

Effects of External Humidification on the Performance of a Polymer Electrolyte Fuel Cell

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Abstract

The dryness of the membrane of a polymer electrolyte fuel cell (PEFC) decreases the ionic conductivity, resulting in performance reduction. In this study, the effects of external humidification to the membrane were investigated by varying the humidification side such as anode humidification, cathode humidification, and both anode and cathode humidification (called as both-side humidification). The amount of required water vapor into the gas was increased rapidly to maintain the relative humidity constant with the increase of cell temperature. The best performance of the cell was achieved by both-side humidification. However, as the humidity condition approached saturation state, anode humidification yielded comparable performance to both-side humidification. In anode humidification, the increase of the cell temperature degraded the performance, even though the amount of water supply to the membrane remained constant. At constant relative humidity conditions with anode humidification, the polarization curves of the PEFC were almost the same, regardless of the cell temperature when the relative humidity was higher than 60%.

Keywords: Polymer electrolyte fuel cell; Relative humidity; Humidity ratio

1. Introduction

The polymer electrolyte fuel cell (PEFC) is one of the prospective power sources for automotive applications, stationary cogeneration systems, and mobile electronic devices. Over the other types of fuel cells, a PEFC offers design simplicity and a moderate range of cell operating temperature. The PEFC consists of a membrane electrode assembly (MEA), a gas diffusion layer (GDL) on each side of the MEA, and two plates on which the gas flow channels are machined. The membrane used in the PEFC serves as an adequate barrier to allow proper mixing of fuel and reactant gases and as a proton conductor. The ionic conductivity of a polymer membrane is strongly dependent on the membrane structure and water content in the membrane [1].

There have been several studies on the effects of humidity and behavior of water molecules inside the PEFC. Zawodzinski et al. [2] determined the water diffusion coefficients in a membrane and presented the numbers of water molecules dragged by the protons as a function of water content in the membrane. Computational studies were conducted on the water transport phenomenon and water effects [3, 4]. Gogerguen et al. [5] presented a novel method to estimate PEFC humidity by analyzing its effect on cell resistive voltage. The water management in a PEFC and the visualization of water buildup were investigated in several experimental studies [6-8]. Since the humidity plays an important role in the performance of the PEFC, comprehensive studies on humidifiers and humidifying methods have been carried out [9-11].

Typically, there are two ways of water uptake of the membrane. The one is external humidification using the reactant gas and the other is self-

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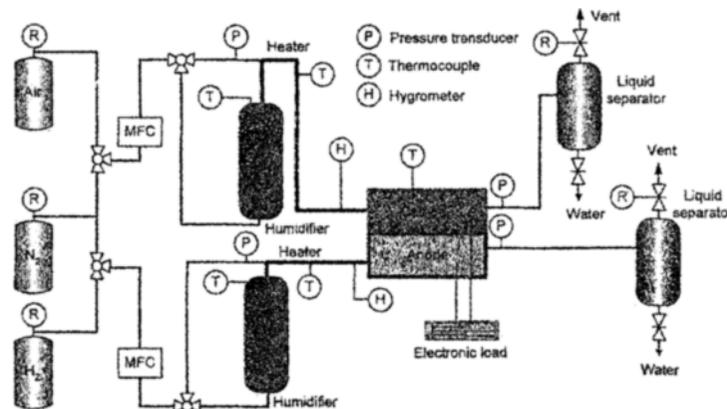


Fig. 1. Schematic diagram of experimental setup.

humidification of membrane by water production as a result of chemical reaction. Because the self-humidification is determined by the current generation, the variation of external humidification is the easy way of controlling the humidity in the PEFC. The water uptake of the membrane with the same amount of external humidification can be varied with the cell temperature. The higher temperature is, the more gas is taken away by the purging gas. Therefore, comprehensive investigations on the cell temperature as well as the external humidification are required, but there are only a few published studies on the effects of humidification related to cell temperature. In this study, the performance of a PEFC was observed at various cell temperatures for two kinds of external humidification conditions (constant humidity ratio and constant relative humidity). In addition, the effects of external humidification side were also investigated, which affects the water transport phenomena in the PEFC.

2. Experiments

2.1 Experimental setup

Fig. 1 shows a schematic of the experimental setup employed in this study. The setup was designed to evaluate the performance of a unit cell of the PEFC. Pure hydrogen was used as the fuel, and air was used as the oxidant. The humidity of the supply gas is one of the main factors in this study. Dry bottled-air was used because the air acquired from the atmosphere already contains some amount of water vapor. The gases were fed into the fuel cell in “flow-through mode” from the gas bottle via a pressure regulator; that is, the exhaust gas from the cell was released into

the atmosphere and the pressure inside the anode and cathode was atmospheric. The flow rates of hydrogen and air were measured and controlled by gas mass flow meters. The hydrogen and the air flow into sparging-type humidifiers, whose temperatures were controlled by PID controllers. The capacities of the humidifiers were high enough that the gas was fully saturated at humidifying temperature for the range of the flow rate tested in this study. A band type heater was wrapped on the gas line between the humidifier and the cell to control gas temperature in the line. A hygrometer with an accuracy of $\pm 2\%$ RH was installed at the inlet of the cell to measure relative humidity of the gas entering the cell.

The humidification conditions were varied at constant humidity ratio and constant relative humidity by controlling the gas temperature supplied into the cell. For the constant relative humidity condition, the humidity was measured by controlling the supplied gas temperature corresponding to the cell temperature. For the constant humidity ratio condition, however, the temperature of reactant gas was kept at a specified value so that the humidity ratio remained constant regardless of the cell temperature.

This study used a 111 cm^2 unit cell with a five-channel serpentine type flow-field. The operating temperature of the fuel cell was controlled by a heater inserted in the endplate and air cooling fan attached on the surface of the endplate. A GoreTM's PRIMEA[®] series MEA whose thickness was $35 \mu\text{m}$ was used in this experiment. The platinum catalyst loading was 0.4 mg/cm^2 for anode and 0.6 mg/cm^2 for cathode. The GDL 35 BC from [®]SIGRACET was used as the gas diffusion layer. An electronic load controls the load of the fuel by varying the current.

2.2 Test procedure

The main operating parameters in this experiment were reactant gas temperature and humidification condition such as humidification side and humidity. The external humidification was conducted alternately at the anode-side, cathode-side, and both sides. The to-be-humidified gas passed through the humidifier, whose temperature was controlled to set the relative humidity to 40%, 80%, and 100% when the cell operated at the temperature of 50 °C. The other gas bypassed the humidifier at dry condition. The hydrogen and air were supplied at the rates of 0.75 slpm and 1.75 slpm, respectively. The flow rates were adjusted to obtain a stoichiometric ratio of 1 when the current density of the fuel cell reached 0.9 A/cm² (100 A/111 cm²).

The second matter of concern was the performance variation according to the humidity and the cell temperature. In this experiment, anode humidification was employed and the humidification condition was varied in two ways. One, the amount of water supplied with reactant gas was maintained constant regardless of cell temperature. The humidifying temperature was controlled to maintain the relative humidity at 40% and 80% when the temperature of hydrogen was 50 °C as the cell temperature was varied from 50 °C to 70 °C. Second, the relative humidity of the supplied hydrogen was controlled. As the cell temperature was varied from 50 °C to 80 °C, the relative humidity of the supplied hydrogen was controlled at 0%, 20%, 40%, and 60% by varying the humidifying temperature. The polarization curves for all experiments were obtained for increase of current from 0. The cell potential at each step of current was recorded for 5 minutes at an interval of 0.5 second. The representative values plotted in the Figs. were obtained by averaging the cell potentials for last 3 minutes before changing to the next step.

2.3 Water content in the reactant gas

In this study, the humidity of the gas is represented by the humidity ratio and relative humidity. The humidity ratio is the ratio of the mass of the water vapor to the mass of the dry gas in the mixture. The relative humidity is the ratio of the mole fraction of the water vapor in a mixture to the mole fraction of the water vapor in a saturated mixture at the same temperature and pressure. Using the perfect gas law, the relation between the relative humidity and the humidity ratio

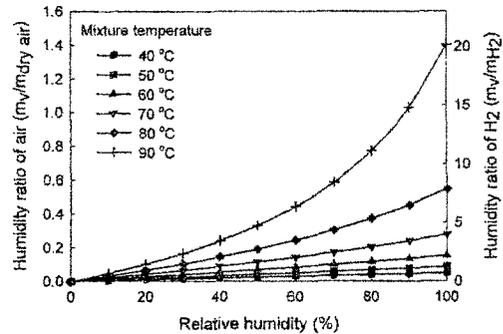


Fig. 2. Variation of humidity ratios for air and hydrogen with relative humidity at various temperatures.

can be derived as

$$W = \frac{M_v p_v}{M_g p_g} = \frac{M_v p_s \phi}{M_g p_g} \quad (1)$$

For the cathode, where the gas is air, Eq. (1) can be rewritten as

$$W = \frac{18.015 p_s \phi}{28.965 p_g} = 0.6219 \frac{p_s \phi}{p - p_s \phi} \quad (2)$$

For the anode, where the gas is hydrogen, Eq. (1) can be derived as

$$W = \frac{18.015 p_s \phi}{2.016 p_g} = 8.936 \frac{p_s \phi}{p - p_s \phi} \quad (3)$$

Fig. 2 shows the humidity ratios of air and hydrogen as a function of relative humidity at various temperatures. Because the molecular weight of hydrogen is approximately 14.4 times smaller than that of air, the humidity ratios of the two gases show a big difference. The increase of humidity ratio with the increase of relative humidity rises rapidly with the increase of the cell temperature. For example, as the air temperature increases from 40 °C to 90 °C, approximately 28.7 times more water is required to maintain saturated state. This implies that more water is required to maintain the same relative humidity at high temperature.

3. Results and discussion

3.1 Effects of external humidification side

The performance variation according to external humidification conditions was investigated. The external humidification was provided by the following

three methods: (1) anode-side humidification, (2) cathode-side humidification, and (3) both anode and cathode-side humidification (both-side humidification). The cell temperature was maintained at 50°C and the relative humidities of hydrogen and air were varied at 40%, 80%, and 100%.

Fig. 3 shows the measured cell potentials at various current densities. The performance of the PEFC is directly affected by the proton conductivity, which is highly dependent on water content in the membrane [12]. When humidity was 40% (Fig. 3 (a)), the highest amount of water molecules was supplied into the cell in both-side humidification. Therefore, both-side humidification showed the highest cell potential, while anode humidification showed the lowest. Even though the hydrogen and air were humidified to the same relative humidity (40%), there was some difference in the amount of water content between them. Table 1 shows the supplied water flow rate mixed with the reactant gases at the temperature of 50 °C. The relative humidity varied from 20% to 100%. The flow rate of dry gas varied from 0.5 to 1.0 slpm for hydrogen and from 1.0 to 2.5 slpm for air. In this case, the water flow rate supplied into anode was 0.00173 kg/h (H₂, 0.75 slpm, 40% RH), and the water flow rate supplied into cathode was 0.00394 kg/h (Air, 1.75 slpm, 40% RH). The flow rate of the water supplied to the cathode was 2.27 times higher than that to the anode. Therefore, in cathode humidification, more water moisturized the membrane to increase proton conductivity. In addition, the water activity was relatively low in the anode because the water in the membrane was dragged to the cathode by the protons. In low humidity conditions, the performance of the PEFC was more sensitive to the amount of water molecules in the membrane.

Table 1. Supplied water flow rate (kg/h) mixed with the hydrogen and air at various relative humidities.

	Flow rate (slpm)	Relative humidity				
		20%	40%	60%	80%	100%
H ₂	0.5	0.00056	0.00115	0.00178	0.00243	0.00313
	0.75	0.00084	0.00173	0.00267	0.00365	0.00469
	1.0	0.00113	0.00231	0.00355	0.00487	0.00625
Air	1.0	0.00110	0.00225	0.00347	0.00475	0.00610
	1.75	0.00192	0.00394	0.00606	0.00830	0.01067
	2.5	0.00274	0.00563	0.00866	0.01186	0.01524

When the relative humidity of the reactant gas was varied, the effects of humidification side showed somewhat different trends. Fig. 3 (b) shows the variation of cell potential when the relative humidity of the reactant gas was 80%. In this case, anode humidification yielded better performance than cathode humidification. The increase of water in the anode increased ionic conductivity, resulting in higher cell potential. However, conflicting phenomena in cathode humidi-

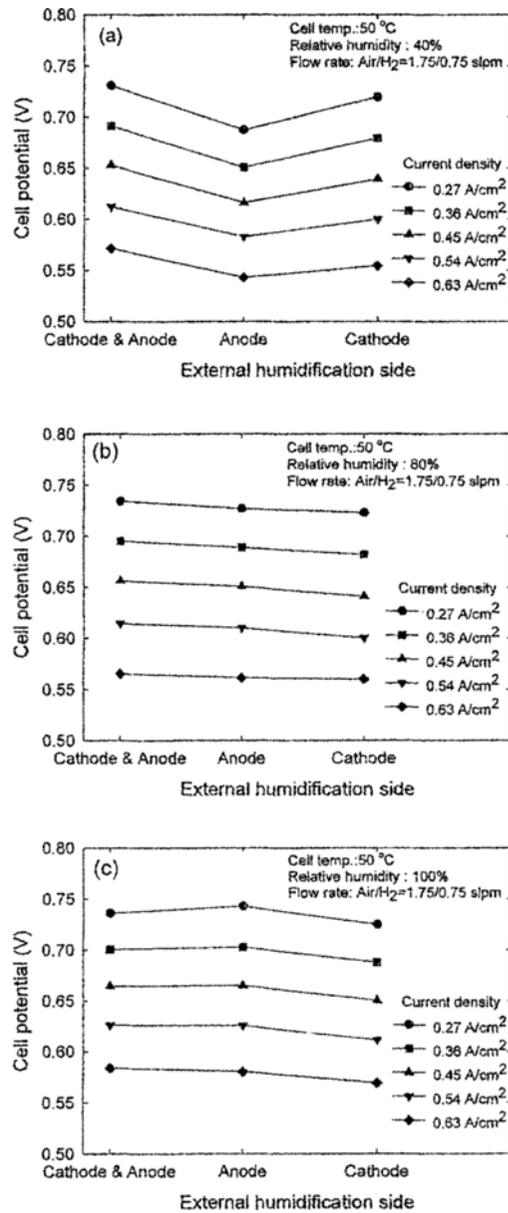


Fig. 3. Variation of cell potential according to humidification side: (a) $\phi=40\%$, (b) $\phi=80\%$, and (c) $\phi=100\%$.

fication were observed at high relative humidity. The water content in the membrane increased with the rise of humidity, while the surplus water decreased the performance of the PEFC due to flooding. Therefore, there was no noticeable increase of cell potential in cathode humidification. When the supplied gas was fully humidified (100%), which is shown in Fig. 3 (c), the cell potential of anode humidification was almost the same as that of both-side humidification. At low current density, anode humidification showed higher performance than both-side humidification. However, as the current density increased, the performance in both-side humidification became higher than that in anode humidification. More water molecules moved from anode to cathode at higher current density, which yielded inadequate humidification of membrane. In that case, both-side humidification showed better performance.

Fig. 4 shows the variation of cell potential as a function of the relative humidity of reactant gas. As shown in Figs. 4 (a) and (c), both-side humidification and cathode humidification do not increase the cell potential noticeably with the increase of relative humidity. However, as shown in Fig. 4 (b), anode humidification increases the cell potential with the increase of relative humidity of the reactant gas. Anode humidification rarely causes flooding in the anode but increases proton conductivity because the water in the anode moves to the cathode along with the protons.

Fig. 5 shows voltage gaps as a function of current density. The solid symbols represent the voltage gaps between both-side humidification and anode humidification. The hollow symbols represent the gaps between both-side and cathode humidification. The latter showed little variation with the increase of current density. On the contrary, the former showed different trends according to humidity. When the humidity was relatively low (40%), the gap between both-side and anode humidification decreased with the increase of the current density. The water generation in the cathode increased the water content in the membrane with current density. The gap was maintained near zero when the relative humidities were 80% and 100%. This indicates that, at the humidity over 80%, water generation in the cathode and external humidification in the anode are enough to moisturize the membrane, and that the surplus water is to be discharged into atmosphere with the excess air, which is composed of nitrogen, unused oxygen, and so on. Consequently, when the reactant gas is humidified

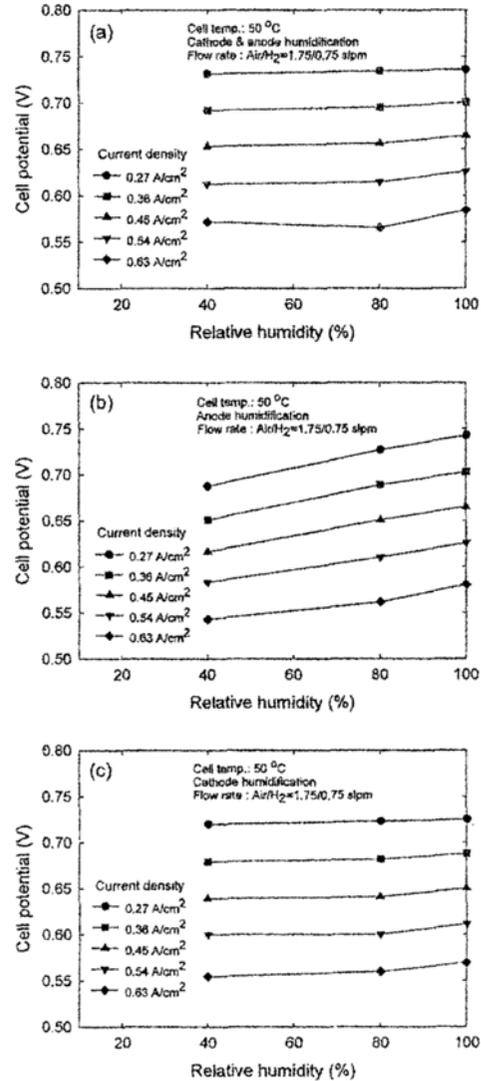


Fig. 4. Variation of cell potential with relative humidity of humidified gas: (a) both cathode and anode humidification, (b) anode humidification, and (c) cathode humidification.

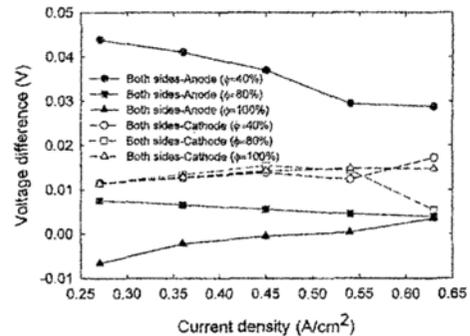


Fig. 5. Variation of potential gap between both-side humidification and one side humidification with current density.

externally at near saturation condition, it is unnecessary to humidify both anode and cathode simultaneously. Anode humidification can show almost the same performance as both-side humidification.

3.2 Effects of humidity associated with cell operating temperature

Generally, the performance of the PEFC is strongly dependent on the cell's operating temperature. Even though the reversible cell potential decreases with increasing temperature, the performance of the PEFC increases due to the increase of chemical reaction rate. With the increase in cell temperature, however, the evaporation rate increases and the reactant gases can take up more water vapor because of higher saturation pressure [12]. Without reliable methods of water management, the MEA structure may start to dry out, resulting in lower ionic conductivity and higher charge transfer resistance across the electrode-electrolyte interface [13,14]. Therefore, this study investigated the performance of a PEFC with respect to cell temperature and humidity. The water content in the PEFC can be varied by the production of water from chemical reactions and external humidification of gases entering the cathode and anode. Because the amount of water production is directly associated with current generation, the control of external humidification level is an effective way to handle the water content in the PEFC. Henceforth, the performance of the PEFC with anode humidification is discussed at constant humidity ratio and constant relative humidity.

Fig. 6 shows the cell potential and power density of the PEFC when the hydrogen was supplied at dry condition at cell temperature ranging from 50 °C to 80 °C. The cell potential dropped rapidly with current density at high cell temperatures ranging from 70 °C to 80 °C. Even though there was absolutely no external humidification, the water produced by chemical reaction moisturized the membrane, resulting in the increase of ionic conductivity. However, at high cell temperatures, the produced water was evaporated by hot gas, so water content was reduced in the membrane.

Fig. 7 shows the polarization curves representing the performance of the PEFC operated at a constant humidity ratio. The humidity ratios of Figs. 7 (a) and 7 (b) were 0.458 and 0.966, respectively. The temperature of hydrogen flowing through inlet line was maintained at 50 °C throughout the experiments,

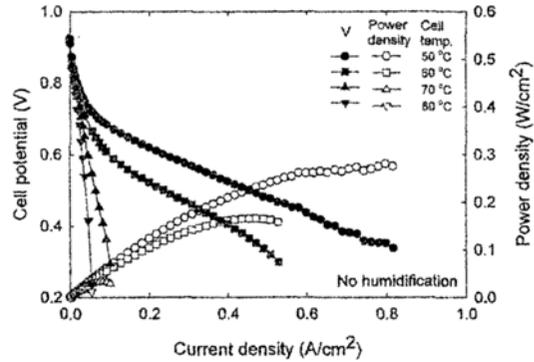


Fig. 6. Polarization curves and variation of power density at no humidification condition.

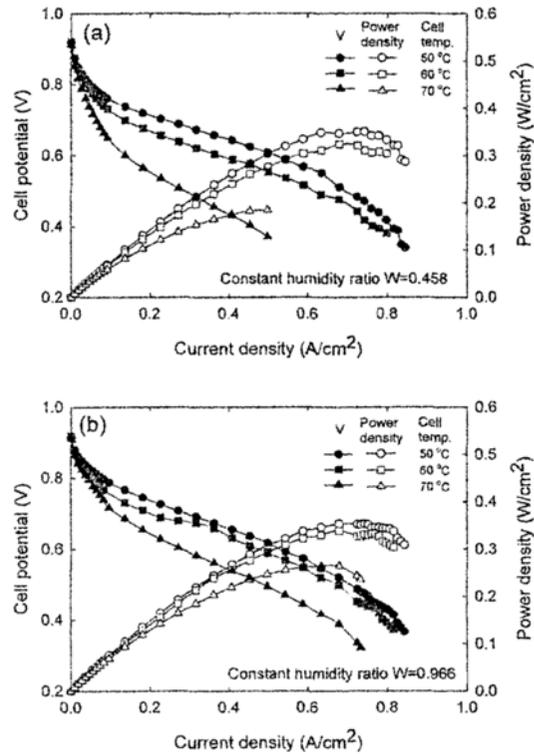


Fig. 7. Polarization curves and variation of power density for anode humidification at constant humidity ratio: (a) $W=0.458$ and (b) $W=0.966$.

while the cell temperature was varied from 50 to 80 °C. The water supply was kept constant throughout the experiments by controlling the relative humidity of supplied gas with respect to the cell temperature. The cell potential and power density decreased with the increase of cell temperature. The reduction of the cell potential at high humidity ratio (Fig. 7 (b)) was lower than that at low humidity ratio (Fig. 7 (a)). Even

though the amount of water vapor supplied into the cell was constant regardless of the cell temperature, the increase of saturation pressure, which corresponded to the increase in cell temperature, allowed the gas to hold more water vapor. At the high cell temperature, the water content in the membrane decreased because a large amount of water vapor had to be discharged from the anode with the excess hydrogen, resulting in the reduction of ionic conductivity of the membrane.

Figs. 8 (a), (b), and (c) show the cell potential and power density of the PEFC at relative humidities of

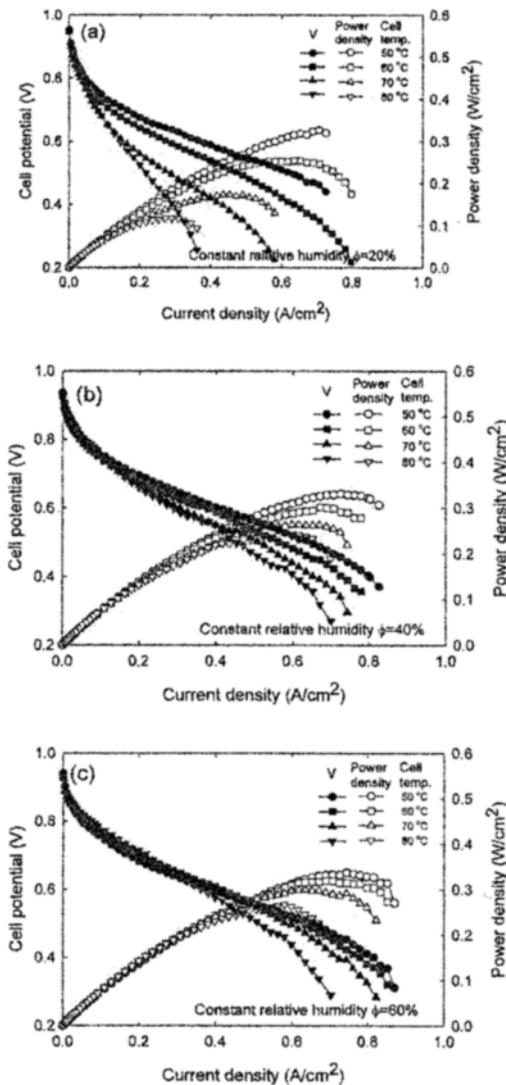


Fig. 8. Polarization curves and variation of power density for anode humidification at constant relative humidity: (a) $\phi=20\%$, (b) $\phi=40\%$, and (c) $\phi=60\%$.

20%, 40%, and 60%, respectively. The cell potential at a cell temperature of 50 °C increased slightly with the rise of relative humidity, while the cell potential at high temperatures ranging from 70 to 80 °C increased dramatically. In Fig. 8 (c), the cell potentials of the PEFC at the temperatures from 50 °C to 70 °C at relative humidity of 60% were almost the same up to the current density of 0.6 A/cm². The humidity ratio increased by 0.7 with the increase of the cell temperature from 50 °C to 80 °C at relative humidity of 20%, while it increased by 2.8 at relative humidity of 60%. This result indicates that much more water is required to maintain constant relative humidity with the increase of cell temperature and even more at high relative humidity. Therefore, it is essential to provide more water into the membrane to minimize the performance reduction of the PEFC at high cell temperatures. However, the degradation of the performance of the PEFC can be minimized by lowering the cell temperature with relatively less humidification.

4. Conclusions

The performance characteristics of a PEFC have been experimentally investigated. The effects of the humidified reactant gas supply methods were measured by varying the humidification side such as cathode, anode and both-side humidification. Both-side humidification yielded the best PEFC performance and anode humidification the lowest performance at low relative humidity. Anode humidification yielded comparable PEFC performance as both-side humidification when the reactant gas was fully humidified. At high current densities, the cell potential gap between both-side and anode humidification decreased. In addition, the effects of reactant gas humidity were examined for anode humidification at constant humidity ratio and constant relative humidity. The performance decreased with the increase of the temperature at constant humidity ratio of hydrogen because excess hydrogen was discharged into air including large amount of water vapor. The variation of cell temperature had little effect on the performance when the relative humidity of hydrogen was maintained constant over 60%.

Acknowledgement

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Nomenclature

M : Molecular mass	(kg/kg mol)
m : Mass	(g)
p : Pressure	(Pa)
W : Humidity ratio	($\frac{g_{\text{water vapor}}}{g_{\text{dry gas}}}$)

Greek letters

ϕ : Relative humidity	(%)
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Subscripts

g : Dry gas
s : Saturation
v : Vapor

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