ANALYSIS OF WATER TRANSPORT IN PEFC BY MRI MEASUREMENT

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ABSTRACT

The management of water is one of the most important problems that limit the operation of polymer electrolyte fuel cells (PEFC). To better understand water transport in polymer electrolyte membranes (PEM), we numerically analyzed a one-dimensional model of water transport in a PEM. To increase the model accuracy, we did magnetic resonance imaging (MRI) experiments to determine the best parameters for the model. Using these parameters, we programmed the measured number of maximum water content of the membrane in a fuel cell and water transfer coefficient of the membrane surface. The resulting water distribution of the PEM under various operation conditions was consistent with previous MRI measurements.

INTRODUCTION

The polymer electrolyte fuel cell (PEFC) is considered to be a useful power source for automotive and other applications. However, the ionic conductivity of polymer electrolyte membranes (PEM) is high only when PEMs are hydrated (1,2). In addition, hydrated PEMs last much longer than dehydrated PEMs(3). The common method to keep a PEM hydrated is to supply humid gas to the PEFC. However, too high a humidity causes flooding of the porous carbon electrode. Thus, it is very important to know the water content distribution in a PEM under fuel cell operation. There are many modeling approaches to understand the water transport in a PEM (4,5), but modeling results strongly depend on poorly known parameters. Thus, as part of our modeling study, we determined the parameters experimentally.

In our previous study, we established a method based on magnetic resonance imaging (MRI) to determine the water distribution in a membrane under various operating conditions. We found that the water in the membrane has a concentration gradient under a high current (6). In this study, we numerically analyzed the water transport in the membrane based on experimental observations by MRI.

First we did the MRI experiment to determine the water transfer coefficient of water into the membrane assembled in the fuel cell. This is because accurate determination of the mass transfer coefficient is essential to describe water transport in the membrane under operation.
Isolated PEMs swell about 10-20% when they are hydrated (7). However, PEMs in a fuel cell are constrained such that they cannot swell; hence, the hydration of a PEM assembled in a fuel cell is poorly understood. In such a situation, we think, we need some model of assembling for analyzing the water content of PEM. Therefore, we used MRI to determine the water content of a PEM in a fuel cell under various conditions. In addition, the microscopic imaging was useful for determining the relation between water content and swell.

Then we programmed the measured water transfer coefficient and limitation of the water content of PEM assembled in a fuel cell. The results of the analyzed water distribution of a PEM under various operation conditions were compared with our previous MRI measurements.

**EXPERIMENTAL**

Because the fuel cell must be exposed to a high field of 7.05 T in the MRI chamber (Varian Unity INOVA 300), we built the fuel cell out of acrylic resin and other non-magnetic materials. Further details of the experimental setup and measurement system are in reference (6). We used a 340-μm-thick Asahi Kasei Aciplex-S® membrane. The membrane was treated with 3 wt.% H₂O₂ solution, then acid-treated with 1 N HNO₃ solution at 60 °C, rinsed with pure water, and then vacuum dried. To form the membrane electrode assemblies (MEAs), the membrane was sandwiched between carbon electrodes with a Pt catalyst of 0.5 mg/cm² by hot pressing them under 0.7 Nm/cm² for 10 min at 120 °C.

To determine the water transfer coefficient, we examined the hydration process of the membrane in the fuel cell. The membrane was initially kept dry. Then we began to supply humidified nitrogen gas to the membrane in the fuel cell. The gas flow rate was 260 ml/min and the pressure was 0.1 MPa. The dew point of the gas was regulated to stay within 40 to 60 °C. We measured the water distribution of the PEM every 5 min.

To determine how much the PEM swelled up for given water content, we measured the membrane thickness using microscopy and the membrane weight. The membrane was initially kept in pure water and fully hydrated. Then we put it on the weighing machine. We measured the membrane thickness and weight about every 3 minutes as the membrane lost weight in the dry room atmosphere (20 °C, 40% RH). The water content of the PEM was calculated from the membrane weight.

**MODEL OF THE WATER TRANSPORT IN A PEM**

Here we model water transport through the membrane as one-dimensional with absorption or evaporation of water at the membrane surface. Diffusion and electro-osmotic drive are included. In addition, we model the membrane’s maximum water
content $\lambda_{\text{max}}$ using the MRI measurement and the measurement of membrane swelling. The water transfer in the PEM follows

$$\frac{\partial \lambda}{\partial t} = \frac{\partial}{\partial \lambda} \left( D \frac{\partial \lambda}{\partial \lambda} \right) - \frac{\partial}{\partial \lambda} \left( n_{\text{osm}} \cdot \frac{\lambda}{F} \right),$$

[1]

where $\lambda$ is the water hydration number per sulfonic acid group, $F=96,485 \text{ C/mol}$ is Faraday's constant, and $i [\text{A/cm}^2]$ is the current density. The water diffusion constant $D$ and the water drag constant for electro osmotic drive $n_{\text{osm}}$ are linearly related to the water content of the membrane (4,5). The dry membrane density $\rho=2.02 \text{ g/cm}^3$ and the equivalent weight value $\text{EW}=1,024 \text{ g/mol}$ are the given values of Asahi-kasei Aciplex S1112 membrane.

As the boundary condition, we consider water absorption or evaporation based on Henry's law and water production due to the electrochemical reaction at the cathode. We assume that water transfer follows

$$J_w = h_c (\lambda_a - \lambda),$$

[2]

where $\lambda_a$ is the water sorption equilibrium value, which is based upon the water vapor activity $\alpha$ of the gas channel. The water transfer constant $h_c \text{ cm/sec}$, which was determined by MRI measurement, models the limits to mass transport that arise from the gas diffusion layer and the water transfer into and out of the membrane. Water production at the cathode follows

$$J_{\text{prod}} = \frac{i \cdot \text{EW}}{2F \rho}.$$

[3]

RESULTS AND DISCUSSION

For each dew point level in the gas, the PEM became hydrated and reached equilibrium within about 15 minutes (Fig. 1). The best fits of the model to the data gave a water transfer coefficient of $h_c = 10^4 \text{ cm/sec}$. It is clear that the water content in equilibrium increased with the dew point of the gas.

We compare the measured equilibrium water content with a typical absorption isotherm for a membrane (8)(Fig. 2). The measured water contents for the dew points of 40 and 50 °C are in good agreement with the results in Hinatsu et al. However, the measured water content at the dew point 60 °C is smaller than one measured by Hinatsu et al. Hinatsu et al. measured water absorption to the membrane. In our study, we measured water absorption to the membrane in the cell. The discrepancy in the two studies suggests that the membrane in the fuel cell has an upper limit on water content due to confinement by the electrode. The upper limit of the water content is about 6.5 per sulfonic acid group in Fig. 2.

To better understand this limiting value per sulfonic acid group of 6.5, we did a measurement to determine the relation between water content and membrane swelling. Figure 3 shows the result. Membrane swelling is not linear with increasing water
content; rather, the swelling increases in two steps as the water content increases. Below water contents of about 6, the membrane thickness does not increase with the water content. At larger water contents, the membrane thickness increases linearly with increasing water content in the membrane.

We think that the membrane in a fuel cell is not able to swell because it is sandwiched between the electrodes with the result that the maximum water content of the membrane in a fuel cell is about 6. This confinement effect was included in our numerical simulation.

The simulation of the water content profile (solid line in Fig. 4) is in good agreement with the MRI results. However, when we removed the confinement effect (broken line in fig. 4), the simulation results gave higher water contents than the MRI. Thus, we conclude that the confinement of the membrane, due to its being in the fuel cell, limits the water content in the membrane and thus has an important influence on the water transport in PEFCs.

To further evaluate this model, we analyzed the water distribution change when the fuel cell starts operation. We measured the water distribution in the membrane using MRI after closing the constant resistant electric circuit. Figure 5 shows the time variation of the current density after the fuel cell started up. The current density decreased because the internal resistance of the fuel cell increased; moreover, the increase of internal resistance was due to a decrease in the water content of the membrane as shown in Fig. 6. Figure 6 shows the time variation of the water content at the anode and cathode side of the membrane. Both the measurements and the model show a rapid decrease of water content at the anode and a slow decrease at the cathode side. The agreement between the model and measurements is good, which further supports the model.

**CONCLUSIONS**

In this study, we used MRI measurements to determine the water transfer coefficient and maximum water content of a membrane in a fuel cell. We found that the maximum water content was consistent with the measured relation between water content and membrane swelling. In our model, we programmed this maximum water content as the confinement effect, which models membranes that have swelled in the fuel cell.

The analysis of steady and unsteady state are in good agreement with the MRI measurements (6). That clearly shows the validity of this model, and we conclude that the limitation of the water content in the membrane assembled in the fuel cell is an important factors for analyzing water transport in PEFCs.
ACKNOWLEDGEMENTS

This study was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan and the Japan Society for the Science Promotion (JSPS). We gratefully thank Asahi Kasei Corp. and Tanaka-Kikinzoku Kogyo for supplying PEFC materials.

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Fig. 1. Average water content in the membrane after the flow of humid gas starts. The points are MRI data for the three dew points and the curves are simulation results that use $h_c=10^{-4}$ cm/s as the water transport constant.

Fig. 2. Water uptake in a PEFC from water vapor. The three data points are from the MRI measurements. The curve is an isotherm from Ref. 8.
Fig. 3. The membrane swelling ratio. The value of 100% represents the dry membrane. In this graph, the abscissa is the water content of the membrane and the means membrane thickness that the dry state membrane thickness is 100%.
Case A; 0 A/cm², 0.844V

Case B; 0.089 A/cm², 0.621V

Case C; 0.222 A/cm², 0.390V

Fig.4: Water content profiles in the membrane. In the MRI image, the left side is the anode.
Fig. 5. Cell current after the cell start-up at 0 seconds.

Fig. 6. Water content in the anode and cathode sides of the membrane after the cell start-up.

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