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Effects of cathode open area and relative humidity on the performance of air-breathing polymer electrolyte membrane fuel cells

Seong Uk Jeong [a], Eun Ae Cho [b,*], Hyoung-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, Sungbuk-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 applications, the, characteristics of passive air-breathing PEMFCs were investigated by examining effects of cathode open area and relative humidity on the cell performance. Among the single cells with cathode open area from 52 to 94%, the single cell with the open area of 77% exhibited the highest performance. The cell performance was improved with increasing RH of atmosphere from 20 to 100% in the low current region while lowered in high current region. Those results were related with the mass transport of oxygen from the atmosphere to the catalyst layer and the degree of membrane hydration determining the ionic conductivity of the membrane.

Keywords: PEMFC; Portable fuel cell; Air breathing; Passive feeding; Cathode structure

1. Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention to replace the battery in portable devices such as cellular phones, PDAs and laptop computers because of its feature of easy fuel supply [1]. However, DMFC has a critical drawback of low power density resulting from the methanol crossover through the membrane and the low reaction rate of methanol oxidation [2]. As an alternative, the polymer electrolyte membrane fuel cell (PEMFC) with a high power density can be considered even though there is still the technical change of hydrogen storage.

Comparing mobile applications and residential power generation for the PEMFC, a portable PEMFC system should be compact and simple since the absolute volume and weight allowed for a mobile power source are limited. Thus, it is necessary to minimize balance of plant (BOP) devices such as pumps, valves and fans [3].

Particularly humidifiers and a water-cooling system are not applicable to portable systems. For that reason, a passive air-breathing PEMFC can be a feasible power source for the portable devices. Although the passive air-breathing PEMFCs have different characteristics from the active air-feeding systems usually applied to fuel cell vehicles and residential power generation systems, the effects of design parameters and operating conditions on the performance of passive air-breathing PEMFCs have not been systematically examined [4–7]. In this study, the characteristics of the air-breathing PEFMC without pump or blower for the air supply to the cathode were investigated by examining the effects of the structure of the cathode current collector and the relative humidity (RH) of air on the cell performance.

2. Experimental

2.1. Cell design

Fig. 1 shows the schematic cell structure for the passive air-breathing PEMFC used in this study. The anode flow field was made of graphite with five-serpentine channels of 1 mm wide and 0.9 mm deep. Polytetrafluoroethylene (PTFE) gaskets were used for gas sealing of both anode and cathode. The cathode current collector was made of 2 mm thick gold-coated copper

* Corresponding author. Tel.: +82 2 958 5279; fax: +82 2 958 5199.
** Corresponding author. Tel.: +82 2 3290 3297.
E-mail addresses: eacho@kist.re.kr (E.A. Cho), kimsh@korea.ac.kr (S.H. Kim).

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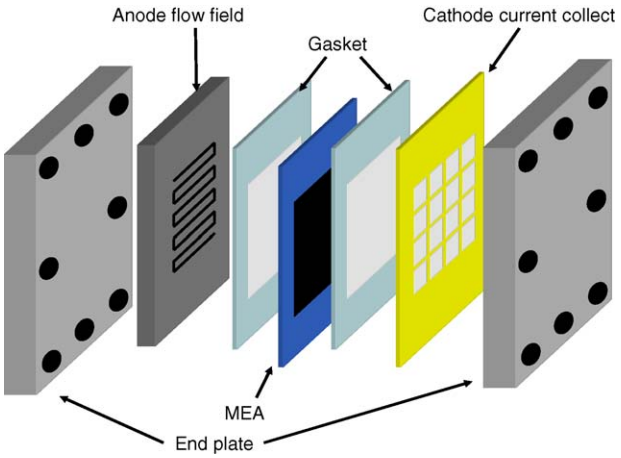

Fig. 1. A schematic structure of the passive air-breathing single cell.

plate. For air-breathing designs, the copper plate was machined to have various open areas with square openings as depicted in Fig. 2 and then coated with gold layer to protect from corrosion. The dimensions of the square openings were 4.5 mm × 4.5 mm, 6.67 mm × 6.67 mm, 11 mm × 11 mm and 24 mm × 24 mm and the total opening areas were 52, 64, 77 and 92%, respectively. The rib width was 2 mm.

2.2. Preparation of membrane electrode assembly (MEA)

A perflurosulfonic acid (PFSA) membrane (NRE-211, DuPont) was used as the electrolyte. The catalyst powder (40 wt.% Pt/C, E-Tek), Nafion solution (5 wt.%, EW = 1100, DuPont) and *iso*-propyl alcohol were mixed to prepare the catalyst ink. The total amount of Nafion ionomer in the electrodes was 33 wt.% of the catalyst weight. Then, the prepared catalyst inks were sprayed on the gas diffusion layer (wet proofing dry 20 wt.% of PTFE, Toray) with a platinum loading of 0.4 mg cm^{-2} for both anode and cathode. The membrane-electrode assembly (MEA) was prepared by placing the above electrodes on both sides of the pretreated Nafion membrane, followed by hot pressing at 140 °C and 100 atm for 90 s. The effective electrode area was 25 cm^2.

2.3. Measurement of cell performance impedance

To measure cell performance, dry hydrogen (99.9%) was used for the anode fuel and the flow rate was fixed at 100 mL min^{-1}. To maintain temperature and relative humidity of the surrounding atmosphere, all experiments were conducted in a controlled temperature and humidity chamber. Relative humidity in the chamber was changed from 20 to 100% at 35 °C. Before all measurements, single cells were pre-activated for 1 h at 100 mA cm^{-2} to eliminate effects of self humidification on ionic conductivity of the membrane. Polarization curves were measured with increasing current by 20 mA cm^{-2}. Each step was kept for 1 min to stabilize the cell voltage. Polarization resistance of the single cells was evaluated by measuring ac impedance of the cell with the air electrode as the working electrode and the hydrogen electrode as the reference and counter electrode. IM6 (ZAHNER) was used for the impedance measurement and the

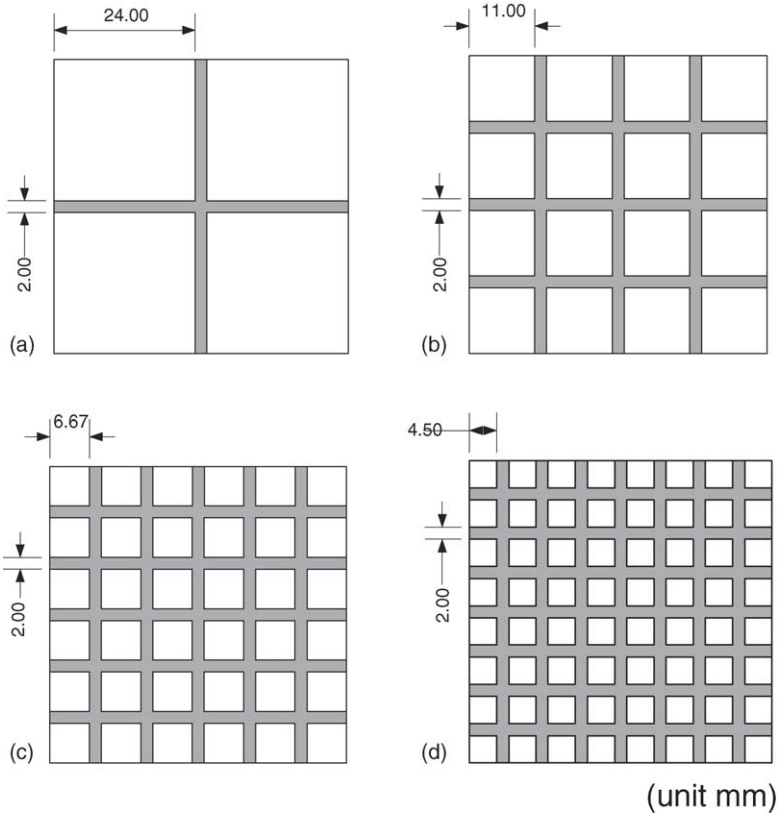

Fig. 2. Design of cathode current collectors with different open area: (a) 92%, (b) 77%, (c) 64% and (d) 52%.

applied frequency was varied from 50 mHz to 10 kHz with an excitation voltage of 20 mV (peak-to-peak) at cell voltage of 0.65 V.

3. Result and discussion

3.1. Effects of cathode open area on cell performance

Fig. 3(a) represents *I–V* curves for the single cells with cathode open area of 52, 64, 77 and 92% measured at RH of 80% and 35 °C. With increasing the open area, open circuit voltage (OCV) was lowered from 0.9 to 0.84 V, lower than that of active air-feeding PEMFCs probably due to a mixed potential of the cathode caused by hydrogen crossover through the membrane and the low activity of the electrode by low ionic conductivity in the electrode. The effects of the cathode open area on cell performance were dependent upon current density, as presented in Fig. 3(b). At low current densities (<100 mA cm^{-2}), i.e. at 40 mA cm^{-2}, the cell voltage was lowered from 0.73 to 0.69 V with the cathode open area since the polarization was mainly controlled by activation loss and ohmic resistance in this low current region. The activation loss and ohmic resistance were increased with the open area due to a lower ionic conductivity of the membrane resulting from faster evaporation of product water and higher in-plane electrical resistance resulting from longer electron pathways through the gas diffusion media. On the other hand, at high current densities (>200 mA cm^{-2}), i.e. at 240 mA cm^{-2}, with increasing the cathode open area from 52 to 77%, the cell voltage increased from 0.3 to 0.55 V due to the improved mass transport of oxygen from the atmosphere to the cathode catalyst layer. However, the single cell with the open area of 92%, even though it did not show fast voltage drop at high current densities by mass transport limitation, exhibited a lowered voltage of 0.43 V due to higher in-plane electrical resistance and lower ionic conductivity of the membrane, as described above. Maximum power density of 138 mW cm^{-2} at 0.46 V was obtained for the single cell with cathode open area of 77%.

At RH of 20%, similar results were obtained, as shown in Fig. 4. With increasing the cathode open area from 52 to 92%, the cell voltage was lowered from 0.67 to 0.63 V at a current density of 40 mA cm^{-2}. At a current density of 240 mA cm^{-2}, the single cell with open area of 77% exhibited the highest cell voltage of 0.56 V and the highest maximum power density of 146.2 mW cm^{-2} at 0.43 V.

Fig. 5(a) and (b) show Nyquist plots for the single cells with various cathode open areas at RH of 80 and 20%, respectively. The Nyquist plots shown in Fig. 5 are semi-circular; the left point

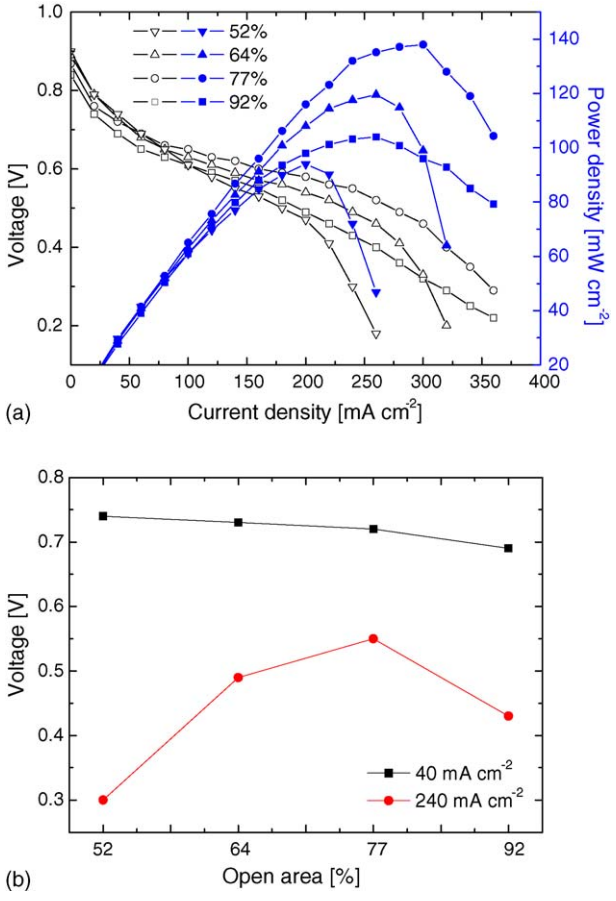

Fig. 3. Effects of cathode open area on cell performance measured at RH of 80%: (a) polarization curves and (b) cell voltage at 40 and 240 mA cm^{-2}.

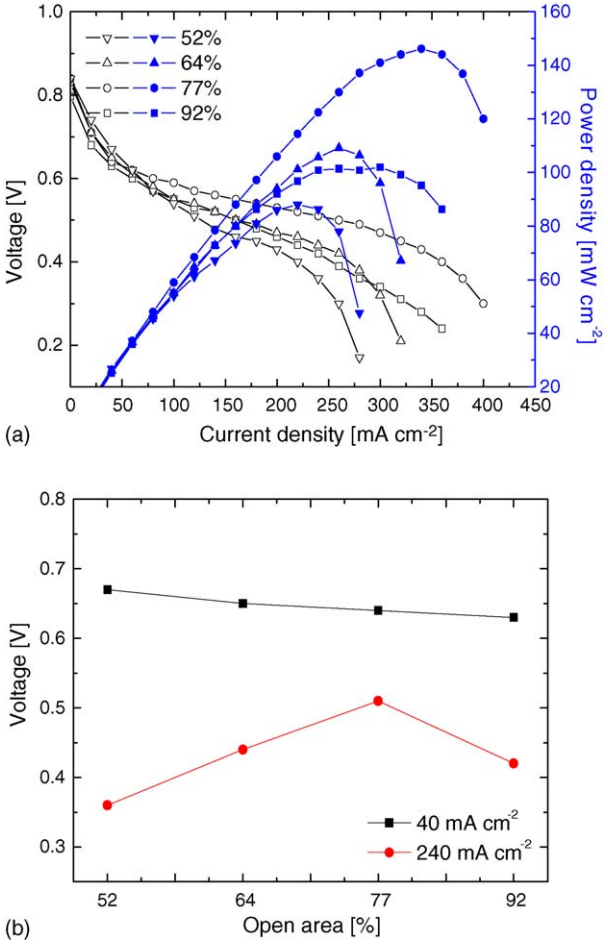

Fig. 4. Effects of cathode open area on cell performance measured at RH of 20%: (a) polarization curves and (b) cell voltage at 40 and 240 mA cm^{-2}.

of intersection with the x-axis corresponds to the ohmic resistance and the diameter of the semi-circle to the charge transfer resistance. In the ac impedance measurement, the air electrode served as the working electrode and the hydrogen electrode as the counter electrode. The counter electrode also served as the reference with its negligible overpotential for the hydrogen oxidation or evolution reaction. Thus, the charge transfer resistance obtained through the ac impedance study primarily could be attributed to the oxygen reduction reaction. From the data in Fig. 5(a) and (b), the ohmic resistance (R_{oh}) and the charge transfer resistance (R_{ct}) were evaluated and represented in Fig. 5(c). At RH of 80 and 20%, the ohmic resistance increased with the cathode open area since water evaporation was facilitated leading to decreases in the degree of hydration and hence ionic conductivity of the membrane. For the same reason, the single cell with the same cathode open area exhibited lower ohmic resistance at a RH of 80% than at a RH of 20%. On the other hand, with increasing cathode open area to 77%, the charge transfer resistance decreased and then increased at 92%. Those results were also associated with the trade-off of mass transport of oxygen from the atmosphere to the cathode catalyst layer and electronic and ion conductivity related with the electron pathway and water evaporations, respectively.

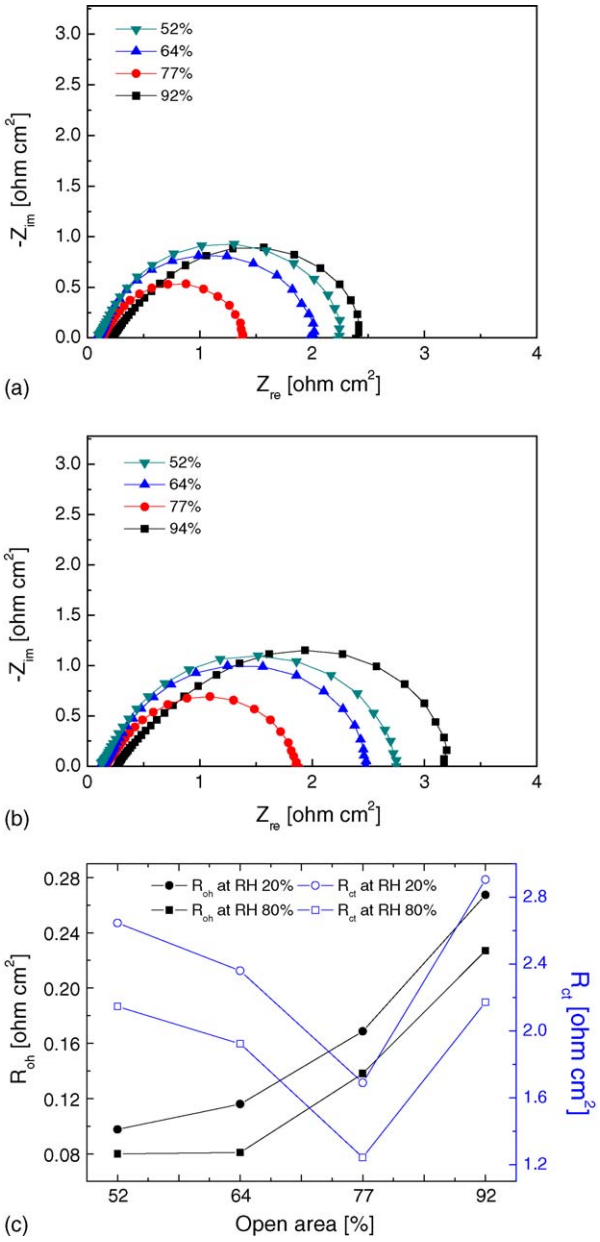

Fig. 5. Effects of cathode open area on Nyquist plots measured at (a) RH of 80% and (b) 20% and on (c) ohmic and charge transfer resistance.

As presented above, the passive air-breathing PEMFCs exhibited severe mass transport limitations, because oxygen was supplied to the cathode only by natural convection. In addition, compared with the active air-feeding PEMFCs where water can be easily removed by forced convection, the mass transport through pores in the catalyst layer and the gas diffusion media is inhibited by residual product water. Therefore, to obtain high performance air-breathing PEMFCs, it is necessary to design and operate a PEMFC under the optimal condition for mass transport and water management.

3.2. Effects of relative humidity on cell performance

Fig. 6 shows *I–V* curves for the single cell with cathode open area of 77% measured at RH from 20 to 100%. As in the case

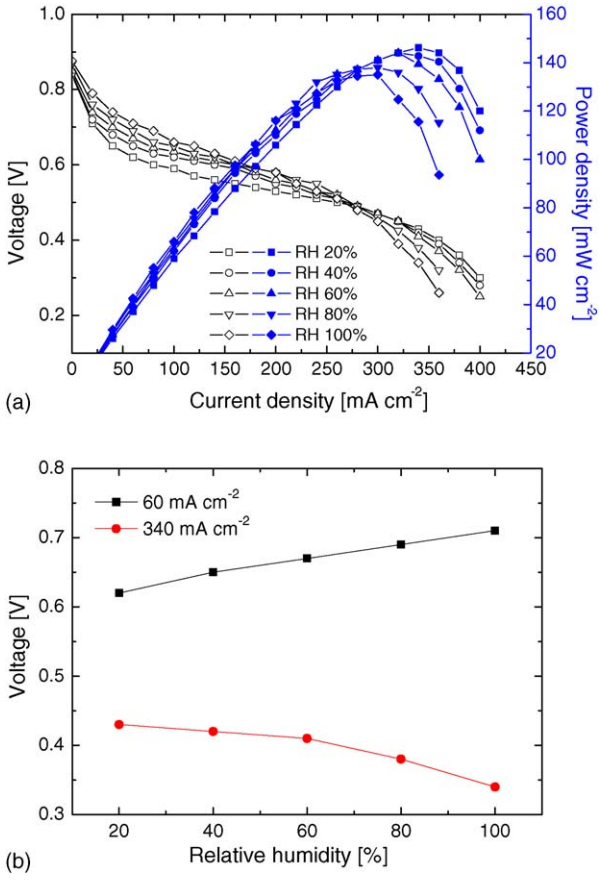

Fig. 6. Effects of relative humidity of atmosphere on cell performance with cathode open are of 77%: (a) polarization curves and (b) cell voltage at 60 and 340 mA cm^{-2}.

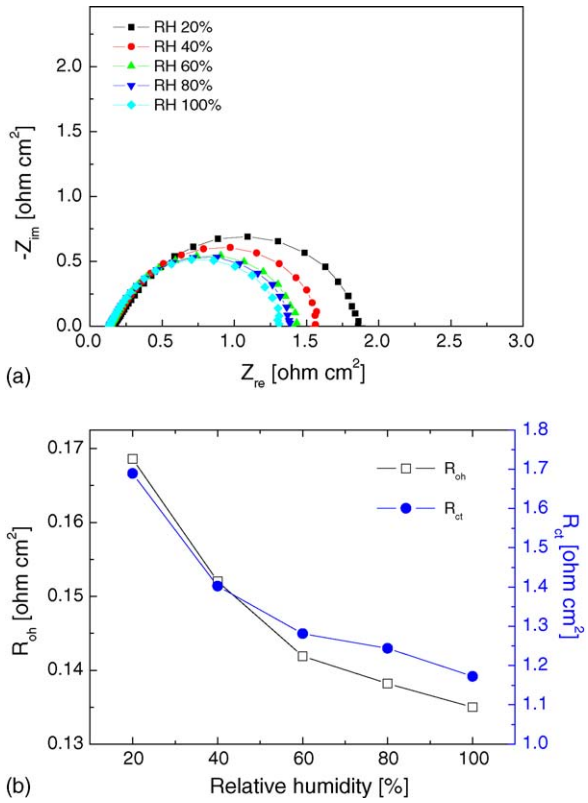

Fig. 7. Effects of relative humidity of atmosphere on (a) Nyquist plots and (b) ohmic and charge transfer resistance.

of the cathode open area, the effects of RH on cell performance were also dependent upon current density as shown in Fig. 6(b). At low current densities below about 200 mA cm^{-2}, i.e. at 60 mA cm^{-2}, the cell voltage increased from 0.62 to 0.71 V with increasing RH from 20 to 100%, due to slower water evaporation and higher ionic conductivity of the electrolyte membrane. High humidity makes conductivity of the ionomer higher and it results in high electrochemical active surface area [8]. In contrast, at high current densities above 300 mA cm^{-2}, higher RH led to a steeper mass transport loss since the product water could not be easily removed from the cathode; cell voltage at 340 mA cm^{-2} was lowered from 0.43 to 0.34 V. The maximum power was 146.2 mW cm^{-2} at RH 20% due to low mass transport polarization.

Nyquist plots for the single cell measured at various RH are presented in Fig. 7(a). In the case of increasing RH in air, the semi-circle shifted to the left with decreasing diameter. This implies decreases of ohmic and charge transfer resistance as shown in Fig. 7(b).

The performance of the passive air-breathing PEMFC is strongly dependent on the competition of evaporation and production of water, especially under dry conditions. Above a certain current density, water production is faster than evaporation and results in severe mass transport limitations. In contrast, below another certain current density, water evaporation is faster than water production and leads to low ionic conductivity of the membrane. Therefore, the operating condition should be controlled to be in the intermediate region.

In the passive air-breathing PEMFC, oxygen transport is divided into three steps: convection and bulk diffusion from the atmosphere to the gas diffusion media (GDM) surface; diffusion through the GDM; and diffusion through the catalyst layer. In the first step, oxygen is transported by weak natural convection and diffusion caused by the concentration difference between the atmosphere and the GDM surface. Thus, mass transport is controlled by the open area of the current collector facing bulk air. In the second step, oxygen travels from the GDM surface to the catalyst layer through pores in the GDL. Oxygen transport possibly can be inhibited by the product water blocking the pores, because there is no forced convection in air-breathing PEMFCs. The product water can be removed by evaporation or back diffusion from the cathode to the anode. Evaporation of water condensed or not condensed can be facilitated under a low RH condition or through a GDM with large pores. In the third step, oxygen diffuses and is consumed to produce water. The product water can diffuse through the membrane to the anode or diffuse through the GDM and evaporate on the surface. Since the back-diffusion of water strongly depends on the RH of the hydrogen gas, RH of hydrogen gas should be controlled for proper water management. It should be noted that, during some measurements of *I–V* curves and impedance spectra shown in Figs. 3–7, water drops were observed in the anode outlet gas, reflecting water back-diffused from cathode to anode.

4. Conclusions

The effects of the cathode open area and the relative humidity (RH) of the atmosphere on performance of the passive air-breathing PEMFCs were examined. At low current densities, the cell performance was lowered with increasing the cathode open area from 52 to 92% due to both faster water evaporation resulting in higher activation loss and ohmic loss and higher in-plane electrical resistance caused by the longer electron pathways through the gas diffusion media. On the other hand, at high current densities, the cell performance was improved by increasing the cathode open area from 52 to 77% due to the improved mass transport of oxygen from the atmosphere to the cathode catalyst layer. The single cell with the open area of 92%, even though it did not show fast voltage drop at high current densities by mass transport limitation, exhibited lowered performance due to higher in-plane electrical resistance and lower ionic conductivity of the membrane.

With increasing RH of atmosphere from 20 to 100%, the cell performance was improved at low current densities due to slower water evaporation and higher ionic conductivity of the electrolyte membrane. In contrast, at high current densities, higher RH led to steeper mass transport loss since the product water could not be easily removed from the cathode.

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