Optimization of Operation Conditions of Polymer Electrolyte Fuel Cell by Numerical Analysis Method
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ABSTRACT
In the development of more efficient and stable Polymer Electrolyte Fuel Cell (PEFC), it is important to propose the optimal operating condition and the optimal shape that can uniform the distribution of current density and relative humidity in a single cell. In this study, the effect of changing operation conditions on the i-V characteristic with a small PEFC was examined experimentally. And the model was created that can express these influences on PEFC reaction characteristics. Furthermore, a PEFC reaction and thermal flow analysis model was constructed. Various operation conditions (membrane thickness, gas diffusion layer thickness, etc.) were evaluated from the viewpoint of average current density and uniformity of current density and relative humidity. As a result, by using the thin membrane, high power density was obtained, and the water management was simplified, but the current density distribution increased. The information that decided the optimal operation conditions was obtained.

KEYWORDS
PEFC, numerical analysis, current density distribution, relative humidity distribution

INTRODUCTION
Now, fuel cells are developed from the viewpoint of the effective utilization of energy and the protection of the environment. Above all, Polymer Electrolyte Fuel Cell (PEFC) is expected as driving power of vehicles and stationary power supply. And the performance of PEFC is greatly improved because of the development of new component and system optimization. As the PEFC power generation characteristic is affected by the structure, the material, and the operating condition, it is greatly important to understand the interrelationship of a complex physicochemical and electrochemical phenomenon in the cell in detail. But there are hardly any researches that understands PEFC internal phenomenon when electricity is generated. As it is very difficult to accurately measure the current density distribution and relative humidity distribution in experiments, the numerical analysis is an effective method to examine them. On the other hand, PEFC that has long life and high durability is demanded recently, and the longevity examination is often carried out. However, the accelerated test of PEFC is difficult because neither the deterioration factor nor the mechanism is clear. It is thought that the numerical analysis can be applied to the investigation of such degradation factor and mechanism.

In our past researches, the effect of changing operation temperature, humidify temperature and H2 and O2 concentration in supply gas on the i-V characteristic of a small PEFC was examined experimentally. And the model was created, which can express these influences on PEFC reaction characteristics (Inoue, et al., 2003). Furthermore, the model was combined with thermal flow analysis, and the PEFC reaction and flow analysis model was made (Inoue, et al., 2003). Using the PEFC reaction and flow analysis model, five kinds of separators were evaluated from the viewpoint of gas flow condition, uniformity of current density and temperature, reduction of pressure drop, and ejection of the remaining water (Inoue, et al., 2003). In this study, we made new PEFC analysis model that includes the flow and heat transfer of cooling water, and we examined about the influence of membrane and gas diffusion layer thickness on cell performance by using this model. Furthermore, we proposed the guideline for optimum operation condition and optimum component shape.
STRUCTURE AND SYSTEM OF PEFC

Figure 1 shows schematic of PEFC single cell that is object in this study. PEFC consists of a membrane electrode assembly (MEA), two gas diffusion layers (GDL) and two separators. Polymer membrane of MEA has proton conductivity, and it is sandwiched between two thin platinum electrode layers. MEA is sandwiched between two GDL and two separators. The specification of MEA, GDL and separator, that are objects in this research, is shown in Table 1. The flow channel shape of the separator is variously proposed. In this study, serpentine separator, shown in Figure 2, was object. The electrode area was a square with 150mm side. Fifteen channels, which have 1mm groove width and shoulder width and 0.5mm groove depth, turned four times. Anode gas and cathode gas were counter flow. Cooling water flowed in the back of the separator, and the channel shape was the same as the separator. The anode gas (hydrogen 75% and nitrogen 25% as reforming gas) and the cathode gas (oxygen 21% and nitrogen 79% as air) were supplied to the cell respectively. The supply gases passed the humidifier set up on the upstream of the cell, and the humidifier temperature was operated to control the humidity. The inlet gas flow rate was set automatically by hydrogen utilization, oxygen utilization and average current density. The inlet cooling water flow rate was set so that the temperature of outlet cooling water could become preset value.

Table 1. Specification of parts in PEFC single cell

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MEA</strong></td>
<td></td>
</tr>
<tr>
<td>Thickness of membrane</td>
<td>10~100 μm</td>
</tr>
<tr>
<td>Size of catalyst layer</td>
<td>2.25×10^{-2} m^2</td>
</tr>
<tr>
<td></td>
<td>(0.15m×0.15m)</td>
</tr>
<tr>
<td>The amount of Pt</td>
<td>3.0g/m^2</td>
</tr>
<tr>
<td><strong>Diffusion layer</strong></td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>2.25×10^{-2} m^2</td>
</tr>
<tr>
<td></td>
<td>(0.15m×0.15m)</td>
</tr>
<tr>
<td>Thickness</td>
<td>10~1000 μm</td>
</tr>
<tr>
<td><strong>Separator</strong></td>
<td></td>
</tr>
<tr>
<td>Number of the groove</td>
<td>15</td>
</tr>
<tr>
<td>Groove width</td>
<td>1mm</td>
</tr>
<tr>
<td>Shoulder width</td>
<td>1mm</td>
</tr>
<tr>
<td>Groove depth</td>
<td>0.5mm</td>
</tr>
</tbody>
</table>

PEFC ANALYSIS MODEL

So far we have been examining the PEFC reaction and flow analysis. In this study, we improved the former model and developed the new model that could be used for real cell calculation in detail.
Model development and assumption

Figure 3 shows the PEFC simulation model. As shown in the figure, gas flow velocity, concentration and temperature were calculated in the gas channel on the anode and cathode. And it was assumed that the temperature distributions of MEA and GDL were same each other, and that they were unified, the temperature and current density were calculated in this unified part. (This unified part is expressed as the solid phase.) The governing equations in this simulation were derived with the following assumption.

1. The gas uniformly flows in each channel of the separator. Similarly, the cooling water uniformly flows.
2. The volume of the condensation water was ignored, and the water moved with the gas flow.
3. The reduction of reaction area caused by flooding of electrode is ignored, and the diffusion prevention caused by water condensation is ignored.
4. Fluid is incompressible Newtonian fluid and ideal gas. Flow condition is laminar flow.
5. Heat transfer between separator and gas is ignored. But those between gas phase, solid phase and cooling water are included.
6. Cell voltage is uniform and constant.
7. Only resistance overvoltage and water transfer in membrane include influence of solid phase temperature.
8. In membrane, ionic conductivity, electro osmosis coefficient and water effective diffusion coefficient that depend on membrane humidity are determined by water activity of anode side.
9. The membrane thickness corresponds to the migration length of the proton and water in membrane, and the GDL thickness corresponds to the diffusion length in GDL. And physical and electrochemical properties of the membrane and GDL are equal in any shape.
10. The gas crossover is disregarded.

Governing equations

In our past method, in order to calculate the gas flow rate distribution of each channel, two-dimensional analysis model was used. But, in this study, one-dimensional analysis as plug flow in each channel was available because of the assumption that the gas flow rate distribution is uniform. Though the separator shape was two-dimension structure to the direction of the membrane face, the quasi-two-dimension analysis model was made by assuming the direction from the inlet to the outlet to be a positive x-direction in each channel and by making the channel meander. As a result, the simplification of the equations and the speed-up of the calculation became possible. However, in case of calculation of the solid phase temperature distribution, it was calculated by two-dimensional analysis model. Moreover, for the purpose of simplification of the calculation, the viscous term in the motion equations, the heat conduction term in the energy balance equations and the diffusion term in the mass balance equations were ignored. Analytical base equations are shown as follows.

Equation of continuity

The equation of continuity is shown by the following expression,
\[
\frac{\partial v^k}{\partial x} = -\frac{1}{l^g_j \rho^k} \left[ \sum_j M_j r^k_j \right] = -R^k_{\text{rea}} \tag{1}
\]

where \( v \) is the velocity of mixed gas, \( l^g_j \) is the depth of gas channel, \( \rho \) is the density of mixed gas, \( M_j \) is the molecular weight of chemical species \( j \), \( r^k_j \) is the reaction or condensation rate per unit area of chemical species \( j \), \( R_{\text{rea}} \) is all reaction rate, and the superscript \( k \) expresses anode side or cathode side.

**Equation of motion**

The equation of motion is shown by the following expression,

\[
\rho^k \frac{Dv^k}{Dt} = -\nabla p^k + \rho^k v^k R^k_{\text{rea}} \tag{2}
\]

where \( p \) is pressure.

**Equation of species**

The equation of chemical species \( j \) is shown by the following expression,

\[
\frac{DC_j^k}{Dt} = \frac{r^k_j}{l^g_j} + C_j^k R^k_{\text{rea}} \tag{3}
\]

where \( C_j \) is the concentration of chemical species \( j \). The equations of species were derived to eight kinds of \( C_{H_2}, C_{N_2}, C_{H_2O(v)}, C_{H_2O(l)}, C_{O_2}, C_{N_2}, C_{H_2O(v)}, C_{H_2O(l)} \) that are hydrogen, oxygen, nitrogen, vapor and condensed water in anode and cathode channel.

**Equation of energy**

The equations of energy are shown by the following expression,

\[
\begin{align*}
\text{(gas)} & \quad \rho^k C_p^k \frac{DT^k}{Dt} = q^k_1 + q^k_2 + \rho^k C_p^k T^k R^k_{\text{rea}} \\
\text{(solid)} & \quad \rho^S C_p^S \frac{\partial T^S}{\partial t} = k^S \nabla^2 T^S + \frac{q^S_3 + q^S_4 + q^S_5 + q^S_6}{l^S} \\
\text{(cooling water)} & \quad \rho^w C_p^{(w)} \frac{DT^L_w}{Dt} = \frac{q^w_{(1)} + q^w_{(2)}}{l^w_w}
\end{align*} \tag{4-6}
\]

in the energy equation of gas, \( C_p \) is specific heat, \( T \) is temperature, \( q_1 \) and \( q_2 \) are heat fluxes from solid phase and cooling water respectively. In the equation of solid phase, \( k \) is heat conductivity, \( l^S \) is the thickness of solid phase, \( q_3 \) is the heat value per unit area the result of electrochemical reaction, \( q_4 \) and \( q_5 \) are heat fluxes from gas and cooling water respectively, \( q_6 \) is latent heat flux of water condensation, and the superscript \( S \) expresses solid phase. In the equation of cooling water, \( l^w \) is the depth of cooling water channel, \( q_{(1)} \) and \( q_{(2)} \) are heat fluxes from gas and solid phase respectively, and the subscript \( w \) expresses water.

**PEFC reaction model equation**

Current density \( i \) was calculated according to PEFC reaction model that authors built in past study (Inoue, et al., 2003). The electromotive force, the resistance overvoltage, the activation overvoltage, and the concentration overvoltage were modeled from theoretical equations respectively. On the other hand, small PEFC with single gas channel was made, which was not much affected by the state of the gas flow and the concentration distribution, and the effects of changing the concentration of the supply gas, the temperature of the cell, the humidifier temperature, the gas mass flow, and the gas channel length were investigated by the power generation examination of this cell. By comparing the experimental results in all operation condition, the parameters of the model equations were decided with the trial and error method. And the calculation data was able to agree with the experimental data by using those parameters. In this model, the current density is calculated by the following equation as the function of local concentration and temperature.

\[
i = f(V, C_{H_2}^a, C_{H_2O}^a, C_{O_2}^c, C_{H_2O}^c, T^a, T^c, T^S) \tag{7}
\]
As an example, in case that concentration of oxygen in the cathode supply gas is changed, the comparison between the experimental data and the calculation data of current density-voltage curve is shown in Figure 4. The experimental data and the calculated data agreed with each other on all conditions. Similarly, it was confirmed that the i-V curve was predictable for other conditions by using this model.

Equation of water transfer coefficient
It is thought that water is moved by two mechanisms of electro osmosis and back diffusion in the electrolyte membrane. When one proton moves from the anode side to the cathode side, the water transfer coefficient \( \alpha \) that shows the net number of water molecules that moves along with proton is obtained from the method of Nguyen and White (1993).

Numerical analysis
The analytical equations were discretized by using the finite difference method and solved as unsteady problem. As the boundary condition, flow velocity, temperature and concentration were constant at the inlet, and those gradients were zero at the outlet. Those variables were calculated until becoming stationary state. The relative errors of balance equation of mass, species and energy became 1% or less in all the calculations.

RESULTS AND DISCUSSIONS

In general, thinning membrane and GDL is effective in the decrease of the resistance overvoltage and concentration overvoltage, respectively. But, it has not been examined how these influence internal phenomenon of a real cell. And the humidifying condition greatly depends on the experience of the power generation experiment because the internal humidity distribution is not clear. So in this study, by calculating with the model of this research, the influences of MEA and GDL thickness on current density distribution, relative humidity distribution and cell performance were examined. The operation condition is shown in Table 2. The reforming gas and air were supplied as anode gas and cathode gas respectively.

The humidifying temperature on both sides was set as 60\(^\circ\)C. The current density distribution when the membrane thickness is changed on 0.7V is shown in Figure 5 and the anode relative humidity distribution is shown in Figure 6. In Figure 5, as the membrane thickness increased, the current density decreased because of the increase of resistance overvoltage. And the position of the high current density and the position of the low

<table>
<thead>
<tr>
<th>Table 2. Operation condition</th>
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<tr>
<td>Pressure</td>
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<tr>
<td>Inlet gas temperature</td>
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<tr>
<td>Inlet cooling water temperature</td>
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<tr>
<td>Outlet cooling water temperature</td>
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<tr>
<td>Humidify temperature</td>
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<td>Operation voltage</td>
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<tr>
<td>Utilization rate</td>
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<td></td>
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<tr>
<td>Inlet gas composition</td>
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current density changed. In the result of 30µm membrane, the current density is high in the upstream of the anode and cathode channel, and it is low in the downstream, because the concentration overvoltage is larger than the other overvoltage. In the result of 50µm membrane, the current density is high in the position of the inlet where the anode vapor concentration is high, because the influence of the resistance overvoltage increases. In the place where the anode gas flows from inlet a little, the anode vapor concentration decreases by the electro-osmosis effect, and the current density decreases. However, in the position from the middle reaches to the downstream, because of the back diffusion from the cathode, the anode vapor concentration is high, and the current density rises gradually. This tendency is more remarkable in 100µm thickness membrane. It is possible to confirm it from the anode side relative humidity distribution of Figure 6 in the above mentioned.

Figure 7 shows the influence of the membrane thickness on the ratio between the maximum current density and the average current density. That rate is increasing by thinning the membrane, and this is the following cause. In case of thin membrane, though the current density is high on the upstream because of the decrease in the resistance overvoltage and the maintenance of anode humidity, on the other hand the current density is low on the downstream.
because of the decrease in the oxygen concentration that results from the consumption for reaction. Moreover, in case of low voltage, the influence of the membrane thickness on the current density distribution becomes small because the concentration overvoltage increases. Because the increase of the current density distribution influences local degradation and the durability of the membrane, it is necessary to decrease this distribution. Accordingly, it is important to design the cell having high power density and uniform current density distribution as much as possible.

Figure 8 shows the influence of the membrane thickness on the ratio between the cathode relative humidity and the anode relative humidity (cathode relative humidity/ anode relative humidity). By the drop of voltage, this ratio increases, because the amount of the water generation and electro-osmosis increase. Moreover in case of thick membrane, this ratio increases because the amount of back diffusion of water decreases.

Next, the influence of the GDL thickness was examined by the calculation. Figure 9 shows the influence of the GDL thickness on the ratio between the maximum and the average current density. It can be confirmed that the current density distribution increases by thinning of GDL, and that this influence is large at the low voltage.

The above calculation result of changing the membrane thickness and the GDL thickness was arranged. And the evaluation chart of the membrane thickness and the GDL thickness concerning the average current density, the current density distribution, anode minimum relative humidity and cathode maximum relative humidity shown in Figure 10, was made. It was confirmed that it is possible to improve the cell output by thinning the membrane more than the GDL in case of 0.7V. Moreover, these evaluation charts can be applied to design the PEFC components. For example, in case of development of the cell satisfying the one requirement, that the average current density is larger than a certain value, that the current density distribution is smaller than a certain value, and that anode and cathode relative humidity are larger or smaller than a certain value, with these evaluation charts, it can be decided that the size of membrane and GDL in intersection of two areas where those conditions are satisfied is the best. Figure 10 is the result only about the influence of the shape of the electrolyte membrane and the GDL on the average current density, the current density distribution and relative humidity. Therefore specific best shape cannot be described still in detail. However, it is thought that the information for the best design of the PEFC component can be obtained by calculating in various conditions by this PEFC numerical analysis model, and by making such an evaluation chart according to the demand condition of each use and operation condition.
A past PEFC numerical analysis model was improved, PEFC internal phenomenon, for which it is difficult to measure in the experiment, can be examined. And the influence of the thickness of membrane and gas diffusion layer on cell characteristics was examined by using this model. As a result, it is found that the current density distribution increases though the output performance improves by thinning the membrane and the gas diffusion layer, and that the changing shapes influences the relative humidity distributions on both anode side and cathode side. The information about the design of the best shape to increase average current density and to decrease the current density distribution could be obtained.

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**NOMENCLATURE**

\[ C_j = \text{molar concentration of species } j \quad [\text{mol/m}^3] \]
$C_p$ = specific heat at constant pressure \ [J/(kg\cdot K)]

$i$ = current density \ [A/m^2]

$k$ = thermal conductivity \ [J/(m\cdot s\cdot K)]

$l_g$ = gas groove depth \ [m]

$l_w$ = cooling water groove depth \ [m]

$l_s$ = thickness of solid phase \ [m]

$M_j$ = molecular weight of species j \ [kg/mol]

$p$ = pressure in Eq.(2) \ [Pa]

$q$ = heat flux between cooling water, gas phase and solid phase
  = heat value generated by reaction
  = latent heat value of condensation \ [J/(m^2\cdot s)]

$r_j$ = molar flux of species j \ [mol/(m^2\cdot s)]

$R_{rea}$ = all reaction rate \ [1/s]

$t$ = time \ [s]

$t_m$ = membrane thickness \ [m]

$T$ = temperature \ [K]

$v$ = flow velocity \ [m/s]

$V$ = operation voltage \ [V]

$x$ = distance \ [m]

$\alpha$ = net water transfer coefficient \ [\cdot]

$\rho$ = density of mixture \ [kg/m^3]

REFERENCES


