Study on performance simulation of polymer electrolyte fuel cell for preventing degradation

T Kobayashi1*, T Fukuda2, M Doi1, R Hashimoto3, H Kanematsu4 and Y Utsumi5
1 Dep. of Electronics & Control Eng., Tsuyama National College of Technology, Okayama, Japan
2 Dep. of Mechanical Eng., Nagoya Institute of Technology, Nagoya, Japan
3 Collaborative Research Center, Hiroshima University, Hiroshima, Japan
4 Dep. of Materials Sci. & Eng., Suzuki National College of Technology, Mie, Japan
5 Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Hyogo, Japan
*E-mail: t-koba@tsuyama-ct.ac.jp; +81-(0)868-24-8215

Abstract. In the present study, the distribution of water content in the membrane of PEFC was analyzed by using a numerical simulation as well as understanding the behavior of internal moisture of PEFC. Eight parameters were selected for the simulation then 18 combinations of the parameters were allocated by design of experiments, thus the data obtained were analyzed by multiple regression analysis to understand the influence factor of operating conditions quantitatively. As a result, the influence of the operating parameters on the dryness of the membrane for the anode side and the cathode side of PEFC was quantitatively shown by using the method of the multiple regression analysis. Further, it was found that the area where cerium carbonate ought to be coated for preventing the degradation without decreasing performance.

1. Introduction
Polymer electrolyte fuel cell (PEFC) is expected as one of the efficient use of fossil fuels. However, there have been still remaining obstacles to be overcome for commercial use. Electrolytic membrane in the PEFC is degraded with decreasing water content in the membrane [1]. It has been reported that low humidity degrades the polymer membrane, resulting in a decrease in cell voltage, a hydrogen cross leak from the anode to the cathode, and finally, stopping power generation [2]. The degraded polymer membrane became much thinner. This damage might be due to radicals formed in the MEA [2]; therefore, a study examined the effect of a radical capturing layer and showed that an MEA with the radical capturing layer exhibits greater endurance—10 to 20 times that of a conventional MEA [3]. However, excessive amount of coating of the radical capturing layer causes performance drop of PEFC [3]-[4].
In the present study, the distribution of water content in the membrane of PEFC was analyzed by using a numerical simulation as well as understanding the behavior of internal moisture of PEFC. The simulation data obtained were analyzed by multiple regression analysis to understand the degree of influence of operating conditions quantitatively. Furthermore, the calculations using the diffusion coefficients of water applied some researchers were conducted to clarify the influence of the properties of the membrane on the dryness [5].
2. Performance Simulation

A two dimensional model considering the transfer of electric charge and mass was constructed. In the simulation model, the direction of gas flow channel can be divided into \( n \) elements, the direction of the membrane thickness is consist of anode gas channel, membrane electrode assembly(MEA), cathode gas diffusion layer and anode gas flow channel. In the present paper, the direction of gas flow channel was divided into 10 elements, and iterative calculation was conducted. Moisture to pass through the polymer membrane is transferred by the following three factors. 1) moisture migration by the reaction. 2) moisture migration by electro-osmosis. 3) moisture migration by diffusion. The above factors are expressed as the following equation which is the sum of each moisture migration.

\[
N(x) = \frac{i(x)}{2F} + n_d \frac{i(x)}{F} + D_w \frac{dc_w}{dy}
\]

(2.1)

Where, \( N(x) \): Molar flux of water in the membrane\([\text{mol/s/cm}^2]\), \( i(x) \): current density\([\text{A/cm}^2]\), \( F \): Faraday constant\([\text{C/mol}]\), \( n_d \): Electro-osmosis coefficient \([-]\), \( D_w \): Diffusion coefficient \([\text{cm}^2/\text{s}]\), \( c_w \): Water content in the membrane \([\text{mol/cm}^3]\). Accordingly, using the equation, the behavior of water can be understood. In addition, the following equation was used for the water content in the membrane obtained in the experiment by Springer et al. [6]

\[
c_w = \frac{\rho_{m,\text{dry}}}{M_{m,\text{dry}}} (0.043 + 17.8a + 39.8a^2 + 36.0a^3)
\]

(2.2)

where, \( \rho_{m,\text{dry}} \): Density of the film dried \([\text{g/cm}^3] \), \( M_{m,\text{dry}} \): Equivalent weight of the membrane dried \([\text{g/mol}] \), \( a \): Water activity \([-]\). The simulation was performed assuming a case of using pure hydrogen as the fuel gas, air as the oxidizing gas \((\text{N}_2:79\%, \text{O}_2:21\%)\). Physical properties required for the simulation, are the same as those in the simulation used by Onda et al. [5]

2.1 Equation for the characteristics of the membrane

Springer et al. [6] expressed as a function of percentage of the water content of the membrane by measuring to the diffusion coefficient and electro-osmosis coefficient in an experimental of PEFC. Here, \( \lambda \) water content ratio defined by water activity, and the relationship between water activity and moisture content is expressed in the following equation.

\[
\lambda_k = 0.043 + 17.81a_k - 39.85a_k^2 + 36.0a_k^3 \quad (0 < a_k \leq 1)
\]

(2.3)

However, \( a_k \) is the water activity of the \( k \) side (anode or cathode). Theoretical water content is a ratio of the number of sulfone group which works as a carrier of proton in the membrane, to the number of water molecule in the membrane. The water content is calculated with the equation. In this paper, this value is referred to as the water content.

\[
cH_2O, k = \frac{\rho_{m,\text{dry}}}{M_{m,\text{dry}}} \lambda_k = \frac{\rho_{m,\text{dry}}}{M_{m,\text{dry}}}(0.043 + 17.81a_k + 39.85a_k^2 + 36.0a_k^3) \quad (0 < a_k \leq 1)
\]

(2.4)

where, \( \rho_{m,\text{dry}} \): Density of the film dried\([\text{g/cm}^3]\), \( M_{m,\text{dry}} \): Equivalent weight of the film dried\([\text{g/mol}]\) The equations of the electro-osmosis coefficient \( n_d \) and the diffusion coefficient \( D_{H_2O} \) are shown in equation (4) and (5).

\[
n_d = 2.522\lambda_a = 0.0049 + 2.02a_a - 4.53a_a^2 + 4.09a_a^3 \quad (0 < a_a \leq 1)
\]

(2.5)
\[ D_{H_2O} = (0.0049 + 2.02a_d - 4.53a_d^2 + 4.90a_d^3)D_0 \exp \left\{ 1268 \left( \frac{1}{303} - \frac{1}{T + 273.15} \right) \right\} \]  

(0 < a_d \leq 1) \quad (2.6)

where, \( D_0 \): the effective water diffusion coefficient in the membrane in the standard condition [cm\(^2\)/s], \( T \): Cell temperature [°C]. The electric conductivity of membrane, which was expressed as a function of the water content in the anode side, is shown below.

\[ \sigma_m = (0.00514\lambda_a - 0.00326)D_0 \exp \left\{ 1268 \left( \frac{1}{303} - \frac{1}{T + 273.15} \right) \right\} \]  

(2.7)

Here, the activity of water in the anode side is

\[ a_a = \frac{x_{H_2O,a} P}{P_{H_2O,a}} = \left( \frac{M_{H_2O,a}^v}{M_{H_2O,a}^v + M_{H_2}^v} \right) \frac{P}{P_{H_2O,a}} \]  

(2.8)

and the activity of water in the cathode side is written in the next formula

\[ a_c = \frac{x_{H_2O,c} P}{P_{H_2O,c}} = \left( \frac{M_{H_2O,c}^v}{M_{H_2O,c}^v + M_{O_2}^v + M_{N_2}^v} \right) \frac{P}{P_{H_2O,c}} \]  

(2.9)

where, \( x_{H_2O} \) is molar fraction. The amount of saturated water vapor required to determine the activity of water is expressed in the following equation.

\[ \log_{10}(P_{H_2O,k}) = 2.95 \times 10 - 2T_k - 9.18 \times 10 - 5T_k^2 + 1.44 \times 10 - 7T_k^3 - 2.18 \]  

(2.10)

3. The simulation conditions

In the simulation, a single cell of one flow path is used as shown in Figure 1, and operating temperature and temperature distribution are kept constant. The initial conditions of the simulation are current density [A/cm\(^2\)], operating temperature [°C], \( H_2 \) humidification temperature [°C], air humidification temperature [°C], \( H_2 \) utilization [%], and the air utilization [%], and the values shown in Table 1 are used.

![Figure 1 Dimensions of the simulation](image-url)
4. Simulation result

The distribution of water content in Polymer Membrane was calculated in 18 conditions using 9 parameters in Table 1. Some examples of the results are shown in Figure 2. It was found that the water content of anode side was higher than that of cathode side probably due to the produced water by power generation. In addition, the water content of cathode side tends to increases from the inlet to outlet direction, on the contrary the trend reverses in the anode side. The reason was suggested that the cathode gas has low humidity due to the lower water saturation temperature in than operation temperature in cathode, and that the water molecules in anode transfer toward cathode by the osmic effect flow. Firstly, dryness and the range of dryness were defined shown in Figure 2. In Figure 2.1 and Figure 2.3, the water contents saturate at around 0.025\(\text{mol/cm}^3\). The saturated value was defined as the dryness of zero. For example, the estimation method of the dryness was shown in Figure 2.1. The average value \(c\) of max and min of water content was determined, then the ratio of \(a\) to \(b\) is defined as the dryness.

\[
\frac{(b-c)}{b} = \frac{a}{b} \times 100 = \text{dryness} \ [%] \tag{4.1}
\]

The range of the dryness was defined as the region not saturated in water content, shown in Figure 2.2 and Figure 2.4. Eight parameters were allocated to 18 conditions using Design of Experiment (DOE), then the dryness and the range of dryness were calculated by the above mentioned simulation.

| Table 1 Eight parameters | First standard | Second standard | Third standard | Range |
|--------------------------|---------------|----------------|---------------|-------|
| \(H_2\) entrance flow quantity | 1 | 2 | 3 | 1 |
| Cell temperature | 50 | 55 | 60 | 10 |
| \(H_2\) humidification temperature | 50 | 55 | 60 | 10 |
| Air humidification temperature | 50 | 55 | 60 | 10 |
| \(H_2\) utilization | 30 | 50 | 80 | 50 |
| Air utilization | 15 | 40 | 60 | 45 |
| Current density | 0.2 | 0.5 | 1 | 0.8 |
| Air entrance flow quantity | 1 | 2 | 3 | 2 |

Figure 2.1 Dryness of membrane (anode side)  
Figure 2.2 The range of dryness (anode side)
From the obtained data, multiple regression analysis on the effects of the parameters on the dryness and the range of the dryness were carried out, and regression equations were created. The obtained coefficients and the equations are shown in the lower part. The influence factor of each parameter is the value multiplied the coefficient of the equation as by the range of each parameter (the range between level 1 to level 13) $\Delta x_i$.

Anode side-dryness

$$Y_1 = -121.24 + 11.961x_1 + 5.081x_2 + 0.199x_3 - 0.095x_4 - 0.027x_5 - 0.011x_6 + 1.97x_7 + 0.434x_8$$

(4.2)

Anode side- range of dryness

$$Y_2 = -5.063 + 0.549x_1 + 0.199x_2 + 0.095x_3 - 0.027x_4 - 0.011x_5 + 1.97x_6 + 0.434x_8$$

(4.3)

Cathode side-dryness

$$Y_1 = -13.863 + 2.032x_1 + 1.643x_2 + 0.199x_3 - 0.095x_4 - 0.027x_5 - 0.011x_6 + 3.111x_7 + 4.572x_8$$

(4.4)

Cathode side- range of dryness

$$Y_2 = -1.915 + 0.239x_1 + 0.094x_2 + 0.067x_3 - 0.008x_4 + 0.014x_5 + 0.487x_7 + 0.159x_8$$

(4.5)

Where, $Y_i$: dryness of membrane [-], $Y_2$: the range of dryness [-], $x_1$: H$_2$ entrance flowing quantity [cc/min], $x_2$: cell temperature [°C], $x_3$: H$_2$ humidify temperature [°C], $x_4$: air humidify temperature [°C], $x_5$: H$_2$ utilization [%], $x_6$: air utilization [%], $x_7$: current density [A/cm$^2$], $x_8$: air entrance flowing quantity [cc/min].

Figure 3 shows the influence factors of the eight parameters. It was found that in anode side, the
influential parameters on the dryness art cell temperature can suppress the drying of the polymer membrane. The parameters influenced on the range of dryness were same as those for the dryness. In cathode side, cell temperature and current density influenced heavily on the dryness, and H₂ utilization ratios and air humidify temperature can suppress the dryness. The parameters influenced on the range of dryness in cathode side are same as those of the dryness, however the parameters suppress drying are air humidify temperature and air utilization ratio.

5. Influence of physical properties
In the above calculation, the physical property values used by Springer and Nguyen were used. To investigate the effect of the physical property values used in the equations, calculation was carried out using the values Zawodzinski were used. In the calculation, current density and H₂ utilization which effect the dryness and the range of dryness respectively were varied keeping the other parameters constant. The diffusion coefficients of water in the polymer membrane compared were shown in Figure 4, where the dependence of relative humidity on the diffusion coefficient is significantly different.
It was found that the difference in dryness was only 5.8% in average, regardless of the significant difference shown in Figure 5 and Figure 6, thus the diffusion coefficient does not influence on the simulation significantly.

6. Coating region of radical capturing layer
In section 4, the multiple regression equations were made for the dryness and the range of dryness in anode and cathode side. Using the equations, the map for coating region of the radical capturing layer was created in order to prevent the polymer membrane from degradation due to radical.

Two parameters having greater influence were chosen in the calculation. The range of dryness in anode side is shown in Figure 8. In this case, cell temperature and air humidity temperature were selected as the two parameters. For the cathode side, current density and air utilization ratio were varied to show the coating region of the radical capturing layer, shown in Figure 7. The vertical axis of Figure 7 and Figure 8 is the distance from inlet of gas flow channel to the region where the coating of capturing layer is required. Regarding the cathode side shown in Figure 7 the region required the coating of the capturing layer was one third of the length of gas flow channel under the condition of high air utilization ratio and low current density. In the case of high air utilization ratio and high...
current density, the coating region was around a half of the length of gas flow channel. When the air utilization ratio is low, the coating region becomes wider. Therefore, it is recommended that an air utilization of around 40% or more and the coating of one third of gas flow channel are applied in the operation condition. There is a report where the degradation occurs in anode side. Therefore, the region required the coating in anode side is shown in Figure 8. The region required coating was only one sixth of the gas flow channel in a condition of high cell temperature and air humidity temperature.

7. Conclusion
The distribution of water content in the membrane of PEFC was analyzed by using a numerical simulation as well as understanding the behavior of interned moisture of PEFC, and the flowing results are obtained.

1) The influence of the operating parameters on the dryness of the membrane for the anode side and the cathode side of PEFC was quantitatively shown by using the method of the multiple regression analysis.

2) Further it was found that the area where cerium carbonate ought to be coated for preventing the degradation without decreasing performance.
2.1) Regarding the cathode side shown in Figure 7 the region required the coating of the capturing layer is one third of the length of gas flow channel under the condition of high air utilization ratio and low current density. In the case of high air utilization ratio and high current density, the coating region is around a half of the length of gas flow channel.
2.2) Anode side region required coating is only one sixth of the gas flow channel in a condition of high cell temperature and air humidity temperature.

8. Reference
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