Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 163 (2007) 708–712
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Behavior of water below the freezing point in PEFCs

Y. Ishikawa[a,*], T. Morita[b], K. Nakata[b],
K. Yoshida[a], M. Shiozawa[a]

[a] Nippon Soken Inc., 14 Iwaya, Shimohasumi-cho, Nishio, Aichi 445-0012, Japan
[b] Toyota Motor Corporation, 1 Toyota-cho, Toyota, Aichi 471-8572, Japan

Received 12 July 2006; received in revised form 21 August 2006; accepted 23 August 2006
Available online 13 November 2006

Abstract

This study investigates the phenomenon of water freezing below the freezing point in polymer electrolyte fuel cell (PEFCs). Water generated on the surface of the catalyst layer was observed simultaneously with visible and infrared images. Surprisingly, it was found that water generated below the freezing point is in the liquid state and that the temperature rises to 0 °C at the time of freezing. It is generally known that heat of solidification is radiated when water in a super-cooled state starts to freeze. This study shows that water generated below the freezing point in polymer electrolyte fuel cells (PEFCs) is in a super-cooled state.

Keywords: PEM; Fuel cell; Freezing point; Ice; Super-cool

1. Introduction

Understanding the mechanism of water freezing is critical to achieving high performance and longevity of polymer electrolyte fuel cells (PEFCs) for cold starts. Below the freezing point, generated water freezes in the PEFC. If the pores in the catalyst layer and gas diffusion layer are filled with ice, or if the catalyst layer surface is clogged by ice to such an extent that the transport of reactant gases to the electrodes is hindered, substantially decreased cell performance results and mass transport limitation due to freezing occurs.

Saito and Hayamizu [1] recently showed that water in a proton exchange membrane freezes below −15 °C. However, the freezing temperature of generated water below the freezing point has not been investigated. Nakamiya et al. [2] showed that many ice particles existed on the catalyst layer surface when they took apart a fuel cell and observed the catalyst layer surface after power generation below the freezing point. However, details about the freezing mechanism are still unknown. Moreover, no one has described the series of physical processes leading to water freezing in PEFCs.

Prior experimental efforts to probe the water distribution and the temperature change of water in an operating PEFC have included neutron radiography [3–5], optical visualization using transparent fuel cell [6,7], and temperature measurement using thermocouples [8] and thermograph [9]. However, these diagnostic tools do not allow observation of both visible and thermal images simultaneously. For the purpose of investigating the behavior of generated water in PEFCs at temperatures of 0 °C or less, a system was developed that enabled us to observe generated water using both visible and thermal images simultaneously.

The results provided by this measurement system indicate that water in a liquid state was generated on the surface of the catalyst layer when the fuel cell was operated below the freezing point. Surprisingly, the water temperature remains below the freezing point.

Furthermore, the temperature of the generated water rose to 0 °C when the generated water began to solidify. This phenomenon was identical to that for the freezing of super-cooled water, leading us to discover that when operating a fuel cell below the freezing point, water is generated in a super-cooled state. This study shows for the first time ever that it is possible to operate a fuel cell under nonfreezing conditions below the freezing point if the generated water can be maintained in a super-cooled state.

---

[*] Corresponding author. Tel.: +81 563 55 1816; fax: +81 563 55 1825.
E-mail address: yuji_isikawa@soken1.denso.co.jp (Y. Ishikawa).

0378-7753/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2006.08.026

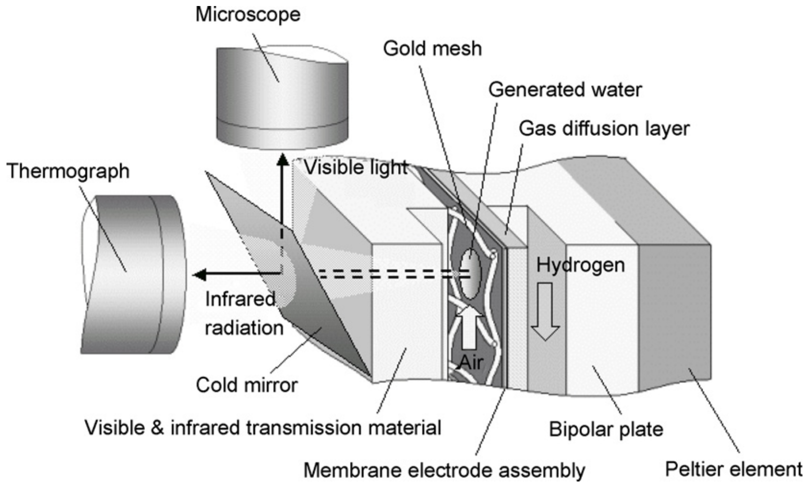

Fig. 1. Experimental set-up to visualize liquid water transport and infrared radiation simultaneously.

2. Experiment

The experimental set-up of the temperature measurement system for generated water is shown in Fig. 1. A cold mirror was installed outside the fuel cell to split the transmission into visible and infrared spectrums. The separator on the cathode side was made from visible and infrared ray transmission material (sapphire glass).

The temperature of the water was measured using thermal imaging, while the behavior of the water was observed using a microscope under appropriate illumination. The gold mesh was used for the current corrector and the gold mesh temperature was not measured accurately because of the difference of radiation rate between gold mesh and water.

This measurement system enabled simultaneous real-time observation of the fuel cell water during power generation using both visible and infrared images.

In the present tests, the total active area of the cell was 1 cm^2 as defined by gaskets. Pure hydrogen and air were used as the fuel and oxidant, respectively. The cell was operated at atmospheric pressure (0 kPa) for both the fuel and the air.

Fig. 2(a) shows the temperature error measurement model. The water temperature was measured by the thermograph and thermocouple. Fig. 2(b) shows the measurement error of the IR temperature from the temperature measurement with the thermocouple (wire: type K). Based on this test, it was confirmed that the water temperature error ($T_{\text{Thermocouple}} - T_{\text{IR}}$) was less than ±1 °C.

In the present experimental set-up, a microscope and thermograph are unable to cool down below the freezing point because of their heat-resistant temperatures. 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 the separator on the anode side, the fuel cell was cooled with the Peltier element, and the cell then compressed with the Peltier element using a pressure jig. The cell was kept constantly cool by the Peltier element during power generation; therefore the thermal energy produced in the catalyst layer did not lead to a rise in the separator temperature. The temperature change of the actual fuel cell is such that, if the fuel cell generates power below the freezing point, the temperature of the separator will rise due to thermal energy from the catalyst layer. In the present experiment, however, the temperature of the separator was kept constant. In the present power generation situation, the cell was cooled more than would be the case for an actual cell.

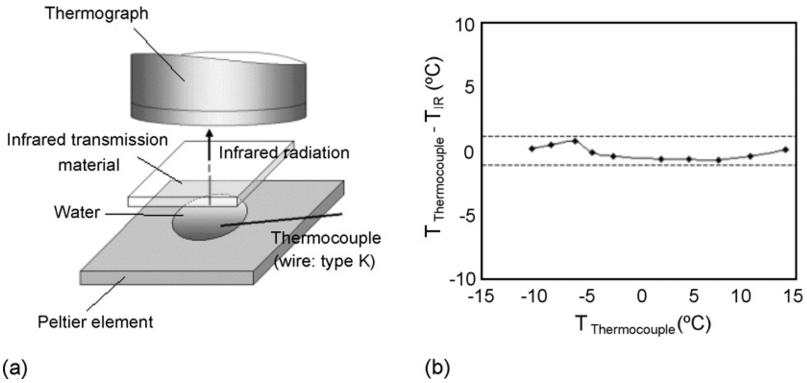

Fig. 2. (a) Temperature error measurement model. (b) Measurement error of the IR temperature from the thermocouple temperature.

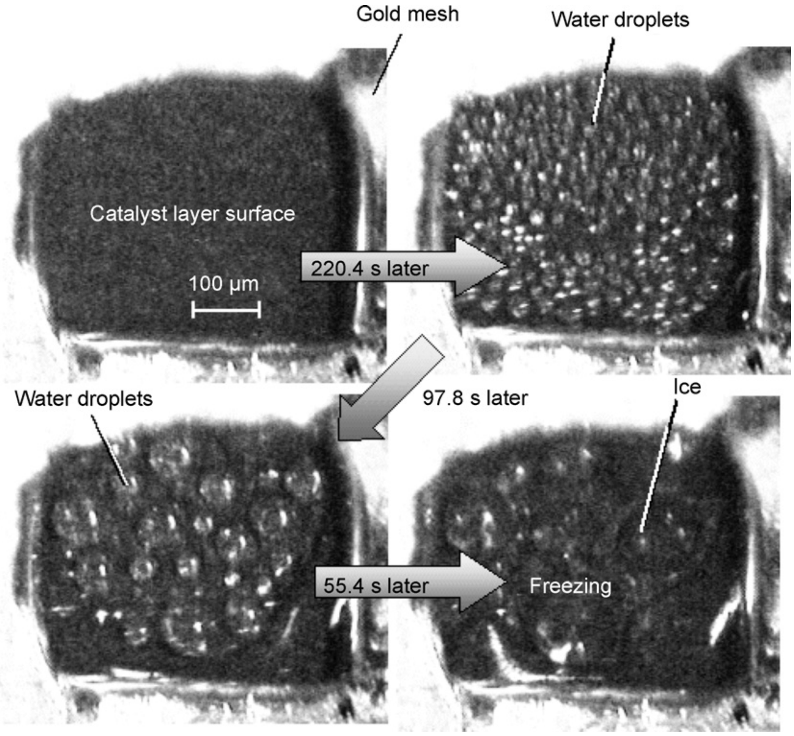

Fig. 3. Water droplets generated on catalyst layer surface at −10 °C.

3. Results and discussion

Under power generation condition, the membrane electrode assembly was cooled to −10 °C using the Peltier element and the voltage was fixed at 0.5 V. The behavior of water generated on the catalyst layer surface is shown in Fig. 3. In the first 380 s, liquid water was generated as the current density increased, the water then subsequently froze. As can be seen in the current profile in Fig. 4, it appears that cell performance drops when the generated water freezes.

This indicates that water generated in the fuel cell does not freeze immediately on the catalyst layer below the freezing point. Furthermore, it also suggests that the water moves in the liquid state to the surface of the catalyst layer and then freezes. In general, transfer of the water in the catalyst layer is assumed to be in a vapor phase. However, the liquid water transfers on the catalyst layer was observed below freezing point. It is considered that the low saturated vapor pressure at −10 °C is the chief factor generating the liquid water. And it is estimated that the liquid water elimination was caused by Laplace pressure.

The temperature measurement results of the generated water droplets are shown in Fig. 5. It can be seen that the temperature is always sub-zero from the point water is generated until the

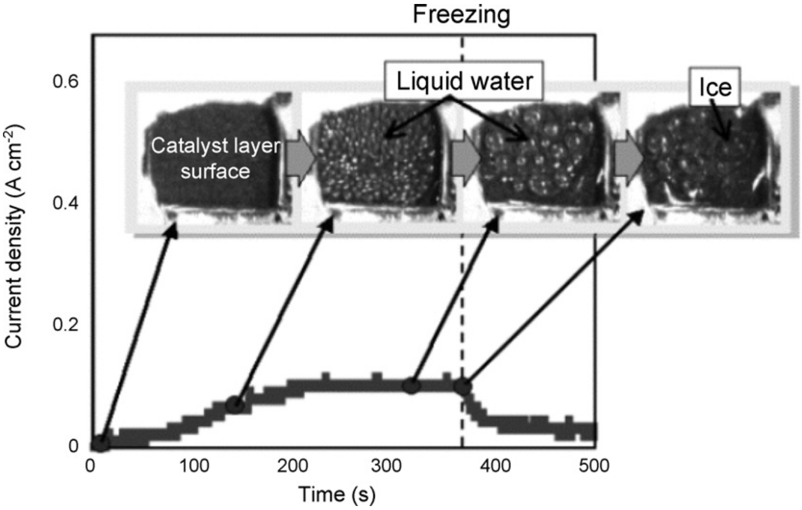

Fig. 4. Cell performance and water generation.

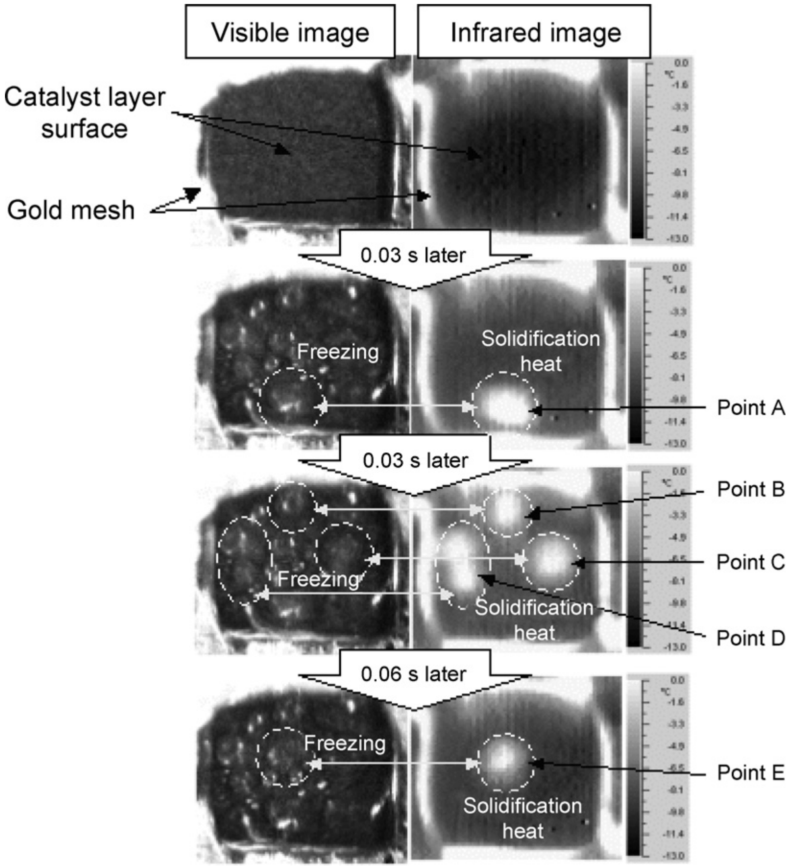

Fig. 5. Liquid water freezing and solidification heat radiation.

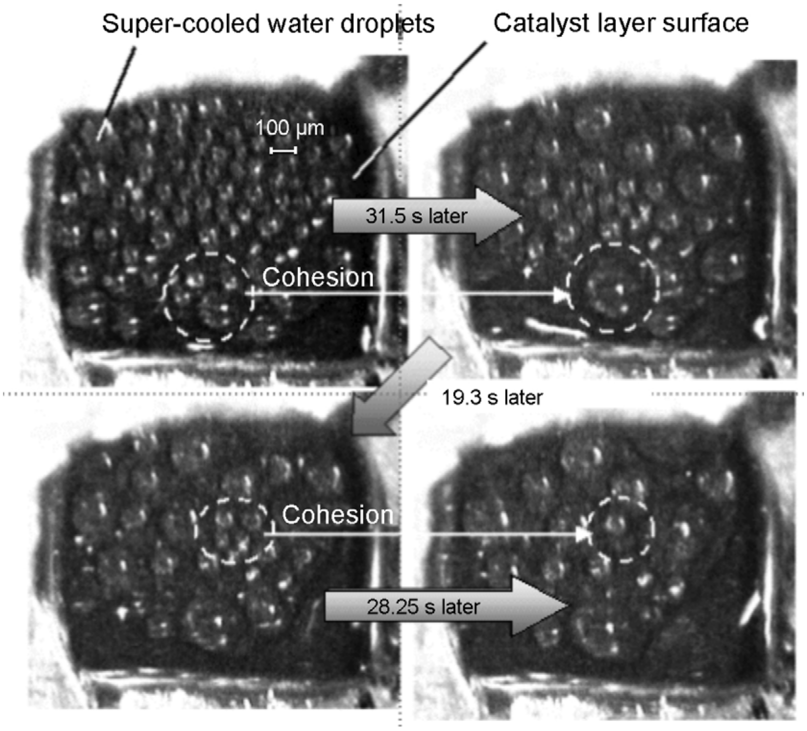

Fig. 6. Behavior of super-cooled water droplets at −10 °C.

Table 1
Maximum temperature of water droplets at time of freezing

Point	Maximum temperature (°C)
A	−0.1
B	−0.1
C	−1.2
D	−1.2
E	−2.2

point it freezes. It also indicates that the temperature rises significantly at the moment the water freezes. It is generally known that when water in a super-cooled state begins to freeze, heat of solidification is emitted and the temperature rises to 0 °C [10]. The present study, therefore, confirms that the phenomenon that results in this temperature rise at the moment generated water in a fuel cell is frozen is the same phenomenon that causes super-cooled water to freeze. Therefore, when a fuel cell is operated below the freezing point, it is expected that water in the liquid state generated on the catalyst layer surface is in a super-cooled state.

Table 1 shows the temperature of the water droplets shown in Fig. 5 (points A–E). Point B (−0.1 °C) is the highest temperature among the five points. Point E shows the lowest temperature, with a high of −2.2 °C. It was confirmed that the highest temperature of these water droplets at the time of freezing is not constant. The temporal resolution of the thermograph in the present experiment was 1/30 s. It is therefore expected that the peak temperatures of points C–E were not measured accurately because the temporal resolution of the thermograph was insufficient to measure the instant radiation of the heat of solidification.

Fig. 6 shows the growth in size of water droplets generated in the super-cooled state. The diameter of the water droplets is approximately 10 μm when generated. The droplets then freeze after growing to a diameter of approximately 100 μm. As the decreasing number of water droplets grow, they absorb nearby smaller water droplets to become larger and fewer. And the super-cooled state did not break when these physical movements occurred.

Generally, the smaller the size of the water droplets, the more easily the super-cooled state is maintained [11]. The present results of fuel cell water freezing correspond to this fact of super-cooled water freezing. Shichiri et al. [12,13] describe how the bursting of air bubbles is the reason for the breakdown of the super-cooled state. However, no burst air bubbles were observed in this experiment. What actually triggers super-cooled water to freeze in PEFCs is therefore still unknown.

4. Conclusions

Water is generated in the liquid state when a polymer electrolyte fuel cell (PEFC) is operated below the freezing point at −10 °C. The temperature of the generated water was measured and found to be below the freezing point. Moreover, the temperature of the generated water rose to 0 °C when the water began to solidify. This phenomenon matches that seen in the freezing of super-cooled water, leading us to discover that when a fuel cell is operated below the freezing point, water is generated in the super-cooled state.

References

[1] M. Saito, K. Hayamizu, The 45th Battery Symposium in Japan, vol. 692, 2004.
[2] H. Nakamiya, K. Kikuta, Y. Tabe, T. Chikahisa, F. Kagami, K. Yoshizawa, Jpn. Soc. Mech. Eng. 5 (2005) 1.
[3] A.B. Geiger, A. Tsukada, E. Lehmann, P. Vontobel, A. Wokaun, G.G. Sherer, Fuel Cells 2 (2003) 92.
[4] R. Satija, D.L. Jacobson, M.A. Arif, S.A. Werner, J. Power Sources 129 (2003) 238.
[5] D. Kramer, J. Zhang, R. Shimoi, E. Lehmann, A. Wokaun, K. Shinihara, G.G. Scherer, Electrochim. Acta 50 (2005) 2603.
[6] K. Tüber, D. Pócza, C. Hebling, J. Power Sources 124 (2003) 403.
[7] X.G. Yang, F.Y. Zhang, A. Lubawy, C.Y. Wang, Electrochem. Solid-State Lett. 7 (2004) A408.
[8] P.J.S. Vie, Signe Kjelstrup, Electrochim. Acta 1069 (2004) 49.
[9] T. Ogawa, N. Nohara, T. Chikahisa, Y. Hishinuma, Thermal Sci. Eng. 12 (2004) 4.
[10] M. Nanjyo, Y. Iwanaga, Encyclopaedia Chim. (1963) 842.
[11] S. Murata, Mizu Handobukku 17 (2003).
[12] T. Shichiri, Y. Araki, J. Cryst. Growth 78 (1986) 502.
[13] T. Shichiri, T. Nagata, J. Cryst. Growth 54 (1981) 207.