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Short communication

Super-cooled water behavior inside polymer electrolyte fuel cell cross-section below freezing temperature

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Abstract

This study investigated the phenomenon of water freezing below freezing point in polymer electrolyte fuel cells (PEFCs). To understand the details of water freezing phenomena inside a PEFC, a system capable of cross-sectional imaging inside the fuel cell with visible and infrared images was developed. Super-cooled water freezing phenomena were observed under different gas purge conditions. The present test confirmed that super-cooled water was generated on the gas diffusion layer (GDL) surface and that water freezing occurs at the interface between the GDL and MEA (membrane electrode assembly) at the moment cell performance deteriorates under conditions when remaining water was dry enough inside the fuel cell before cold starting. Moreover, using infrared radiation imaging, it was clarified that heat of solidification spreads at the GDL/MEA interface at the moment cell performance drops. Compared with a no-initial purge condition, liquid water generation was not confirmed to cause ice growth at the GDL/MEA interface after cell performance deterioration. Each condition indicated that ice formation at the GDL/MEA interface causes cell performance deterioration. Therefore, it is believed that ice formation between the GDL/MEA interface causes air gas stoppage and that this blockage leads to a drop in cell performance.

Keywords: PEM; Fuel cell; Cold start; Freezing point; Ice; Super-cooled water

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been attracting much attention as a clean source of power for vehicles, and researchers have been actively pursuing ways of utilizing these fuel cells in recent years. The problem, however, is that when operating a fuel cell below freezing point, water generated in the catalyst layer is frozen inside the fuel cell, resulting in a drop in fuel cell performance. Therefore, understanding the mechanism of water freezing is critical to achieving high performance of polymer electrolyte fuel cells for cold starts. As noted previously, generated water freezes in PEFCs below freezing point if the pores in the catalyst layer and gas diffusion layer are filled with ice, or if the catalyst layer surface is clogged with ice to such an extent that the transport of reactant gases to the electrodes is hindered. Both cases lead to substantially deteriorated cell performance.

In spite of the importance of PEFC cold-start capability, very few studies in the literature have focused on PEFC cold-start water dynamics.

Ge et al. [1] point out that liquid water generation was visualized using a transparent fuel cell at −3 °C. Nevertheless, details about the water freezing mechanism and temperature change dependency on the ice formation process were not carried out. Saito et al. [2] have discussed that water in the proton exchange membrane freezes below −15 °C. However, water behavior of the generated water below freezing point was not investigated. Nakamiya et al. [3] took apart a fuel cell and observed the catalyst layer surface after cold start and found that many ice particles formed on the catalyst layer surface. However, they mention that details about the freezing mechanism were still unknown.

So far, we have clarified the interesting phenomenon that water maintains a super-cooled state when the water is gen-

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erated on the catalyst layer surface below freezing point [4]. However, details of super-cooled water freezing phenomena inside the PEFC are not completely clarified yet and many items remain that should be discussed. Therefore, based on what we know about super-cooled water generation on the catalyst layer surface, we investigated the super-cooled water behavior inside the PEFC cross-section. In this experiment, water freezing phenomena inside the PEFC cross-section were clarified under different gas purge conditions using a real-time cross-sectional observation system in order to explain the freezing area that causes the cell performance deterioration.

Prior experimental efforts to probe the water distribution and temperature change of water in an operating PEFC have included neutron radiography [5–7], optical visualization using transparent fuel cells [8–10], and temperature measurement using thermocouples [11] or a thermograph [12]. It is noted that neutron radiographic imaging enables non-destructive analysis of water behavior. However, confirming the phase change (liquid water/ice) of water and measuring the water temperature is difficult to achieve using neutron imaging.

Instead of neutron imaging, traditional optical diagnostics tools could be used to observe the liquid water in the fuel cell but these tools are not applicable to thermal imaging because of the transmission properties of the windows material. So far no reports are known to have realize visible and infrared simultaneous and coaxial observation inside the PEFC cross-section using these fuel cell optical visualization tools.

Accordingly, we developed a system that enables observation of water transport and the spread of heat of solidification inside the PEFC cross-section using simultaneous visible and infrared imaging.

In an actual environment of a fuel cell in a vehicle, the fuel cell is controlled above freezing point before cold start. Thus, an initial operation was performed at room temperature before cold start. Generally speaking, the gas purge process is critical when starting the fuel cell below freezing point. Nevertheless, the behavior of super-cooled water inside the PEFC cross-section depends on the gas purge conditions, which are still unknown. Therefore, in the present experiment the behavior of super-cooled water inside the PEFC cross-section was visualized in two different gas purge conditions. And each condition indicated that ice formation at the GDL/MEA interface causes cell performance deterioration.

2. Experiment

2.1. Water visualization and temperature measurement method of generated water

The experimental setup for in situ visualization of PEFC super-cooled water behavior inside PEFC cross-section in order to clarify the details of water freezing phenomena is shown in Fig. 1. To realize cross-sectional imaging inside the PEFC, visible and infrared transmission material (sapphire glass) is placed at the edge of the cathode bipolar plate. This window provides optical access to the GDL cross-section, enabling water behavior there to be visualized using a microscope from outside the fuel cell. Furthermore, the spread of heat of solidification was confirmed by simultaneously using a thermograph.

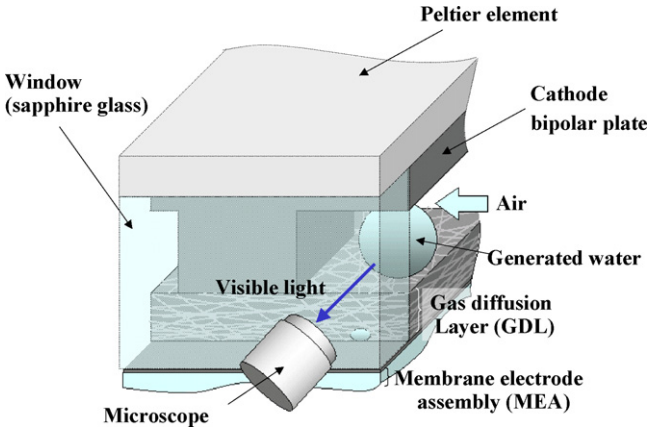

Fig. 1. Schematic image of system for visualizing inside PEFC cross-section.

The water temperature was measured using thermal imaging (space resolution 10 μm, temporal resolution 1/30 s frame^{-1}), while the water behavior was observed using a microscope under adequate illumination. This measurement system enabled simultaneous real-time observation of the fuel cell cross-section during power generation using both visible and infrared imaging.

In the present tests, carbon papers (SIGRACET GDL 25BC by SGL GROUP) were used as a gas diffusion layer (GDL), and the total active area of the cell was 13 cm^2 as defined by gaskets. Pure hydrogen and ambient air were used as the fuel and oxidant, respectively. The cell was operated at atmospheric pressure (0 kPaG) for both the fuel and the air.

Based on our previous test that investigates the measurement error of the thermal images, the water temperature was measured using thermocouples and a thermograph simultaneously. In this result it was confirmed that the water temperature error ($T_{\text{Thermocouple}} - T_{\text{IR}}$) was less than ±1 °C [4]. Moreover, the infrared radiation rate of the GDL (0.9) made from carbonate material is equal to the rate of water (0.9), leading to the belief that the measurement error of the GDL is equal to that of the water.

In the present experimental setup, the microscope and thermograph are unable to cool down below the freezing point because of the operating temperature range (0–40 °C). Therefore, a device to cool only the test cell was needed. A Peltier element was used to cool only the test cell (Fig. 1). The Peltier element was placed against both sides of the anode and cathode separator, the fuel cell cooled with the Peltier element, and the cell compressed with the Peltier element using a pressure jig. The cell was kept constantly cool with the Peltier element during power generation; therefore this system enables isothermal cold-start testing.

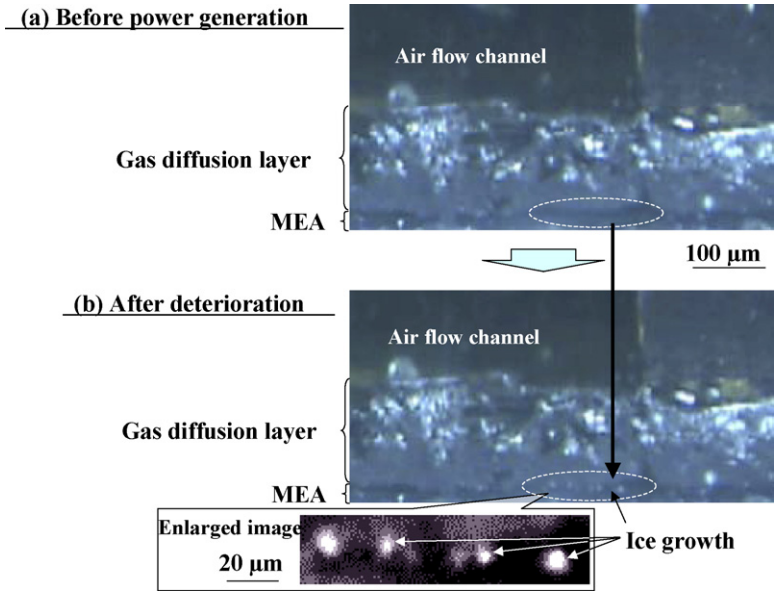

Fig. 2. Visible image inside PEFC cross-section with no purge: (a) before power generation and (b) after performance deterioration.

3. Results and discussion

3.1. Cell performance and super-cooled water behavior when initial gas purge was not performed

Fig. 2 shows the visible images inside the PEFC cross-section before and after cell performance deterioration at −10 °C in the no-purge condition. After cell performance deterioration, ice growth was confirmed at the interface between the GDL and MEA (Fig. 2(b)). This result indicates that super-cooled water did not cause ice to grow at the GDL/MEA interface when the fuel cell was operated below freezing point in the no-purge condition. In this condition, current density was very low (0.17 A cm^{-2}) and cell performance dropped immediately (Fig. 3).

3.2. Super-cooled water transport inside the PEFC cross-section below freezing point after initial purge was performed

Before cold starting the fuel cell, residual water inside the test cell was purged using non-humidified reactant gas (ambient air and H_2, 55 °C) until the visible image showed that all remaining water had disappeared inside the PEFC cross-section. Under power generation, the test cell had a fixed operating temperature of −10 °C using the Peltier element, and the voltage was held at 0.5 V.

Fig. 4 shows an image of super-cooled water transport at cold start with the purge process. It is demonstrated that super-cooled water is generated on the GDL surface at 142.5 s (Fig. 4(b)). Thereafter, the water droplet growing on the GDL intermittently

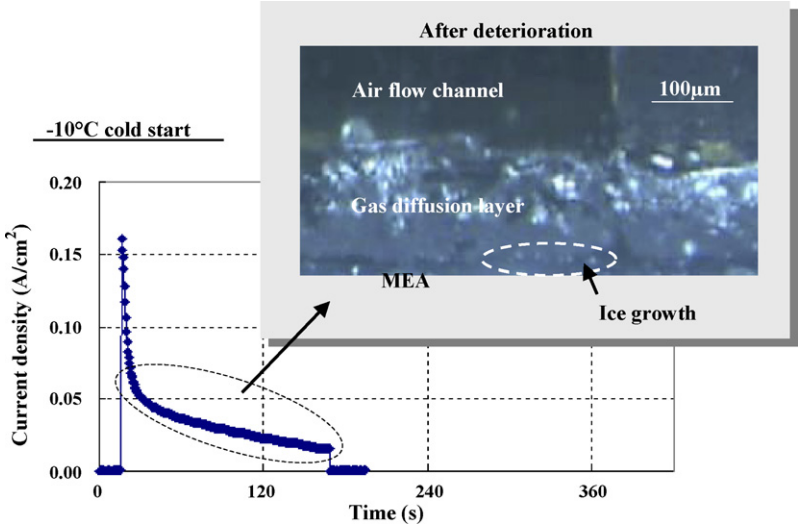

Fig. 3. Current profile at −10 °C cold start with no purge, with image of ice formation at GDL/MEA interface.

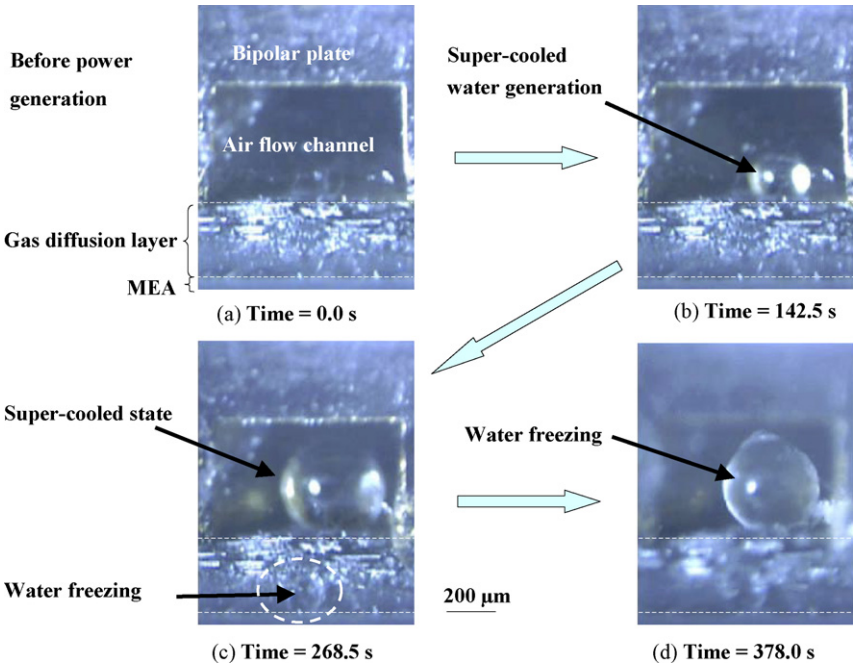

Fig. 4. Super-cooled water behavior inside PEFC cross-section with purge: (a) before power generation, (b) liquid water generated on GDL surface, (c) water freezing at GDL/MEA interface, and (d) water droplet on GDL surface freezes.

remains in a liquid state. Clarification is then seen of water freezing at the GDL/MEA interface at 268.5 s (Fig. 4(c)), at the moment of cell performance deterioration (Fig. 5). At this moment, water droplets on the GDL surface help maintain a super-cooled state (Fig. 5). Moreover, it was confirmed that the water droplet on the GDL surface freezes after the cell performance drops at 378.0 s (Fig. 4(d)). After freezing, the upper shape of the water droplet changes to a triangular shape as the water crystallizes. This result shows that it is possible to generate water in a super-cooled state below freezing point if the purge process is performed after initial operation.

3.3. Spread of heat of solidification at moment of freezing with purge condition

Fig. 6 shows visible and thermal simultaneously observed images inside the PEFC cross-section. In the thermal image here, because the infrared radiation rate was adjusted for the GDL radiation rate, the temperature of the bipolar plate cannot be measured accurately due to the difference in radiation rates between the GDL (0.9) and bipolar plate (0.3). Based on these images, it was revealed that the GDL temperature is approximately −10 °C (Fig. 6(a)).

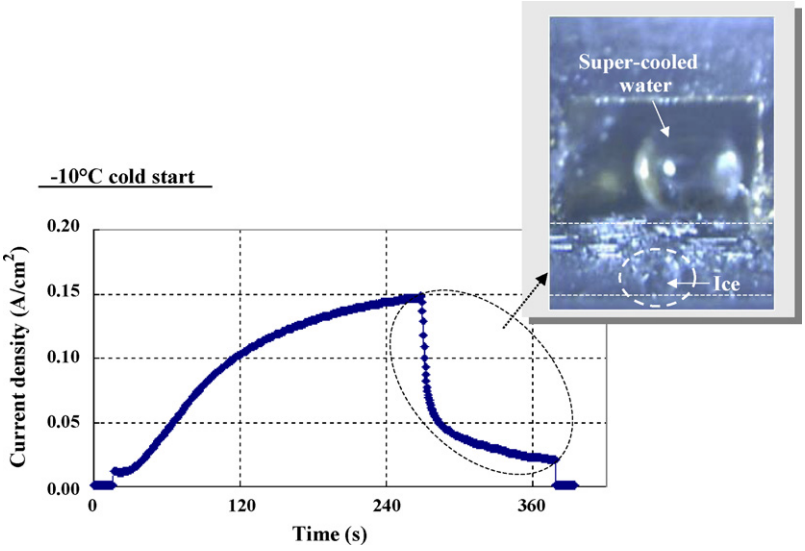

Fig. 5. Current profile at −10 °C after purging, with image of ice formation at GDL/MEA interface.

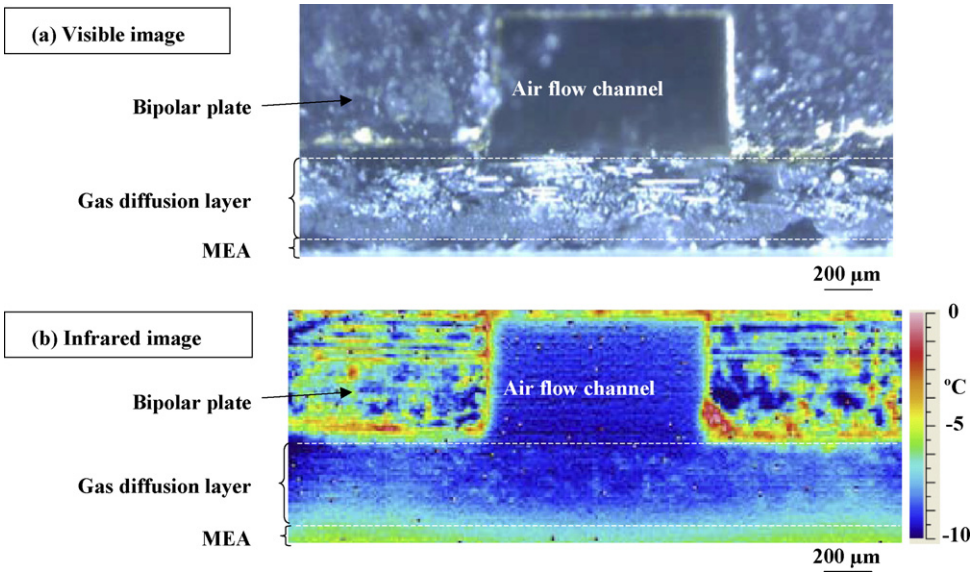

Fig. 6. Visible and infrared simultaneous observation images inside PEFC cross-section.

Fig. 7(b) shows the infrared radiation at the moment super-cooled water freezing occurs inside the PEFC cross-section. It is generally understood that when water in a super-cooled state begins to freeze, heat of solidification is emitted and the temperature rises [13]. The present study shows that the heat release that results from fuel cell water freezing is the same phenomenon that causes super-cooled water to freeze. Consequently, when a fuel cell is operated below the freezing point, it is determined that water is in a super-cooled state.

Fig. 7(b) confirms that heat of solidification radiates to the right side of the GDL. Fig. 7(c) shows the 1/30 s after freezing, the heat of solidification spreads to the left side of the GDL. Therefore, the thermal imaging results here indicate that super-cooled water freezing spreads momentarily at the GDL/MEA interface.

3.4. Water freezing phenomena and cell performance deterioration

Fig. 8 shows the ice formation inside the PEFC cross-section and current profile at −10 °C cold start under different gas purge conditions. When there is no-initial purge, liquid water generation was not confirmed in the visible image and ice grew at the interface between the GDL and MEA. In comparison, when an

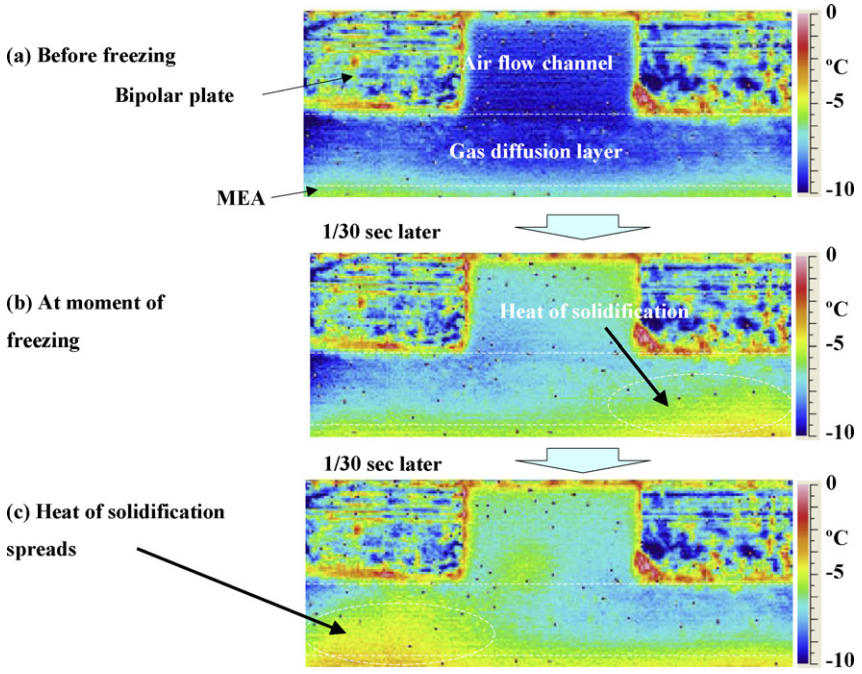

Fig. 7. Infrared images inside PEFC cross-section: (a) before freezing, (b) at moment of freezing, and (c) 1/30 s after freezing.

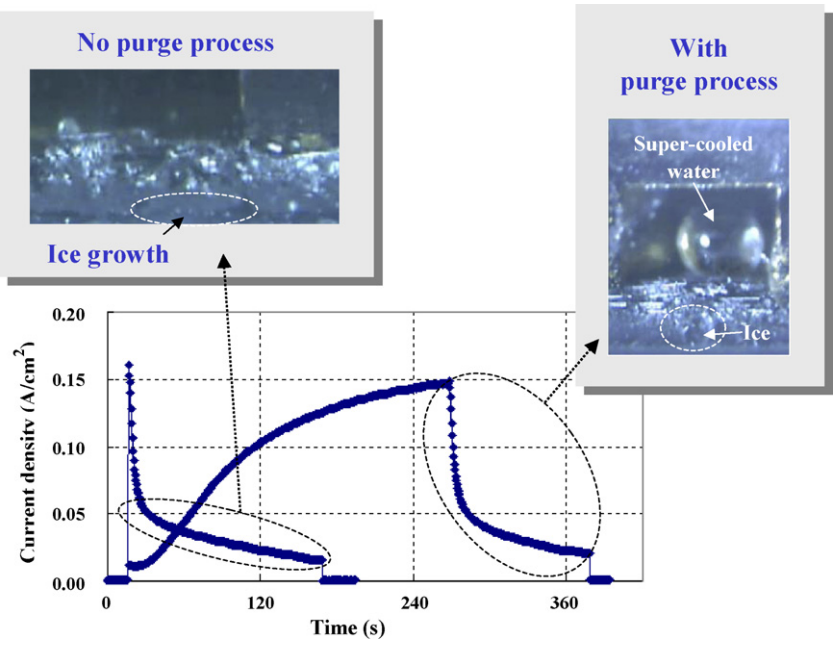

Fig. 8. Water freezing phenomena and cell performance deterioration with and without purge.

initial purge was performed, super-cooled water was generated on the GDL surface as the current density increased in the first 268.5 s, and water freezing at the GDL/MEA interface causes cell performance to drop (Fig. 8). Each condition therefore indicates that ice formation between the GDL/MEA interface causes cell performance deterioration.

These results highlight the reasons why super-cooled water generation was not confirmed in the no-purge condition. Generally speaking, a liquid below its freezing point will crystallize in the presence of a seed crystal or nucleus. However, lacking any such nucleus, the liquid phase can be maintained. In the fuel cell, it is assumed that the residual water turns to ice below freezing point and that this residual ice will crystallize into super-cooled generated water. Moreover, it is believed that a short purge time causes a large amount of residual water to remain in the GDL, and that these nucleuses of ice prevent liquid water generation on the GDL surface, thus causing ice growth at the GDL/MEA interface.

4. Conclusion

A system was actualized that enables real-time observation using visible and infrared images inside a PEFC cross-section. Using this system it was clarified that super-cooled water was not generated, and that when no-initial gas purge was performed, maximum fuel cell current density was very low ($0.15\ A\ cm^{-2}$) and ice grew at the GDL/MEA interface following cell performance deterioration. However, maintaining water in a super-cooled state is possible if the water remaining inside the gas flow channel and gas diffusion layer is adequately purged prior to a freezing start. Moreover, it was confirmed that water freezing at the interface between the GDL and MEA causes cell performance to drop. In general, it is well known that super-cooled water begins to freeze with core of ice. Therefore, it is reasonable to expect that the starting point of any super-cooled water freezing in the PEFC is the ice that remains after the purge process. In observing infrared images at the moment super-cooled water freezing occurs inside the PEFC cross-section, it was clarified that the heat of solidification spreads momentarily at the GDL/MEA interface. As a result, it is expected that ice formation at the interface between the GDL and MEA causes air gas blockage and that this blockage leads to decreased cell performance.

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