

A study on cathode structure and water transport in air-breathing PEM fuel cells

Seong Uk Jeong^a, Eun Ae Cho^{b,*}, Hyung-Jhun Kim^b,
Tae-Hoon Lim^b, In-Hwan Oh^b, Sung Hyun Kim^{a,**}

^a Department of Chemical and Biological Engineering, Korea University, 1 5-ka, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea

^b Fuel Cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolkok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

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Abstract

For portable electronics, air-breathing PEMFCs are being developed without external air-feeding and humidification systems. To optimize the cathode structure and to investigate characteristics of such air-breathing PEMFCs, the effects of catalyst loading and gas diffusion layer (GDL) properties on the cell performance are examined. Water transport in air-breathing PEMFCs is interpreted in terms of the net water drag coefficient, which was obtained by changing the current density, relative humidity, temperature and the hydrogen stoichiometry to understand the water transport phenomena under various conditions.

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1. Introduction

Newly developed portable electronics require power supplies with a higher energy density and longer operation time. As a substitute for currently used batteries, fuel cells are being considered based on their potential to fulfil these requirements. Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has many advantages for portable electronics such as a low operating temperature, fast response, design flexibility, high power density and so on. However, as a portable power source, PEMFCs have some limitations; use of power-consuming auxiliary devices like pumps, valves, fans and humidifiers should be minimized so as to obtain a high power density. The space and weight allowed for those devices are also very limited. To overcome these limitations, air-breathing PEM fuel cells are being developed.

Air-breathing fuel cells have their cathode structures open to air. Therefore, the performance of an air-breathing fuel cell is strongly affected by the atmospheric conditions including relative humidity and temperature. To operate a PEMFC efficiently, water should be supplied to the cell so that the electrolyte and the electrodes are properly hydrated to maintain a high ionic conductivity. However, for air-breathing portable electronics, an external water supply is not available due to the system complexity. Instead, product water generated at the cathode by the electrochemical reaction can hydrate the anode and the electrolyte as well as the cathode by back diffusion induced by the difference in water content between the anode and the cathode. Thus, water transport through the membrane is crucial to performance improvement of air-breathing PEMFCs. In addition to water supply to the cell, oxygen transport to the cathode can limit the performance of air-breathing PEMFCs, since oxygen is supplied to the cathode only by passive feeding like natural convection. In this study, the effects of the cathode structure on the performance of air-breathing PEMFCs were examined to optimize the cathode structure. Based on the results, water transport phenomena in air-breathing fuel cells were investigated with reaction equations.

* Corresponding author. Tel.: +82 2 958 5279; fax: +82 2 958 5199.

** Corresponding author. Fax: +82 2 958 6102.

E-mail addresses: eacho@kist.re.kr (E.A. Cho), kimsh@korea.ac.kr (S.H. Kim).

Nomenclature

A	active area (cm^2)
F	Faraday constant ($96,485 \text{ C mol}^{-1}$)
I	current density (A cm^{-2})
N	molar flow rate (mol s^{-1})
P	total pressure (bar)
P_{sat}	saturation pressure (bar)
T_{cell}	cell temperature ($^{\circ}\text{C}$)
T_{hum}	humidification temperature ($^{\circ}\text{C}$)
x_j	molar fraction of species j in dry gases ($^{\circ}\text{C}$)
$\alpha_{\text{net,drag}}$	net drag coefficient
λ	stoichiometry

Subscripts

w_an	water at the anode
w_prod	water produced by reaction

2. Experimental

2.1. Cell design

Single cells were prepared as described in previous work [1]. For the anode gas supply, a graphite plate was machined with five-serpentine channel with an active area of $5 \text{ cm} \times 5 \text{ cm}$. Polytetrafluoroethylene (PTFE) gaskets were used for gas sealing of the electrodes. A 2 mm-thick gold-coated copper plate was used as the cathode current collector. A cathode current collector that exhibited the highest cell performance in previous work [1] was used where the size of the square openings was $11 \text{ mm} \times 11 \text{ mm}$ with 2 mm-wide ribs.

2.2. Preparation of membrane electrode assembly (MEA)

A perfluorosulfonic acid (PFSA) membrane (NRE-211, DuPont) was prepared by a solution casting method. Catalyst ink was prepared from a mixed catalyst powder (40 wt.% Pt/C, E-Tek), Nafion solution (5 wt.%, $E_W = 1100$, DuPont) and *iso*-propyl alcohol. The weight ratio of the Nafion ionomer to the catalyst powder was 1/3. The prepared catalyst ink was coated onto a gas diffusion layer by the spraying method. For the cathode, the platinum loading was in the range from 0.3 to 1.6 mg Pt cm^{-2} and various types of carbon paper (Toray TGPH-030, 060, 090 and 120 with wet proofing of 0–50% by PTFE) were used as the gas diffusion layer. For the anode, the catalyst loading was 0.4 mg Pt cm^{-2} on TGPH-060 with a wet proofing of 20% by PTFE. The prepared anode, cathode and membrane were hot-pressed at 140°C and 100 atm for 90 s. The active electrode area was $5 \text{ cm} \times 5 \text{ cm}$.

2.3. Measurement of cell performance and impedance

To measure cell performance, dry hydrogen (99.9%) was supplied to the anode. All experiments were carried out in a temperature and humidity chamber. The relative humidity in the

chamber was controlled from 30 to 60% at a controlled temperature of 25 or 35°C . To eliminate effects of self-humidifying on the ionic conductivity of membrane, the cells were activated for 1 h at 100 mA cm^{-2} before cell testing. The impedance of the cells was measured in the potentiostatic mode with an excitation voltage of 20 mV over a frequency range from 0.05 to 10,000 Hz at 0.65 V versus at NHE using an IM6 electrochemical impedance analyzer (ZAHNER Elektrik, Germany).

2.4. Water measurement

From the anode outlet, back-diffused water was collected using a desiccant (CaCl_2) for water absorption. CaCl_2 was put in a U-tube, which was connected to the anode outlet through a tube kept at 50°C to prevent water condensation. Since the cathode was directly open to atmosphere, water could not be collected from the cathode. The collected water in the U-tube was weighed before and after cell operation.

3. Results and discussion

3.1. Effects of cathode catalyst loading on cell performance

To optimize the cathode structure for air-breathing fuel cells, the effects of catalyst loading on cell performance were investigated by measuring I - V curves for the single cells with cathode Pt loading from 0.3 to 1.6 mg cm^{-2} at a relative humidity (RH) of 30 and 60%. As shown in Fig. 1(a), at a RH of 30%, the cell voltage in the low current region below about 100 mA cm^{-2} , increased with catalyst loading while the cell voltage in the higher current region was almost constant with Pt loading above 0.6 mg cm^{-2} . On the other hand, at a RH of 60% presented in Fig. 1(b), the cell voltage in the high current region above 200 mA cm^{-2} increased with Pt loading up to 1.2 mg cm^{-2} and then was lowered while the cell voltage in the lower current region increased. Fig. 2 demonstrates the cell voltage at 60 and 200 mA cm^{-2} measured for a RH 30 and 60%. These results are attributed to the higher catalyst loadings that could facilitate the electrochemical reaction by increasing the active catalyst surface area but also interfere with mass transport of the reactants and products to and from the catalyst surface. The cell performance was slightly higher at a RH of 60% than at a RH of 30%, since more water could be fed to the cathode from the atmosphere to make the catalyst more active. Since the cell voltage increased significantly with Pt loading up to 0.6 mg cm^{-2} and then remained almost constant, single cells were fabricated with a Pt loading of 0.7 mg cm^{-2} for the following experiments.

3.2. Effect of GDL structure on cell performance

To examine the effects of thickness and water proofing of the gas diffusion layer (GDL) on cell performance, single cells were prepared using various types of carbon paper. Fig. 3(a) exhibits I - V curves measured at a RH of 30% for the single cells with TGPH-030, 060, 090 and 120 whose thickness was 100, 190, 280 and $370 \mu\text{m}$, respectively. For all the single cells, compression of the GDL was 60% to keep the electrical contact

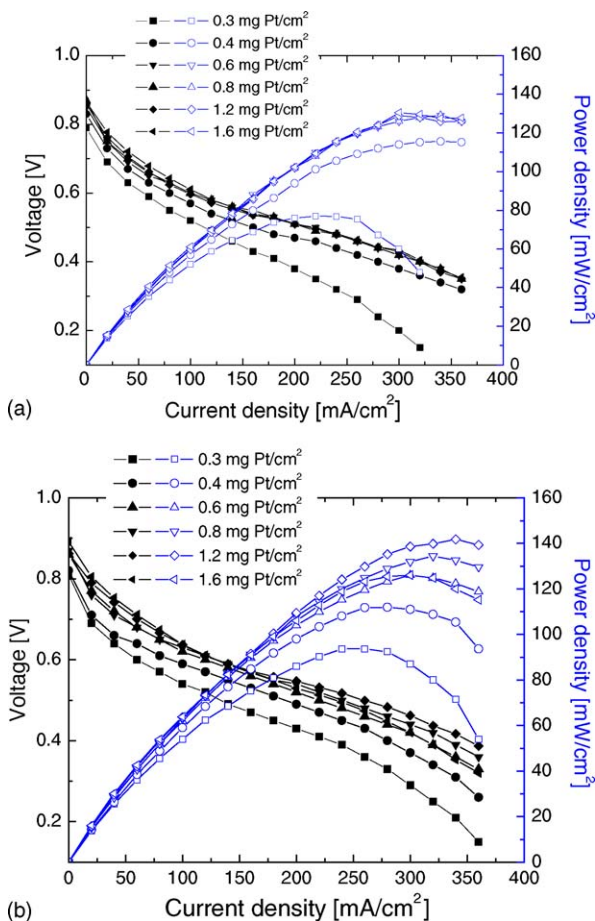


Fig. 1. Effects of catalyst loading on I - V curves at 35 °C RH of (a) 30% and (b) 60%.

resistance and pore structure constant. With increasing GDL thickness to 280 μm , the cell performance was improved in the measured current region. However, for the GDL with a thickness of 370 μm , the cell performance was lower than that with a thickness of 280 μm . Those tendencies were more clearly confirmed by impedance analysis presented in Fig. 3(b) and (c). With increasing GDL thickness, the ohmic and charge transfer

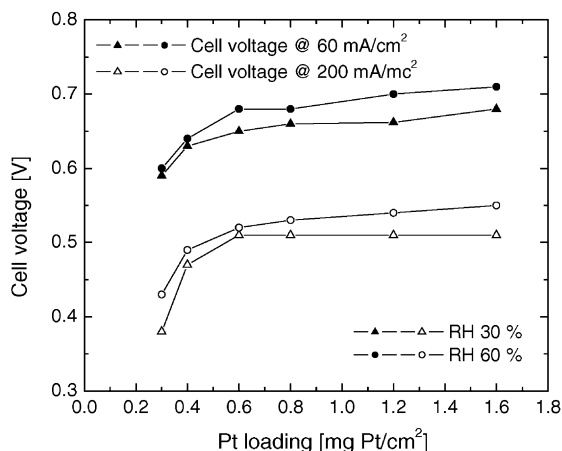


Fig. 2. Effects of catalyst loading on cell voltage at 60 and 200 mA cm^{-2} measured from the data in Fig. 1.

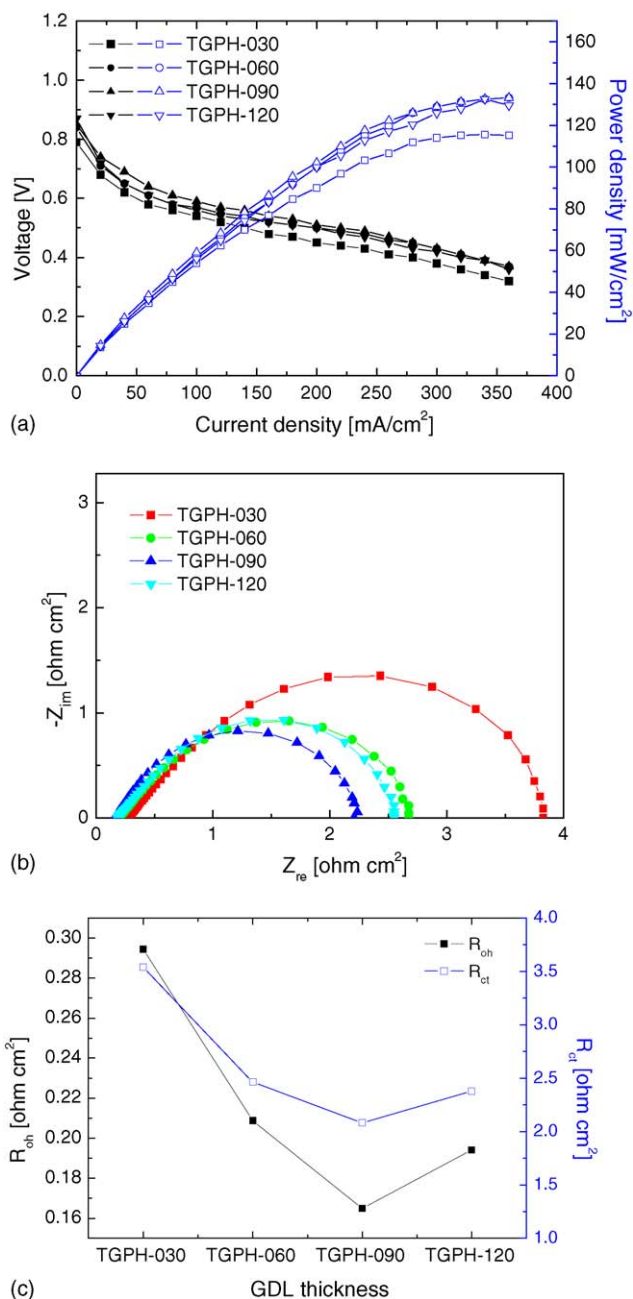
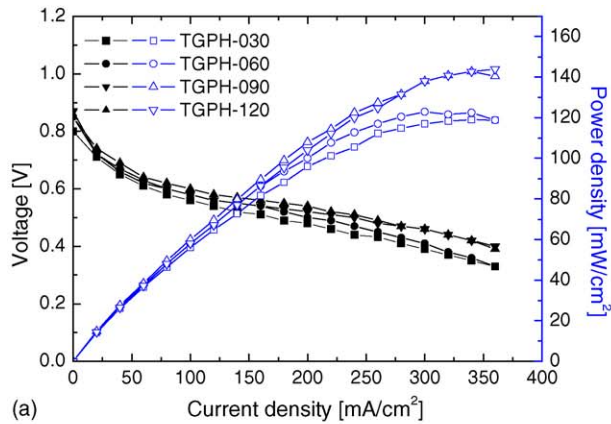


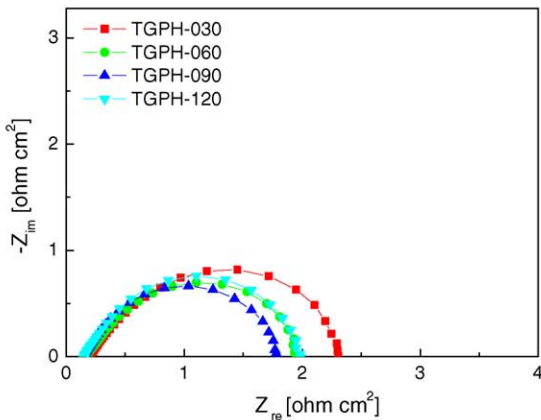
Fig. 3. Effects of GDL thickness on cell performance at 35 °C and RH 30%. (a) I - V curves, (b) Nyquist plot, and (c) ohmic and charge transfer resistance.

resistance were reduced up to 280 μm and then increased. Similar results were obtained at a RH of 60% as given in Fig. 4. A thinner GDL probably could not effectively prevent water evaporation from the MEA resulting in membrane dehydration and hence a reduction of ionic conductivity. On the other hand, thicker membranes could induce a mass transport limitation. Thus, the best performance was obtained with a GDL with an intermediate thickness of 280 μm .

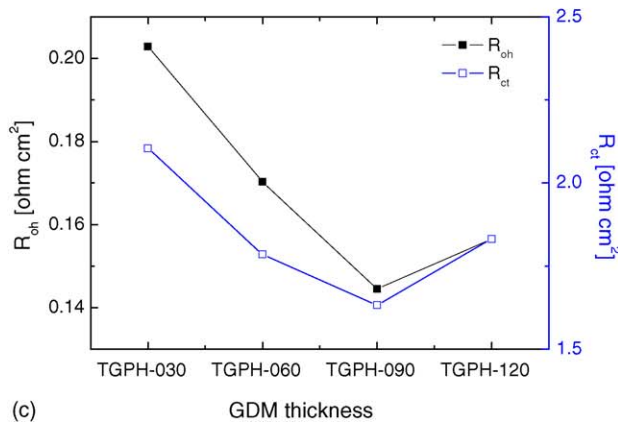
In addition to thickness, water proofing of the GDL is an important factor in determining cell performance. Fig. 5 demonstrates I - V curves measured at a RH of 30 and 60% for single cells fabricated using TGPH-060 with PTFE of 10–50%. At current densities below about 100 mA cm^{-2} , the voltage difference



(a)



(b)

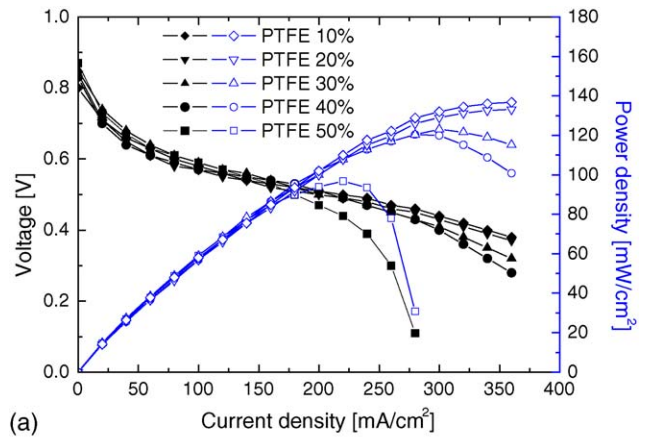


(c)

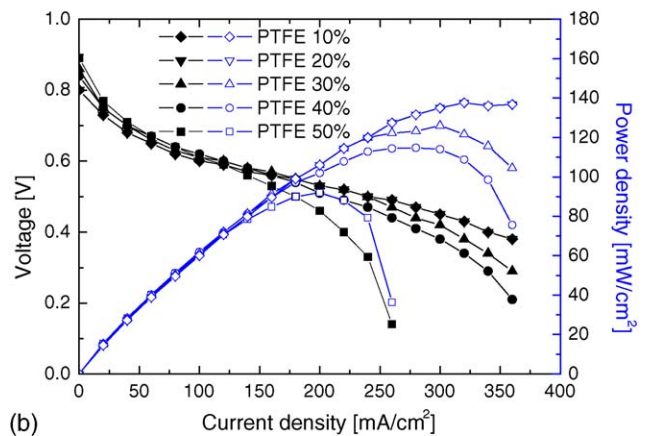
Fig. 4. Effects of GDM thickness on cell performance at 35 °C and RH 60%. (a) *I*–*V* curves, (b) Nyquist plot, and (c) ohmic and charge transfer resistance.

was not remarkable. However, with increasing current density above 240 mA cm⁻², the voltage difference became more distinguishable probably due to mass transport losses caused by the PTFE layer. Generally, the pore size and the porosity decreased with content of PTFE in the GDL [2] leading to a higher mass transport resistance.

Fig. 6 shows *I*–*V* curves measured at a RH of 30 and 60% for the single cells fabricated using TGPH-090 with PTFE of 0–20%. Even though the performance difference was not so significant, the single cells using the GDL with PTFE of 5–10% exhibited the best performance. The GDL without PTFE showed a lower performance since water could not be properly removed



(a)



(b)

Fig. 5. Effects of PTFE contents on cell performance with TGPH-060 at 35 °C and (a) RH 30%, (b) RH 60%.

from the cathode and blocked the pores in the GDL, resulting in mass transport limitation.

3.3. Water transport in air-breathing fuel cells using dry hydrogen

Performance of air-breathing PEMFCs depends on the ionic conductivity of the membrane electrolyte, which is a function of the water content in the membrane [3,4]; ionic conductivity increases with the hydration level. In an air-breathing PEMFC for portable electronics, water can be fed to the cell only in the form of product water from the electrochemical reaction at the cathode since usually there is no external humidification system. A schematic diagram for water transport in an air-breathing PEMFC is depicted in Fig. 7 [5] with related reaction equations.

In an air-breathing PEMFC, the water production rate by electrochemical reaction is calculated using Eq. (1). The water content at the anode inlet is zero since dry hydrogen is supplied. Generally, the water quantity for the anode is calculated by Eq. (3) for conventional cells, which have channels on both the anode and cathode sides. The air stoichiometry was assumed to be unity since oxygen is transported to the cathode by diffusion only when the current is externally loaded. The rate difference between electro-osmotic drag and back diffusion through the

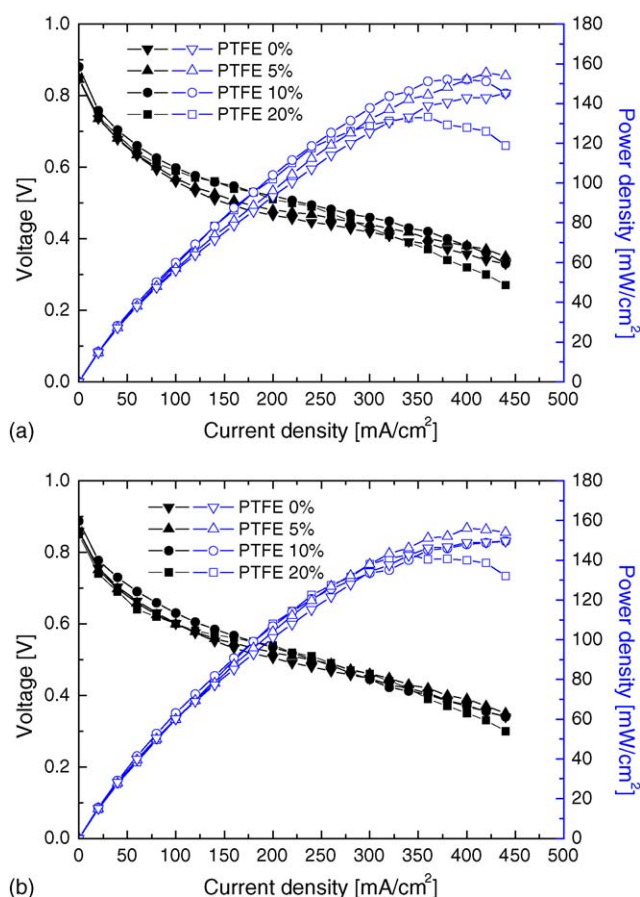


Fig. 6. Effects of PTFE contents on cell performance with TGPH-090 at 35 °C and (a) RH 30%, (b) RH 60%.

membrane results in net water drag and is defined by Eq. (4). Protons are transported with water when current is flowing and the average number of water molecules per proton is called the electro-osmotic drag coefficient. It was reported that the electro-osmotic drag coefficient was in the range from 1 (equilibrated with water vapor) to 2.5 (equilibrated with liquid water) in Nafion membranes [6–8]. The net drag coefficient could be

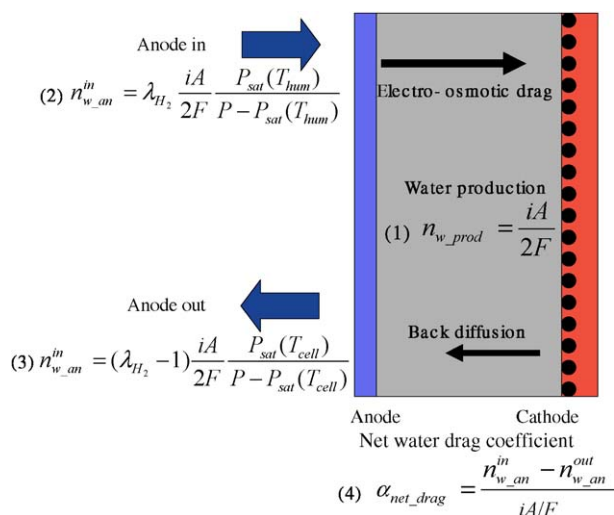


Fig. 7. A schematic diagram for water transport in air-breathing PEMFCs.

Table 1
Effects of current density and relative humidity on the net water drag coefficient at 35 °C with a hydrogen stoichiometry of 5

Current density (mA cm ⁻²)	Relative humidity (%)		
	30	60	100
50	-0.2277	-0.3005	-
100	-0.1564	-0.1810	-0.3197
200	-0.0882	-0.1113	-

The cell employed TGPH-090 with 5% PTFE. The Pt loading for the cathode was 0.7 mg Pt cm⁻².

simply calculated by measuring the water at the anode since there was no external input of water.

The net water drag coefficient measured under various conditions is listed in Table 1. All the values were negative reflecting that water was transported from cathode to anode and the back diffusion was faster than the electro-osmotic drag. The water concentration at the anode was lower than that at cathode in air-breathing PEMFCs using dry hydrogen where the difference of water concentration between anode and cathode would be higher than under fully-humidified operating conditions. The absolute value of the net water drag coefficient increased with the RH of the atmosphere. As the RH increases, the water level at the cathode increased and the difference of water concentration between anode and cathode also increased resulting in a high back diffusion rate. At low RH, water evaporation at the cathode is facilitated, and water level at the cathode decreases, and hence the back diffusion rate is reduced.

The absolute value of the net water drag coefficient was lowered with increasing current density. With increasing current density, the weight of water collected at the anode outlet increased since more water was produced by the electrochemical reaction, resulting in increases in the cathode water level and back diffusion rate. However, since the increase in electro-osmotic drag from anode to cathode was greater than the increase in the back diffusion from cathode to anode, the absolute value of the net drag water coefficient was lowered. Water transport from anode to cathode by electro-osmotic drag, not by back diffusion, was directly proportional to the current density. For example, when the current density doubled, the number of the water molecule transported by electro-osmotic drag was doubled. However, the rate of back diffusion does not increase by twice since the difference of water level between anode and cathode is not doubled.

The net water drag coefficient was lowered with temperature as summarized in Table 2. At a constant current density of 100 mA cm⁻², water transport by back diffusion was faster at 35 °C than at 25 °C, resulting in a higher absolute value of the net water drag coefficient. The difference of the net water drag coefficient between RH 30 and 60% at 25 °C was smaller than at 35 °C, reflecting that water transport at 25 °C was not so strongly affected by RH as at 35 °C. The net water drag coefficient was lowered with the hydrogen stoichiometry due to faster back diffusion at a hydrogen stoichiometry of 5 than at 2.5. As the hydrogen flow rate increases, water is more effectively

Table 2
Effects of temperature and hydrogen stoichiometry on the net water drag coefficient at a current density of 100 mA cm^{-2}

	Relative humidity (%)	
	30	60
Temperature ($^{\circ}\text{C}$)		
25	-0.0877	-0.0897
35	-0.1562	-0.1812
Hydrogen stoichiometry		
2.5	-	-0.1017
5	-	-0.1810

The cell employed TGPH-090 with 5% PTFE. The Pt loading for the cathode was $0.7 \text{ mg Pt cm}^{-2}$.

removed from the anode. Then, the water level at the anode was lowered resulting in higher back diffusion.

4. Conclusions

The effects of cathode catalyst loading and GDL properties on the performance of air-breathing PEMFCs were examined. With increasing cathode catalyst loading from 0.3 to 1.6 mg cm^{-2} , the cell performance was improved significantly up to a Pt loading of 0.6 mg cm^{-2} and then increased slightly due to the trade-off of an increase in active catalyst surface area and an increase in mass transport resistance. With increasing GDL thickness, water

evaporation could be reduced while the mass transport limitation increased. Thus, the GDL with an intermediate thickness of $280 \mu\text{m}$ exhibited the best performance in the range from 100 to $370 \mu\text{m}$. As the PTFE content in the GDL increased, the cell performance was lowered particularly in the high current region since a GDL with a higher PTFE content has a smaller pore size and a lower porosity. In contrast, a GDL without PTFE seemed not to properly remove water from the cathode. The GDL with 5–10% PTFE was found best for the air-breathing PEMFCs fabricated in this study. Based on the results, water transport in air-breathing PEMFCs were interpreted in terms of the net water drag coefficient.

References

- [1] S.U. Jeong, E.A. Cho, H.-J. Kim, T.-H. Lim, I.-H. Oh, S.H. Kim, Effects of cathode open area and relative humidity on performance of air-breathing polymer electrolyte membrane fuel cells, *J. Power Sources*, in press (available online 22 November 2005).
- [2] G.-G. Park, Y.-J. Sohn, T.-H. Yang, Y.-G. Yoon, W.-Y. Lee, C.-S. Kim, *J. Power Sources* 131 (2004) 182–187.
- [3] A.V. Anantaraman, C.L. Gardner, *J. Electroanal. Chem.* 141 (1996) 115–120.
- [4] F.N. Buchi, S. Srinivasan, *J. Electrochem. Soc.* 144 (1997) 2767–2772.
- [5] G.J.M. Janssen, M.L.J. Overvelde, *J. Power Sources* 101 (2001) 117–225.
- [6] T.F. Fuller, J. Newman, *J. Electrochem. Soc.* 139 (1992) 1332–1336.
- [7] T.A. Zawodzinski, J. Davey, J.A. Valerio, S. Gottesfeld, *Electrochim. Acta* 40 (1995) 297–302.
- [8] M. Ise, K.D. Kreuer, J. Maier, *Solid State Ionics* 125 (1999) 213–223.