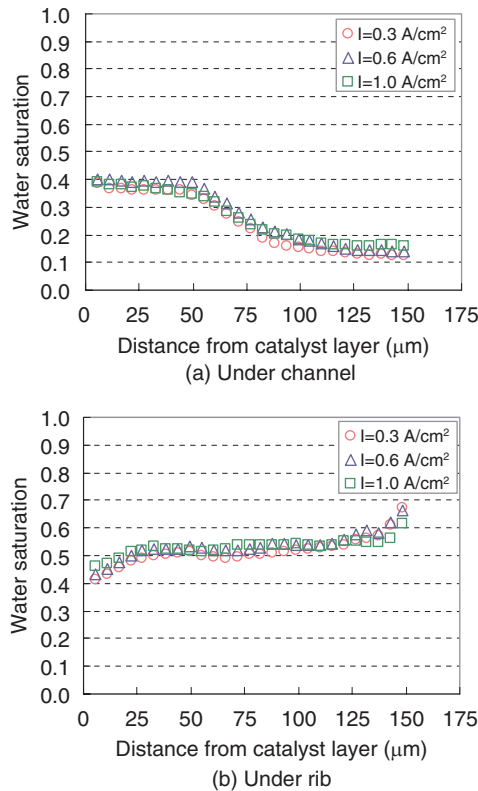


Fig. 11 Water saturation in GDL

3. Analysis of Water Transport Using X-ray Radiography

3.1. Overview of X-ray Radiography Imaging

The X-ray radiography method acquires X-ray transmission images without rotating the observation subject in the manner of X-ray CT. This means that the structure and water distribution cannot be measured in three dimensions, but real-time observation is possible. In the X-ray radiography tests, the X-ray tube used lanthanum hexaboride (LaB6) as the filament material, and a transmission-type open tube with tungsten as the target material. The detector used a 5 M-pixel CCD with an image intensifier, and measurement was performed at a tube voltage of 70 kV and a tube current of 110 μA . The exposure time was 3 s, and measurement was performed at a spatial resolution of 4.3 μm . Figure 12 shows the fuel cell used in the X-ray radiography tests. The electrode area was 10 mm x 9.3 mm, and used a 15 mm diameter carbon separator with three trapezoidal straight channels having a lower side length of 2.1 mm, an upper side length of 0.58 mm, and a height of 0.58 mm. The test procedure and image processing procedure conformed to the X-ray CT tests. Hydrogen moisturized at a dew point temperature of 310 K was supplied to the anode side at a rate of 50 ml/min, air moisturized at a dew point temperature of 317 K was supplied to the cathode side at a rate of 200 ml/min, and the test was performed at the three cell temperature conditions of 323 K, 328 K and 333 K.

3.2. X-ray Radiography Measurement Results

The effects of cell temperatures on the internal water distribution were analyzed. Figure 13 shows an image transmitted in the X direction through the fuel cell shown in Fig. 12, with each cell component labeled. The top part is the anode, and the bottom part is the cathode. In addition, the green areas indicate the gas channels, the orange areas

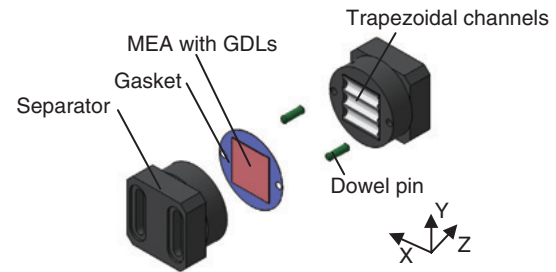


Fig. 12 Fuel cell for X-ray radiography imaging

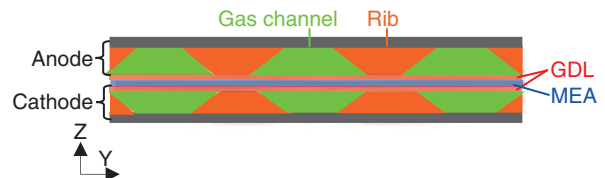


Fig. 13 X-ray radiography image of PEFC

indicate the separator ribs, the red areas indicate the GDL, and the blue area indicates the MEA. Figure 14 shows the change over time in the water content distribution inside the PEFC during the 1 A/cm² constant current test at a cell temperature of 328 K. The water content was normalized and calculated using the dry condition image and the image of the completely water-saturated condition after degassing. These images confirm that starting from the dry condition in Fig. 14(a), water produced by generation accumulates in the GDL under the ribs [Fig. 14(b), (c)], and this water is then discharged from under the ribs along the channel wall surfaces to the gas channels [Fig. 14(d), (e)]. Figure 15 shows the change over time in the water content inside the cathode GDL and gas channels at the cell temperatures of 323 K, 328 K and 333 K. At 328 K and 333 K the internal water content reaches a steady state, but at 323 K the water did not reach a steady state and continued to increase. This is thought to occur because, at a cell temperature of 323 K, the water vapor contained in the supplied gas and the water vapor produced by generation cannot be completely eliminated, and condense in the GDL and channels. Figure

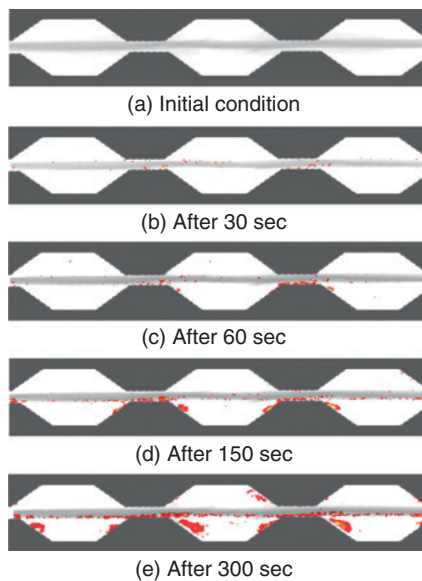


Fig. 14 X-ray radiography images

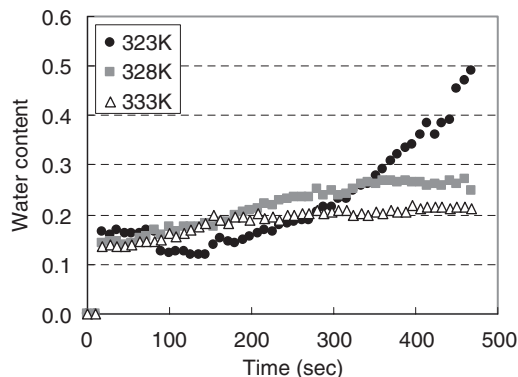


Fig. 15 Effect of operating temperature on water content in GDL and gas channels

16 shows a graph of the water content inside the cathode GDL and gas channels at 450 s after the start of generation. Figure 16 shows that when the cell temperature increased from 323 K to 328 K, the water content in the gas channels decreased by more than the water content in the GDL, and when the cell temperature increased from 328 K to 333 K, this difference became smaller. This indicates that the water inside the channels dried faster than that inside the GDL. In this manner, the change in water distribution over time could be measured using X-ray radiography.

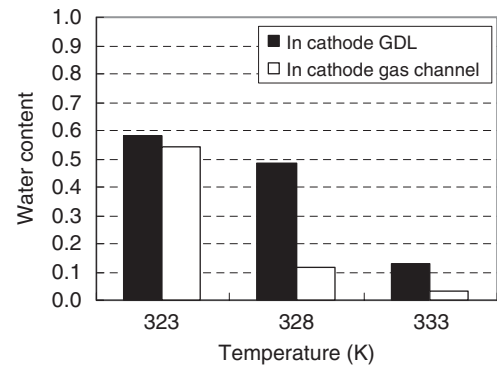


Fig. 16 Water content in GDL and gas channels

4. Conclusion

An X-ray CT measuring system that can measure the water distribution in a generating fuel cell in three dimensions with high spatial resolution and contrast, and an X-ray radiography system that can analyze the dynamic behavior of water with high temporal resolution were developed. Image processing technology was also developed, and the water distribution was quantitatively analyzed. The results showed that water produced by generation easily accumulates inside the GDL near the catalyst layer and under the ribs and water is discharged from the GDL to the channels along the separator. In addition, the plugging phenomenon, water condensation on the channel wall surfaces, and the growth process of the condensed water were also observed.

In the future, X-ray CT, which has high 3D spatial resolution, and X-ray radiography, which has high temporal resolution, will be combined to analyze the effects of operating temperature and the supply gas velocity and humidity on water discharge behavior. In addition, the optimal materials and structure will also be investigated.

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