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Simultaneous Measurements of Water Distribution and Electrochemical Characteristics in Polymer Electrolyte Fuel Cell

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Abstract. In this study, neutron radiography and electrochemical impedance spectroscopy (EIS) were simultaneously used to evaluate the relation between the water amount and the electro chemical characteristics in a polymer electrolyte fuel cell (PEFC). Two-dimensional water distributions in the through-plane direction of the proton exchange membrane (PEM) were measured every 60 s during the PEFC operation. The results were compared with ionic and the polarization resistances obtained from EIS. The ionic conductivity through the PEM increased with an increase in the liquid-water content in the membrane. The effects of water content on the ionic conductivity were much smaller in comparison to the Springer's model at a water content was less than 1. The polarization resistance increased with an increasing in liquid-water accumulation in the gas diffusion layer.

Introduction

Water management is a key topic of a polymer electrolyte fuel cell (PEFC). If condensed water exists in the gas diffusion layer (GDL) and the gas channel, it may depress the gas diffusion as flooding. However, the generated water must be appropriately supplied to the proton exchange membrane (PEM) for proton conduction. Hence, water management is significantly important for PEFC performance, and clarification of the water-transport mechanisms between the PEM, GDL, and gas channels is of great concern. Several investigations on water management have been carried out concerning water movement inside the PEM, water flooding in the GDL, and water plugging in the channel [1, 2].

Loss in electric power generation in the PEFC is due to resistances such as ionic, activation, concentration, etc. Many of these resistances are related to the mass transport in the PEFC. To evaluate the resistances in a PEFC, electrochemical impedance spectroscopy (EIS) has been widely used [3]. However, the effect of water in the PEFC on the resistances has not been fully understood. Aim of this study is to clarify the effect of water in the PEM and the GDL on the resistances. Simultaneous measurements of the water distribution and the electrical impedance were carried out by using neutron radiography and EIS. Changes in water accumulation in the PEM and the GDL were compared with the resistances.

Experimental setup and method

A schematic diagram of the PEFC is shown in Fig. 1. A proton exchange membrane was sandwiched between the gas diffusion layers and the gas channels. The separators were made of gold-plated aluminum having nine-parallel gas-channels with a cross-sectional area of 1 × 1 mm^2. The length of the channel was 10 mm. Nafion® NR-212 was used as the PEM with a thickness of approximately 90 μm, having catalyst layers on both the anode and the cathode sides. The electrode area was 10 × 19 mm^2. The GDL was carbon paper (Toray Ind.) with thickness of 190 μm at the cathode side and 280 μm at the anode side. The porosity of the GDL was approximately 78%.

Two-dimensional water distributions were measured using neutron radiography during PEFC operation. The neutron radiography facility at B-4 port in the Kyoto University Reactor (KUR) was used in this study. The total neutron flux at the beam exit was approximately 5 × 10^7 /cm^2 s with a nominal thermal output of 5 MW [4]. Neutrons entered from the side-view direction and were attenuated by the PEFC including the accumulated water. The transmitted neutrons were converted to visible rays using a scintillator screen, and the 16-bit gray-scale radiographs were taken using a cooled CCD camera (PIXIS 1024, Princeton Instruments) with an array of 1024 × 1024 pixels. Exposure time for obtaining an image was set at 1 min. Obtained water-distribution represents the average value over 1 min exposure time. The details of the measurement methods are described in reference [2].

The equivalent electric circuit for the EIS analysis used is shown in Fig. 2. As the polarization resistance of the cathode is much higher than that of the anode, associated elements of the anode can be neglected [5]. C_{dl} is the double-layer capacitance, R_{PEM} is the ionic resistance through the PEM, and R_{pol} is the polarization resistance consisting activation and concentration polarization resistances at the cathode. Impedance analysis took approximately 40 s for one measurement with a frequency range of 0.5 to 30 kHz. Therefore, an impedance measurement was complete within the time taken for a neutron radiograph measurement. Comparisons of the water distribution and the electro chemical characteristics were carried out over 1 min. Impedance analysis can be applied for steady state conditions, however, if the water distribution changes rapidly, results might be affected. Therefore, to change the water distribution gradually, the experiments were carried out at a relatively lower current density, i = 158 mA/cm^2 and 316 mA/cm^2. The air and hydrogen flow rates were 66 Ncc/min and 28 Ncc/min, respectively. The oxygen utilization was 7.5% at i =158 mA/cm^2 and 15% at i =316 mA/cm^2 and a hydrogen utilization was 7.5% at i =158 mA/cm^2 and 15% at i =316 mA/cm^2. The experiments were carried out at room temperature, while the temperature of the PEFC varied between 25 – 30 °C.

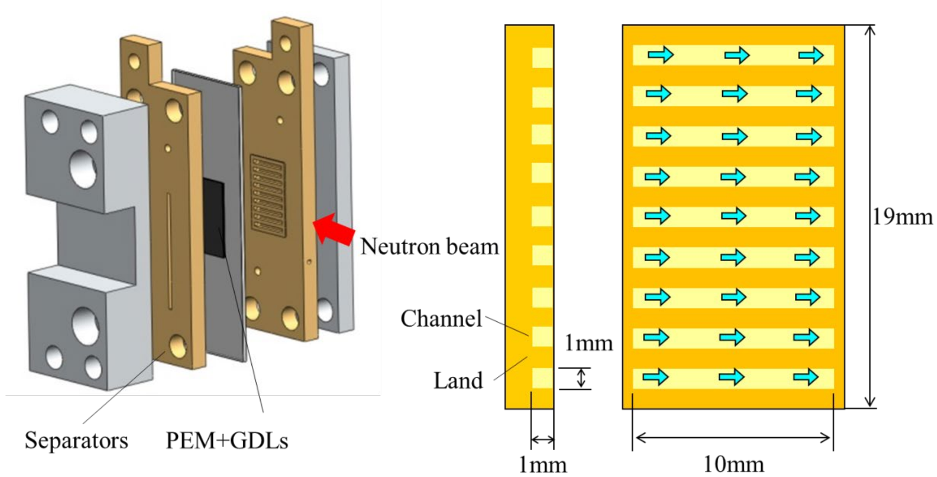

Fig. 1. *Schematic diagram of the polymer electrolyte fuel cell and geometry of the gas channel.*

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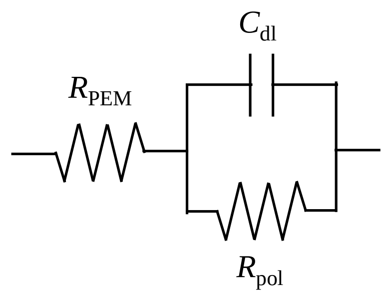


Fig. 2. *Equivalent electric circuit.*

Evaluation of the ionic conductivity

Springer et al. [6] proposed a correlation between ionic conductivity of the PEM, σ, and the water content in the PEM as

$$\sigma(T_{cell}) = (a\lambda + b)\exp\left[1268\left(\frac{1}{303} - \frac{1}{273+T_{cell}}\right)\right] \qquad \text{for } \lambda > 1 \tag{1}$$

Where λ [-] is the water content of the electrolyte and is defined as mol-H_2O / mol-SO_3^- ; T_{cell} [°C] is the cell temperature. The correction factors were proposed as a = 0.5139 and b = -0.326. To evaluate Eq. (1), λ was calculated using the following equation [7].

$$\lambda = \frac{t_w h t_{PEM} \rho / M_{H_2O}}{mS / EW}. \tag{2}$$

Where t_w [m] is the average water thickness inside the PEM, h [m] is the electrode height, t_{PEM} [m] is thickness of the PEM, ρ [g/m^3] is density of the liquid water, M_{H_2O} [g/mol] is the molar mass of water, EW [kg/mol] is the mass of PEM per mol of the sulfonic acid group, m [kg/m^2] is the mass per area of PEM, and S [m^2] is the area of PEM. Ionic conductivity from the impedance measurement results can be expressed by the following equation, using R_{PEM} and the active area of A [m^2].

$$\sigma = \frac{A}{R_{PEM} t_{PEM}}. \tag{3}$$

The PEM properties are listed in Table 1.

Table 1. *PEM properties*

PEM thickness, t_{PEM}	[m]	: 90×10^{-6}
Electrode height, h	[m]	: 19×10^{-3}
Liquid water density, ρ	[kg/m^3]	: 997.04
Molar mass, M_{H_2O}	[g/mol]	: 18
Equivalent weight, EW	[kg/mol]	: 1100
Basic weight of Nafion® NR-212, m	[g/m^2]	: 100
Area of PEM, S	[m^2]	: 0.00168

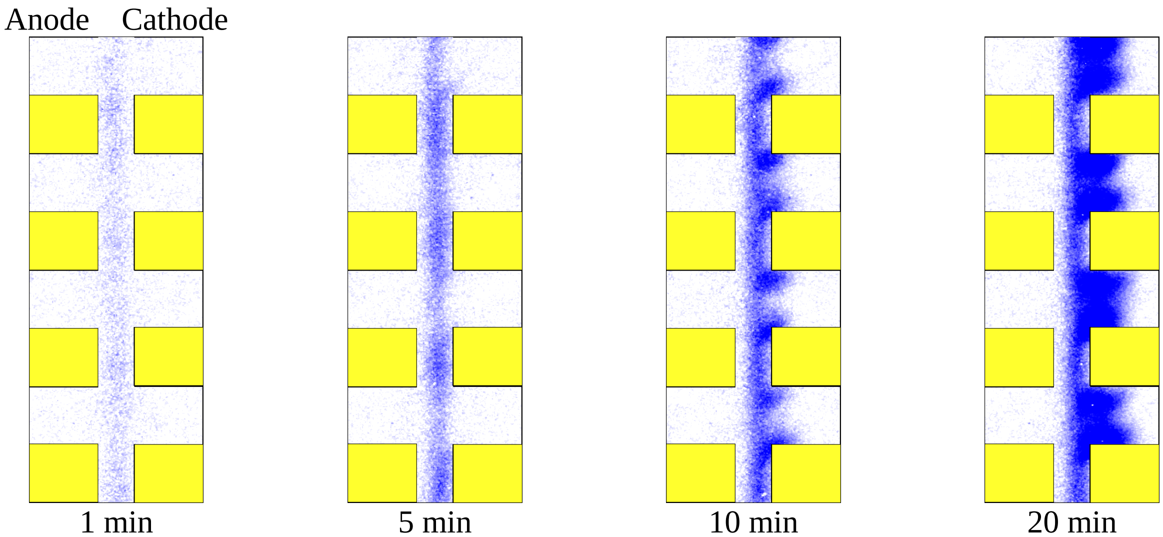


Fig. 3. *Two-dimensional water distributions at i =158 mA/cm²*.

Two-dimensional water distributions

Two-dimensional water distributions at i =158 mA/cm^2 are shown in Fig. 3. Blue color represents the liquid water. Water accumulation in the PEM and the GDL increases with the PEFC operation time. The amount of water accumulation in the GDL under the lands is greater than that under the channels at 5 min. It indicates that water accumulation in the GDL at the cathode started under the lands. The liquid water, then reaches the channel and gets concentrated at the land corners. Liquid water droplets formed in the channels grow at the interface between the channels and the GDL along the channel walls.

Relation between water saturation and the resistances

Two-dimensional water distributions measured using neutron radiography expressed the relative water accumulation based on the initial condition. In this study, changes in λ (Δλ) and changes in σ (Δσ) from the initial condition are evaluated. Fig. 4 represents the relation between Δλ and Δσ at all times in each current density. It was confirmed that Δσ increases with Δλ. However, effect of water contents on the ionic conductivity was much less than that proposed by Springer et al. [6]. It is difficult to determine the absolute value of λ in the PEM precisely using the neutron radiography. However, it was confirmed that a small change of the water amount in the PEM with supplying dry nitrogen was confirmed before each experiment. Therefore, it is expected that λ in the PEM before operation is less than 1. These results show that change in the ionic conductivity with respect to the water content becomes small in low water content range.

Fig. 5 shows the relationship between water saturation, s, in the GDL and the polarization resistance. The water saturation was calculated from the average two-dimensional water distribution in the GDL area. The results show that R_{pol} increases with the water saturation in the GDL. Tendencies at i = 158 mA/cm^2 and 316 mA/cm^2 are almost the same at $s < 0.2$. However, R_{pol} increases rapidly at $s > 0.2$. This indicates a blockage in the gas supply due to flooding in the GDL and the channel significantly degraded the power generation.

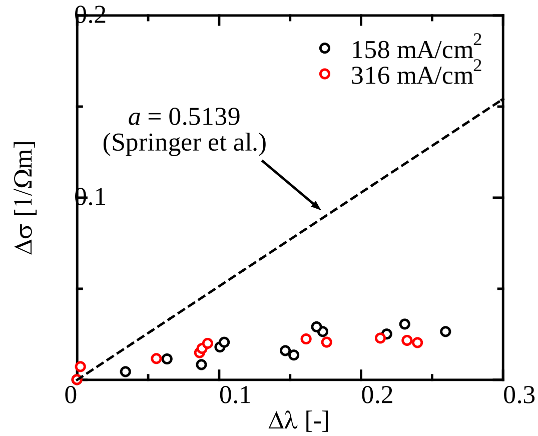


Fig. 4. *Relation between water content in MEA and the ionic conductivity.*

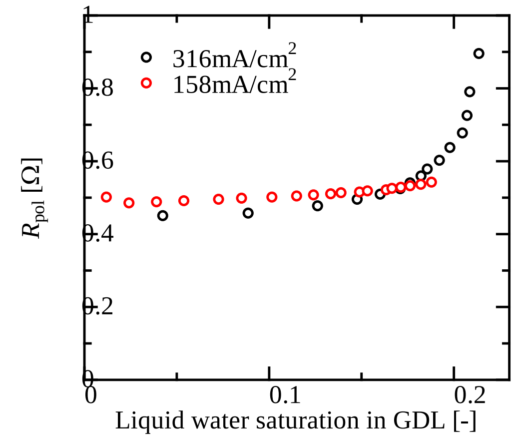
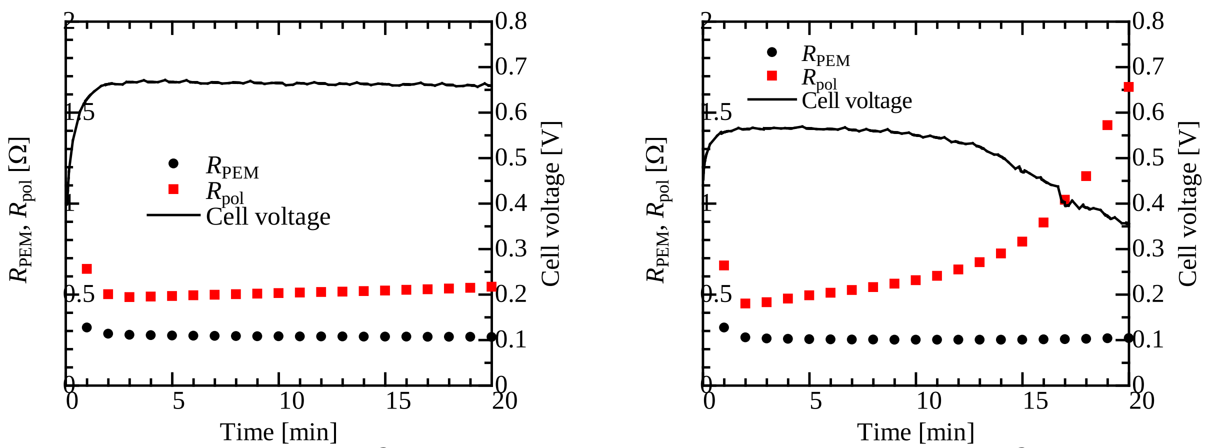


Fig. 5. *Relation between liquid saturation in GDL and the reaction resistance.*



(a) 158 mA/cm^2 (b) 316 mA/cm^2

Fig. 6. *Relation between the cell voltage and the resistance.*

Fig. 6 shows time series of the cell voltage, the polarization and the ionic resistances. The large periodical fluctuations in the cell voltage were caused by EIS. For an easier understanding, a moving average was applied to the original cell voltage data during the impedance measurements, resulting in a smooth change in the cell voltages, as shown in Fig. 6. The cell voltage rapidly recovers after start of the power generation and is approximately constant at i = 158 mA/cm^2. The polarization resistance increases slightly, and the ionic resistances decreases slightly, with the operation time. Alternatively, the cell voltage rapidly decreases due to an increase in the polarization resistance after 10 min at i = 316 mA/cm^2. The tendency of the ionic resistance at i = 316 mA/cm^2 is approximately same as at i = 158 mA/cm^2. Because of the power generation, water accumulates in the PEM and the GDL. Increase in water accumulation in the PEM leads to a slight decrease in the ionic resistance. However, difference in the ionic resistance was not significant at 158 mA/cm^2 and 316 mA/cm^2. As discussed in Fig. 4, the effect of water content on the ionic conductivity was not significant. Thus, water accumulation influenced the polarization resistance and affected the cell performances.

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Summary

In this study, simultaneous measurements of water distribution and the electrical impedance were carried out by using neutron radiography and electro-chemical impedance spectroscopy. The relation between the water amount in the PEFC and the electro chemical characteristics was evaluated.

Ionic conductivity increased with an increase in the membrane water content. However, effects of the water content on the ionic conductivity was much less than proposed by Springer et al. Springer's model cannot be applied for $\lambda < 1$. Polarization resistance increased with an increasing in liquid water in the GDL. This effect was dominant when water saturation reached 0.2. This indicates a blockage in the gas supply due to flooding in the GDL and the channel significantly degraded power generation. The polarization resistance, consisting of activation and concentration polarization resistances had a dominant effect on the degradation of the power generation if water accumulation in the membrane and the GDL was high.

Acknowledgement

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