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Study of external humidification method in proton exchange membrane fuel cell

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Abstract

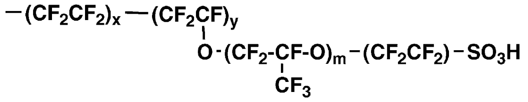
Water management is essential for performance enhancement of a PEMFC because proton conductivity depends on hydration of the polymer. An external humidification method is used in a fuel cell experiment. Humidity and temperature of the gas are measured using humidity and a dew-point transmitter. An E-tek electrode and a Nafion 115 membrane was used to check the relationship between humidity and performance of a fuel cell. The Fuel cell performance experiment was carried out using a control program that is made in laboratory using HP VEE. Humidity data on the steady state was used to understand the effect of humidity on fuel cell performance. An experiment was performed to improve fuel cell efficiency at lower humidity and temperature condition. The relative humidity of hydrogen gas was lower by about 10–15% than that of air or oxygen but the temperature was higher by about 2.5 °C.

Keywords: Humidity; Hygrometer; Heat capacity; PEMFC

1. Introduction

Environmental concerns and increasing dependence on imported fuels suggest alternative energy sources, and better utilization of existing energy sources are needed. The proton exchange membrane fuel cell (PEMFC) is a promising alternative energy source because of the simplicity of its design and operation. Some attractive characteristics of the PEMFC system are lightweight, high energy density, no or low emissions and low temperature operation.

Perfluorinated ionomer membranes are used in the PEMFC as proton conductor with the following chemical formula [1].



$$-(CF_2CF_2)_x-(CF_2\underset{\underset{\displaystyle O\cdot(CF_2\text{-}\underset{\underset{\displaystyle CF_3}{|}}{C}F\text{-}O)_m-(CF_2CF_2)-SO_3H}{|}}{C}F)_y$$

This type of membrane requires water to maintain proton conductivity. Water management is essential for performance enhancement of a PEMFC because protons transferred from anode to cathode as hydronium ions (H_3O^+) and proton conductivity depends strongly on hydration of the polymer [2–5]. A continuous supply of water is needed to prevent drying of the membrane that result in performance degradation. Various humidification designs such as internal humidification, external humidification, and direct injection methods are used in the PEMFC to maintain hydration level of the polymer membrane.

Porous membrane is located between the gas channel and the water channel in the internal humidification method [6]. Water droplets permeate through the membrane from the water side to the gas side. The heat produced in the stack could be used as an energy source for vaporizing water in this method. If the water side is not purged after system is shut down, water permeate through the membrane and form stagnant water on the gas side. The stagnant water could cause a flooding problem during fuel cell start up.

Gas is passed through a water column of a humidifier bottle in the external humidification method. The humidifier bottle temperature controlled independently from cell fixture temperature to get the desired gas temperature and relative humidity. The external humidification method is widely used in small scale laboratory fuel cell experiments due to its simplicity.

An additional amount of liquid water is injected directly into the fuel cell in the liquid injection design. Lately, direct vapor injection and humidification with a porous dipolar plate have been studied [7–9].

In this paper, basic research has been conducted using an external humidifier, which is mainly used for unit cell

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or small size stacks. Experiments have been performed to check the influence of the humidifier bottle temperature, gas flow rate, and the type of gas on relative humidity. The humidifier bottle temperature on the anode side showed more influence on cell performance than the cathode side. The relative humidity of the hydrogen gas was lower than that of oxygen gas due to the difference in heat capacity.

2. Experimental

2.1. Humidity test

As shown in Fig. 1, the external humidification test system was composed of a humidifier vessel from which the gas received humidity and a hygrometer vessel in which relative humidity and temperature of the humidified gas was measured and the data was stored in a computer file. The humidifier bottle size was 1600 cm^3 for a single cell experiment. Gas goes through the diffuser to be distributed as small bubbles. The temperature difference between the outlet gas from humidifier and the water in the humidifier could be reduced when the humidifier volume was increased to 1500 cm^3 to give enough residence time for the gas. The mass flow controller (MFC) is used to control the gas flow rate.

The humidity and temperature of the gas were measured accurately using a humidity and dew-point sensor. A few types of gas inlet and outlet schemes were tested to insure less fluctuation in the humidity reading. The gas outlet is positioned in the bottom for easy removal of water residue. The remaining water in the hygrometer vessel could be removed with a purge gas that flows into the top of the vessel. The temperature of the hygrometer vessel is controlled with a thyristor power regulator (TPR) and a flexible heating tape. Relative humidity and temperature of the humidified gas measured and stored automatically at regular time intervals through a personal computer connection.

2.2. Performance test

An E-tek electrode with 2 mg Pt/cm^2 and a Nafion 115 membrane was used to make a 5 cm^2 membrane and electrode assembly. A current vs. potential experiment was performed automatically using a control program. A personal computer was connected to a Hewlett Packard electronic load (HP-6060B) and perform control and data acquisition in the fuel cell experiment.

3. Results and discussion

3.1. Steady state performance

A stability test was conducted to measure the humidification value at constant temperature and gas flow rate in order to insure reliability of data for the external humidification method. Steady state performance is shown in Fig. 2. The temperature of the external humidifier is controlled equal to the hygrometer vessel, and the flow rate of gas was kept at 1 l/min. Various gases such as oxygen, air and hydrogen are

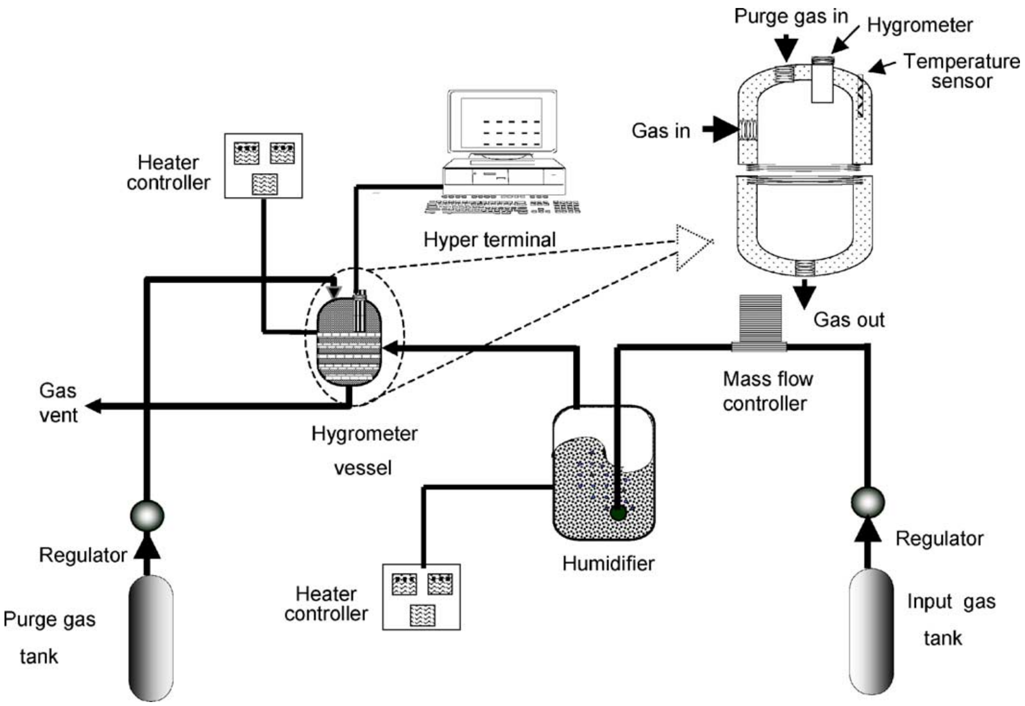

Fig. 1. Humidity measurement system.

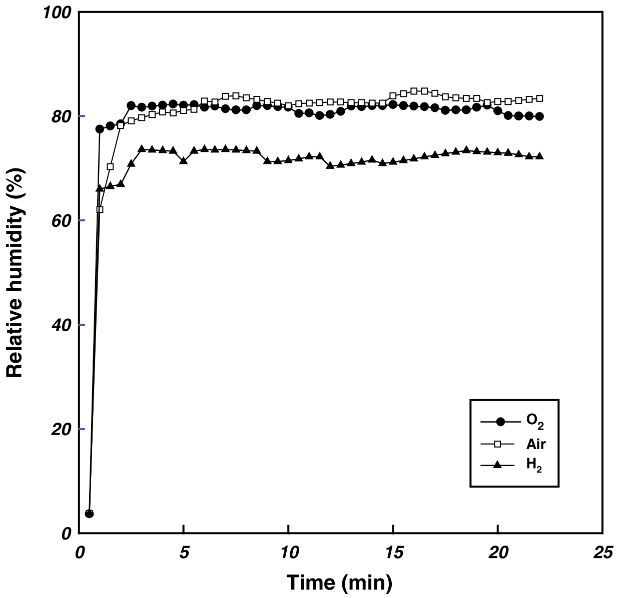

Fig. 2. Transient response of relative humidity (temperature: 60 °C, gas flow rate: 1 l/min).

used. As shown in Fig. 2, the steady state of humidity value was achieved within a few minutes. The humidity data of steady state was used to understand the effect of humidity on fuel cell performance.

The humidity value became unstable if water condense inside hygrometer vessel. This problem could be avoided by increasing the hygrometer vessel temperature compared to that of humidifier vessel. As shown in *x*-axis of Fig. 3, the hygrometer vessel temperature was controlled in ranges from −5 to 10 °C compared to humidifier temperature that is controlled at 30, 50 and 70 °C. Oxygen is supplied at flow rate of 1 l/min. As the hygrometer vessel temperature is increased, the relative humidity of oxygen is decreased accordingly.

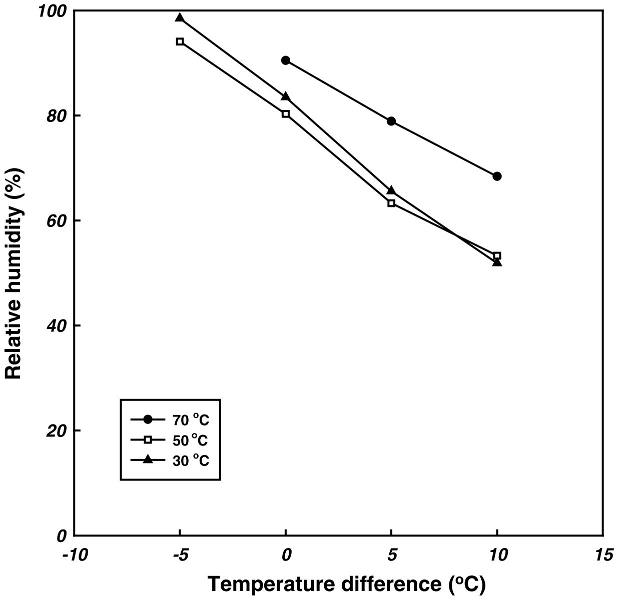

Fig. 3. Relative humidity and temperature difference, $T_{\mathrm{hygrometer}} - T_{\mathrm{humidifier}}$.

It is necessary to analyze not only relative humidity but also vapor pressure at various temperatures. Vapor pressure could be calculated with the temperature of hygrometer vessel and relative humidity data. The amount of water supplied to fuel cell at a certain flow rate could be calculated with Eq. (1). The subscript A and B in Eq. (1) represent water vapor and dry gas, respectively:

$$N_{\mathrm{A}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}}\frac{P_{\mathrm{B}}V_{\mathrm{B}}}{RT} = \frac{P_{\mathrm{A}}V_{\mathrm{B}}}{RT} \tag{1}$$

where N is the water phase (mol/min), P the vapor pressure (mmHg), V the input gas volume rate (l/min), R the gas constant (l mmHg/mol K) and T the absolute temperature (K).

Even though the hygrometer vessel temperature is different from that of the humidifier, the vapor pressure was kept within a tolerable range as shown in Fig. 4. The hygrometer vessel temperature could be controlled higher than that of humidifier to avoid water formation in the hygrometer vessel.

3.2. Gas flow rate effect

As shown in Fig. 5, measurement of the humidity and temperature was conducted at various flow rates with oxygen, air and hydrogen. Both hygrometer and humidifier vessel temperature were kept at 60 °C. Relative humidity was increased as gas flow increased. However, the increment of relative humidity was not directly proportional to the flow rate, and the tendency of increment was a small reduction at higher flow rate. A peculiar phenomenon was observed between gases. The relative humidity of hydrogen was lower

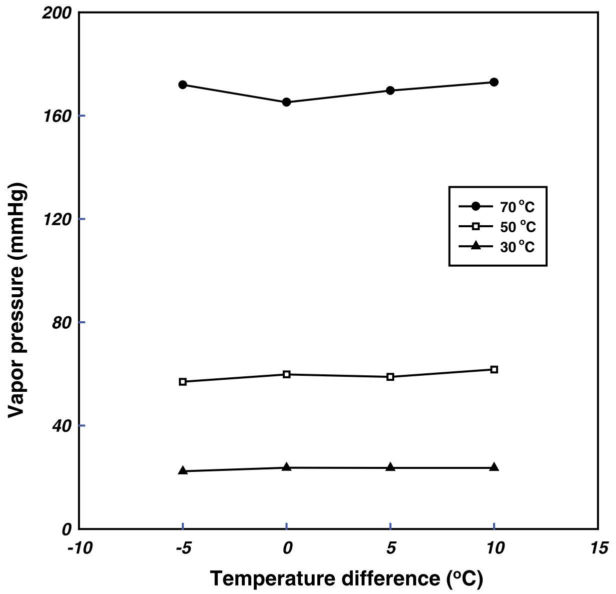

Fig. 4. Vapor pressure and temperature difference, $T_{\mathrm{hygrometer}} - T_{\mathrm{humidifier}}$.

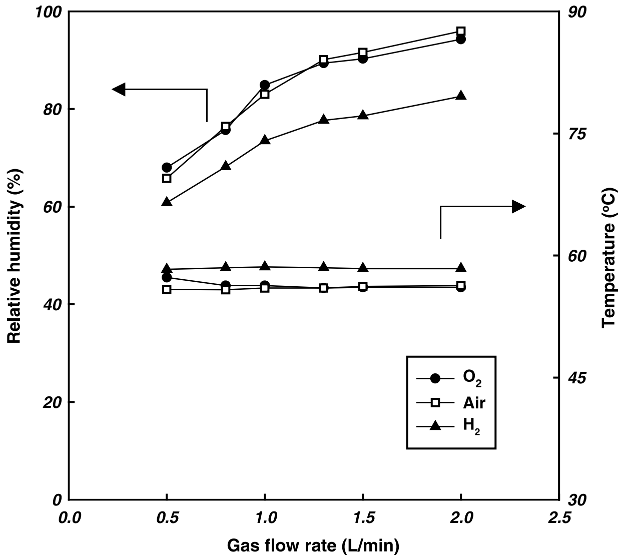

Fig. 5. Relative humidity, temperature and gas flow rate at 60 °C.

by about 10–15% than that of other gases but the temperature was higher by about 2.5 °C, as shown in Fig. 5.

Fig. 6 shows the amount of humidified water that is calculated from relative humidity and temperature data at various temperatures. The amount of water fed to the fuel cell was directly proportional to the gas flow rate. Also, the amount of humidified water appeared to be similar for hydrogen and oxygen under the same conditions. The mass of water vapor carried by unit mass of vapor-free gas is dependent only on the partial vapor pressure in the mixture at fixed total pressure [10,11].

The difference of relative humidity and temperature between hydrogen and oxygen could be explained by the heat

Table 1
Heat capacity parameters of gases

	A	$B \times 10^3$	$C \times 10^6$	$D \times 10^{-5}$
Air	3.355	0.575	–	−0.016
Hydrogen	3.249	0.422	–	0.083
Oxygen	3.639	0.506	–	−0.227

capacity of the gases. Humidified gas passes through the external humidifier and can be expressed as Eqs. (2) and (3)

$$H_{2,A} \xrightarrow{\text{humidifler}} H_{2,B} + \alpha H_2O \quad (2)$$

$$O_{2,A} \xrightarrow{\text{humidifler}} O_{2,B} + \alpha H_2O \quad (3)$$

where α is the amount of humidified water (g/min).

The subscript A and B represent dry gas at room temperature and humidified gas at higher temperature. In this process, an enthalpy change occurs which could be expressed by Eq. (4) [12].

$$\Delta H = \int C_P \, dT + \alpha H_{H_2O} \quad (4)$$

where H is the enthalpy (J/mol), and C_P the heat capacity (J/mol K).

The heat capacity (C_P) can be calculated with Eq. (5):

$$C_P = A + BT + CT^2 + DT^{-2} \quad (5)$$

where A, B, C and D are the heat capacity parameters of gases shown in Table 1. The amount of humidified water in hydrogen and oxygen have similar values as shown in Fig. 6. The difference of enthalpy change between two gases is calculated with heat capacity. Fig. 7 shows the enthalpy change of gases from 15 to 90 °C with a gas flow rate of 1 l/min. Each gas appeared to have a different enthalpy change value with temperature. The hydrogen gas temperature would be

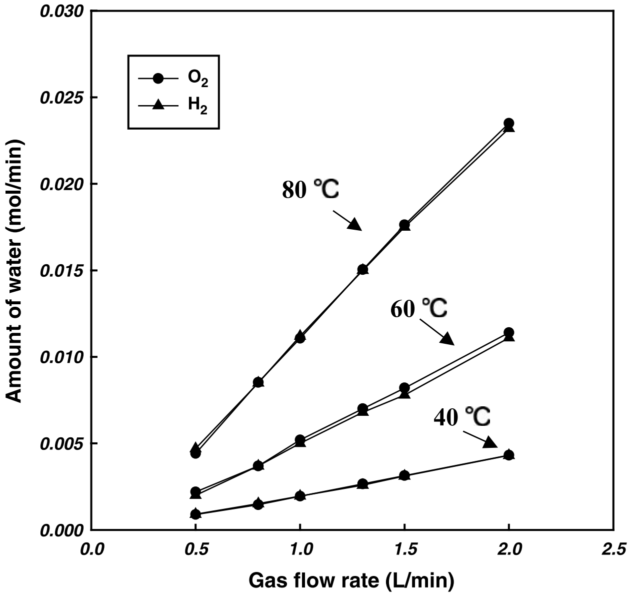

Fig. 6. Amount of water and gas flow rate for different temperatures.

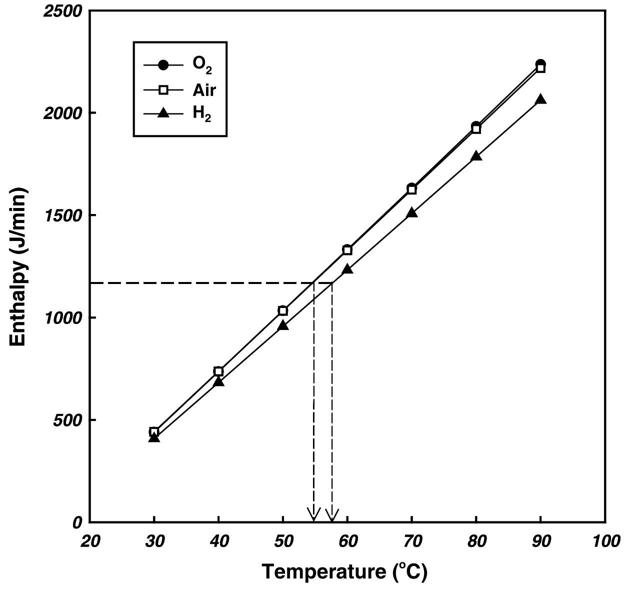

Fig. 7. Effect of gas heat capacity on temperature.

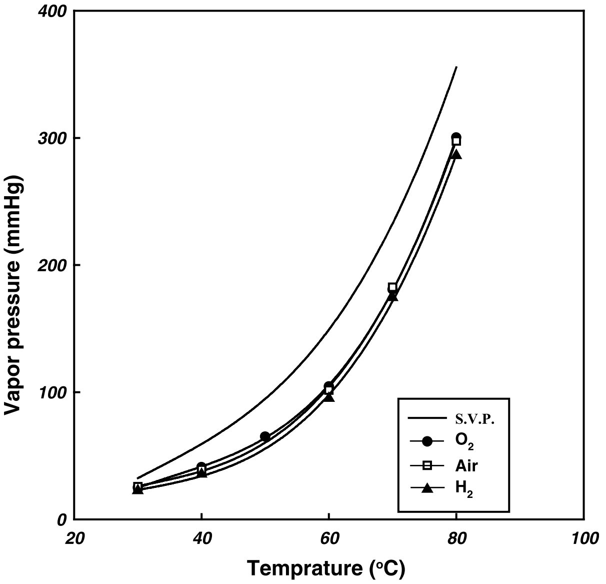

Fig. 8. Comparison of vapor pressure and saturated vapor pressure (SVP) (gas flow rate: 1 l/min).

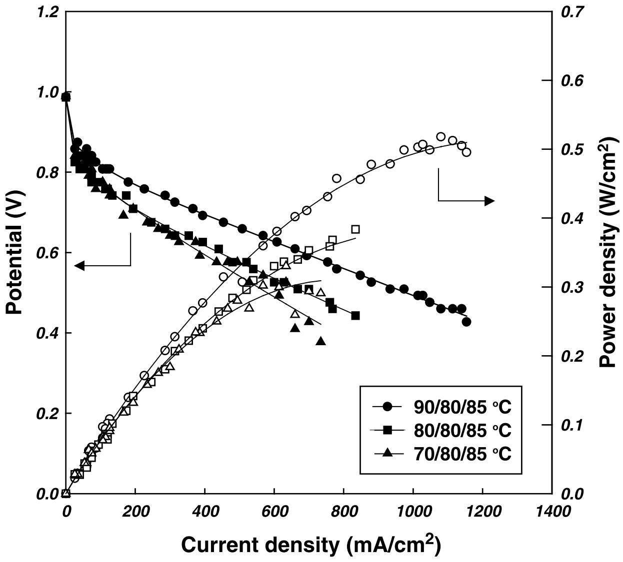

Fig. 9. Effect of anode humidifier temperature on performance.

increased from 15 to 57.5 °C when 1180 J/min is supplied as shown in Fig. 7. The oxygen gas temperature would be increased to 55 °C with same energy supply of 1180 J/min. This temperature difference of 2.5 °C between hydrogen and oxygen was the same as observed in Fig. 5. The heat capacity of hydrogen is smaller than that of oxygen. Thus, the temperature of hydrogen was higher than that of oxygen, and the relative humidity of hydrogen was lower than that of oxygen with same energy supply.

3.3. Temperature effect

A vapor pressure experiment was performed with various gas flow rates and temperatures. The hygrometer and humidifier vessel were controlled to the same temperature. Fig. 8 shows the vapor pressure change of the reaction gas with temperature compared to saturated vapor pressure under a fixed gas flow rate of 2 l/min. The vapor pressure increase as the temperature rose. As shown in Fig. 8, the vapor pressure was increased 30–40 mmHg while heating from 30 to 50 °C, 30–40 mmHg from 50 to 60 °C, and 50–70 mmHg from 60 to 70 °C. The rate of increment for vapor pressure increased with increasing temperature. The amount of water supplied to the fuel cell by the gas was greatly affected by gas temperature. The relative humidity as well as the amount of water is important to improve and stabilize the fuel cell performance. The relative humidity and the amount of water should be examined separately and then combined to improve fuel cell performance.

Fig. 9 shows the effect of the anode side humidifier temperature on fuel cell performance. The cell fixture temperature was kept at 80 °C and cathode side at 85 °C and atmospheric pressure. The performance of the fuel cell at 0.6 V was 700 mA/cm^2 with the anode side 90 °C, 445 mA/cm^2 with 80 °C, and 390 mA/cm^2 with 70 °C. The performance was affected much by the anode side humidifier temperature.

Fig. 10 shows the effect of the cathode side humidifier temperature on fuel cell performance. The cell fixture temperature was kept at 80 °C and the anode side at 90 °C atmospheric pressure. The performance of fuel cell at 0.6 V was 700 mA/cm^2 with cathode side of 85 °C, 690 mA/cm^2 with 75 °C, and 610 mA/cm^2 with 65 °C. The performance little affected by the cathode side humidifier temperature.

An experiment was performed to improve the fuel cell efficiency at a lower humidity and temperature of the gas without sacrificing performance. Fig. 11 shows the performance at a cell temperature of 80 °C at atmospheric pressure. RTD

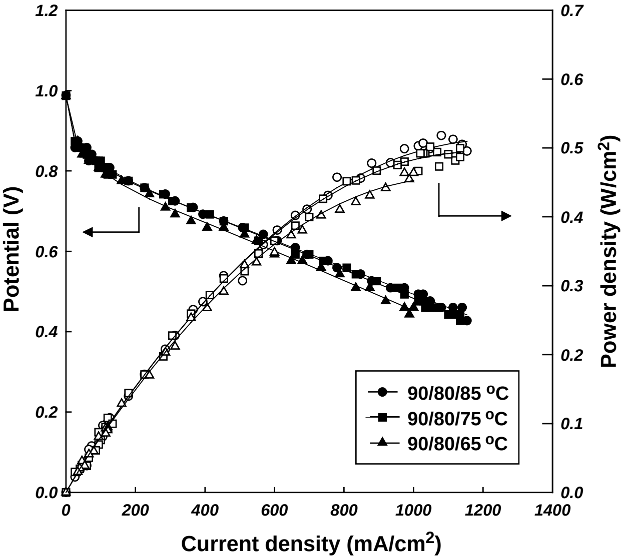

Fig. 10. Effect of cathode humidifier temperature on performance.

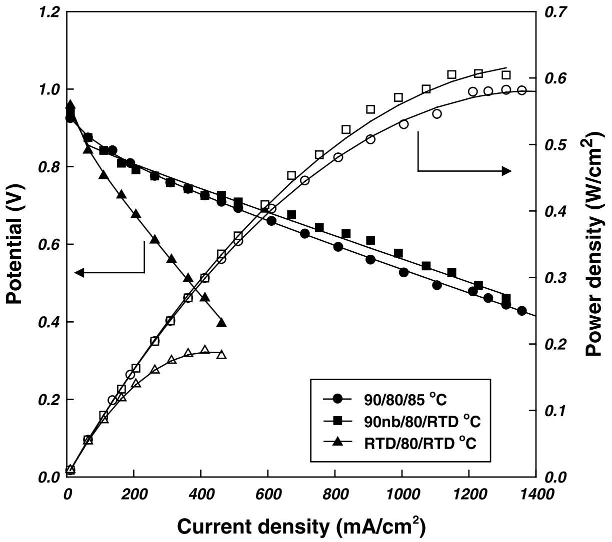

Fig. 11. Effect of humidity on performance (nb: no bubble, RTD: room temperature dry gas).

in Fig. 11 represents room temperature dry gas, and nb represents no bubbling of the gas. When the humidifier temperature of the hydrogen is controlled at 90 °C and oxygen is controlled at 85 °C, the relative humidity of the reaction gas at the cell fixture should be more than 100%. It is considered that decreased performance appeared as a result of the flooding on cathode at a high current density. Hydrogen gas passes over surface of water in the humidifier instead of bubbling, and room temperature oxygen without humidification was fed to the fuel cell. Performance of the above case with less humidification was about equal or better than that with both side humidifications. The performance of the fuel cell dropped a lot when both gases were fed at room temperature without humidification. Product water at low current densities such as 500 mA/cm^2 seem to be not enough to maintain conductivity of the membrane. Humidity on the anode side is needed to keep the proton conductivity of the membrane and cell performance. The amount of supplied water to the fuel cell was directly proportional to the gas flow rate as shown in Fig. 6, therefore improved performance would be established by correlation of gas humidity and utilization in future studies.

Acknowledgements

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References

[1] L.J. Blomen, M.N. Mugerwa, Fuel Cell System, Plenum press, New York, 1993.
[2] K. Kordesch, G. Simader, Fuel Cell and Their Applications, VCH, New York, 1996.
[3] J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, M.G. Klett, Fuel Cell Handbook, 4th ed., US Dept. of Energy Office, 1998.
[4] B. Baradie, C. Poinsignon, J.Y. Sanchez, Y. Piffard, G. Vitter, N. Bestaoui, D. Foscallo, A. Denoyelle, D. Delabouglie, M. Vaujany, J. Power Sources 74 (1998) 8.
[5] M.C. Wintersgill, J.J. Fontanella, Electrochim. Acta 43 (1998) 1533.
[6] K.H. Choi, D.J. Park, Y.W. Rho, Y.T. Kho, T.H. Lee, J. Power Sources 74 (1998) 146.
[7] P.L. Reid, S.C. Duncan, Gas humidification process, US Patent 4,759,882 (1988).
[8] D.L. Wood III, J.S. Yi, T.V. Nguyen, Electrochim. Acta 43 (1998) 3795.
[9] C.Y. Chow, B.W. Wozniczka, Electrochemical fuel cell stack with humidification section located upstream from the electrochemically active section, US Patent 5,382,478 (1995).
[10] W.L. McCabe, J.C. Smith, P. Harriott, Unit Operations of Chemical Engineering, 5th ed., McGraw-Hill, New York, 1993.
[11] R.H. Perry, D.W. Green, J.O. Maloney, Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill, New York, 1997.
[12] J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 5th ed., McGraw-Hill, New York, 1996.