

Simulation of Current Density Distribution at PEMFC by using Measured Electro-Chemical and Physical Properties of Membrane

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Introduction

Establishing precise numerical model of the proton exchange membrane fuel cell (PEMFC) provides a useful method to estimate and improve the PEMFC performance. The first objective of the present investigation is to build a numerical model, which can describe the PEMFC performance such as a $V-i$ characteristics and current distributions inside the cell. For building properly the PEMFC model, it is necessary to know the water management factors such as transmissivity and electro-osmotic coefficient of water vapor through the membrane-electrode assembly (MEA), and power loss factors such as activation and resistive overpotentials, since these factors have significant impacts on performance of PEMFC. Nevertheless, the effects by these factors on PEMFC have not been cleared sufficiently. Then, obtaining the basic information for PEMFC is a second objective of this study. The comparison of measured and calculated current distributions is finally conducted to verify the reliability of our numerical model.

Measurement of water management factors and power loss factors

To obtain the diffusive properties of MEA, the cell outlet humidities at both anode and cathode were measured with supplying air or nitrogen with different humidities to fuel cell inlets. The measurement procedure is essentially the same as those described previously⁽¹⁾. The measured water vapor diffusivity through MEA D_{diff} did not change much against relative humidity and was described by the relation $D_{diff} = f \cdot D_{H_2O-Air}$, where D_{H_2O-Air} is water vapor diffusivity in air, and f is the porosity of diffusion electrodes. In our case of carbon cloth, f was calculated to be about 0.25. The measured transmissivity through MEA T_r was about 7 times higher than that by Nguyen *et al.*⁽²⁾ and lower than by Yamada *et al.*⁽³⁾. However, the increasing tendency of T_r against relative humidity increase was consistent with that by Nguyen *et al.* Therefore we approximate T_r to be 7 times greater than that by Nguyen *et al.* Electro-osmotic coefficient n_d is determined similarly to the diffusion coefficient, except the electric current flowing condition to transport water electro-osmotically. The measured n_d increased when the relative humidity increases. n_d at of 50°C agreed with that by Nguyen *et al.*, but showed a different tendency against relative humidity when compared to n_d by Yamada *et al.*, who performed similar experiment with us using carbon cloth.

Resistive and activation overpotentials are also important factors to decide PEMFC power generation performance. The ionic resistance of MEA was measured by AC impedance meter (SO-LARTRON SI1280B), supplying air with the same humidity to both anode and cathode to avoid the water movement through MEA. Parameters for MEA resistance are membrane temperature T_{mem} and relative humidity a . The resistivity did not depend on T_{mem} , but depended only on a . When the activation overpotential η_{act} was measured, the relatively high flow rate of 600cc/min was supplied to keep the low utilization rates of H_2 and O_2 , in order to prevent the change of η_{act} by distributed current density along flow. η_{act} was obtained by subtracting the cell voltage V_{cell} and the resistive

overpotential η_{ohm} from the Nernst potential V_{Nernst} , *i.e.*, $\eta_{act} = V_{Nernst} - V_{cell} - \eta_{ohm}$. Spatially average partial pressures of active materials were used to determine V_{Nernst} considering water vapor pressures. The experimental conditions to measure η_{act} were FC temperature of 60°C, cathode O_2 partial pressure ratio P_{O_2} of 0.05, 0.2, 1.0, anode gas of pure H_2 and atmospheric pressure of cathode and anode gas. The measured η_{act} increased almost linearly against P_{O_2} except for a region where current density is very small.

Numerical model of PEMFC

Our model basically consists of the steady state two-dimensional mass, charge and energy conservation equations with an equivalent electric circuit of PEMFC. Following assumptions are adapted to derive governing equations⁽²⁾.

1. Fuel cell is a parallel flow type.
2. Gas flow along a channel is plug flow.
3. Owing to the constant-temperature water circulation through separators, the separator temperature is constant.
4. The volume of the condensed water is so small that effect by condensed water at cathode can be neglected.
5. The total gas pressure is constant, neglecting pressure drop along flow channel.

The mass conservation equations are as follows by using mole flow rate M_j of each chemical species j , and current density i through MEA. The subscripts a , c and k denote at anode, cathode and either anode or cathode, respectively. d is height (thickness) of channel (layer) and h is channel width.

$$\text{Hydrogen : } \frac{dM_{H_2}}{dx} = -\frac{hi}{2F} \quad (1) \quad \text{Oxygen : } \frac{dM_{O_2}}{dx} = -\frac{hi}{4F} \quad (2)$$

$$\text{Water liquid : } \frac{dM_{water,k}^{liquid}}{dx} = \left(\frac{hd_{channel}}{R(T_k + 273.15)} \right) \left(\frac{M_{water,k}^{vapor}}{M_{water,k}^{vapor} + M_{H_2}} P - P_{water,k}^{saturated} \right) \quad (3)$$

$$\text{Water vapor (anode): } \frac{dM_{water,a}^{vapor}}{dx} = -\frac{dM_{water,a}^{liquid}}{dx} - \frac{dM_{vapor}}{dx} \quad (4)$$

$$\text{(cathode) : } \frac{dM_{water,c}^{vapor}}{dx} = -\frac{dM_{water,c}^{liquid}}{dx} + \frac{dM_{vapor}}{dx} + \frac{hi}{2F} \quad (5)$$

Here M_{vapor} is the water vapor mole flow rate from anode to cathode.

$$\frac{dM_{vapor}}{dx} = \frac{R_{MEA} \left(-T_r \frac{dC_w}{dy} + n_d \frac{i}{F} \right) - R_{diff,c} \frac{i}{2F}}{R_{MEA} + R_{diff,a} + R_{diff,c}} h \quad (6)$$

where R_{MEA} is $d_{MEA}/(Tr \cdot A)$ and $R_{diff,k}$ is $d_{diff,k}/(D_{diff,k} \cdot A)$

Five energy conservation different equations for five layers (two gas channels, two diffusion electrodes and one MEA) are derived, but only two equations for MEA and diffusion electrode are shown below due to limitations of space.

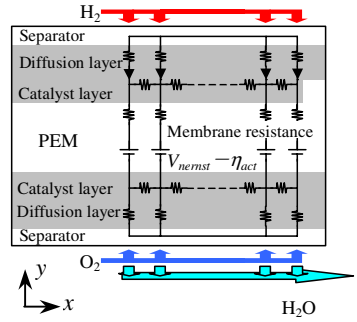
$$\text{MEA: } t_{mem} \frac{d}{dy} \left(k_{mem} \frac{dT_{mem}}{dy} \right) = k_{diff,a-mem} \frac{T_{mem} - T_{diff,a}}{\Delta x_{diff,a-mem}} + k_{diff,c-mem} \frac{T_{mem} - T_{diff,c}}{\Delta x_{diff,c-mem}} - \left(\sum_j N_{j,a} H_{j-T_{diff,a}} - \sum_j N_{j,c} H_{j-T_{diff,c}} \right) - N_{H_2} \Delta H_{LHV} + i (V_{Nernst} - \eta_{ohm} - \eta_{act}) \quad (7)$$

$$\text{DE: } \sum_j (M_j c_{p,j}) \frac{dT_k}{dx} = (H_{water,k}^{vapor} - H_{water,k}^{liquid}) \frac{dM_{water,k}^{liquid}}{dx} + U(T_s - T_k) \quad (8)$$

Here N_j and H_j represent the mole flux along y direction and enthalpy of the j species, respectively. U is heat transfer coefficient. η_{ohm} is resistive overpotential by eq. (9) as a function of the MEA resistivity ρ .

$$\eta_{ohm} = \left(\frac{1}{a_a - a_c} \int_{a_c}^{a_a} \rho da \right) t_{mem} i \quad (9)$$

The equivalent electric circuit for PEMFC is shown in Fig. 1. Due to the high electric conductivity of the separators, the cell voltage along channel can be kept constant. Control volume method and Tri-diagonal matrix algorithm (TDMA) were used to solve simultaneously equations (1) - (8) with an equivalent circuit.



Measurement of current distribution

Current distributions were measured by two different methods to confirm its reliability. One method adopted the segmented electrodes cell to measure the current distribution by shunt resistances. Another method adopted the gas chromatography to measure gas composition changes to be converted to the distributed current through the decreased flow rate of H_2 or O_2 . N_2 mixed fuel and air were employed in this measurement to reserve the constant flow rate of N_2 as reference. H_2 mixed with 20% of N_2 (not CO_2) was used as fuel, because CO_2 is apt to be absorbed in water and not giving the proper reference. Figure 2 shows the measured current density distributions for two average

Fig 1 Equivalent electric circuit for the PEFC

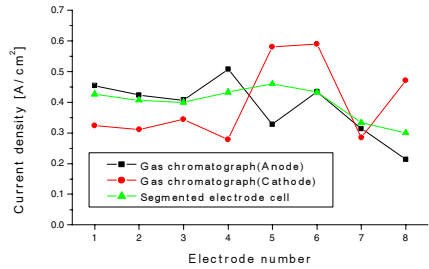
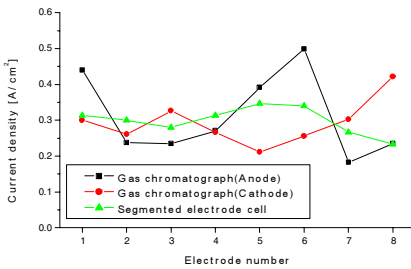


Figure 2 Comparison of measured current distributions i_c mean $i_m = 0.3 \text{ A/cm}^2$ (left), $i_m = 0.4 \text{ A/cm}^2$ (right)

current densities i_m of $0.3\text{A}/\text{cm}^2$ and $0.4\text{A}/\text{cm}^2$. The current density by gas chromatography fluctuated to some extent, but compatible with the one by segmented electrodes cell. Thus we could confirm the measurement reliability of current density distribution.

Results of numerical simulation and comparison with measured current distribution

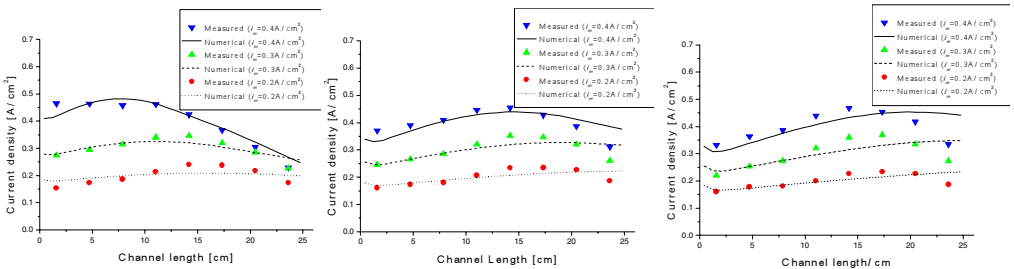
The current density distributions calculated by the numerical model are shown in Fig. 3. The conditions for the analysis are summarized in Table 1. The good agreement between the numerical and measured results indicates that our numerical model using the measured water management and power loss factors can provide a useful tool to estimate the PEMFC power generation performance. The measured showed higher current density at inlet, and lower current density at outlet than the calculated, especially for higher oxygen utilization ratio of 80%. This discrepancy might be due to the flooding by generated water at a downstream cathode, hindering the site for electrochemical reaction. Further studies are needed on empirical formula for the activation overpotential, water management factors and diffusion overpotential through diffusion electrode.

Reference

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- [2] T.V.Nguyen and R.E.White, J. Electrochem. Soc., Vol.140, No8, p.2178 (1993).
- [3] H.Yamada and Y.Morimoto, Proc. 70th anniversary Jpn. Electrochem., p316 Soc. (2003). (in Japanese)

Table 1 Experimental conditions used in the numerical model

	left	center	right
Cell temperature[°C]	60		
Anode flow rate[cc/min]	48		
Cathode flow rate[cc/min]	91	136	182
Anode dew temperature[°C]	60		
Cathode dew temperature[°C]	Not humidified		
Fuel and oxygen utilization ratio($i_m=0.2\text{ [A}/\text{cm}^2\text{]}$)	0.4, 0.4	0.4, 0.26	0.4, 0.2
Fuel and oxygen utilization ratio($i_m=0.3\text{ [A}/\text{cm}^2\text{]}$)	0.6, 0.6	0.6, 0.4	0.6, 0.3
Fuel and oxygen utilization ratio($i_m=0.4\text{ [A}/\text{cm}^2\text{]}$)	0.6, 0.6	0.8, 0.53	0.8, 0.4



(Air flow rate : 91cc/min)

(Air flow rate : 136cc/min)

(Air flow rate : 182cc/min)

Figure 3 Comparison between the measured and the numerical current distributions