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Electrochemical reaction and fluid flow analysis in PEMWE

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Abstract

In this study, a numerical model is developed to analyze the electrochemical reaction and fluid flow in a polymer electrolyte membrane water electrolyzer using OpenFOAM®. The activation overpotential distributions of hydrogen reduction reaction, and oxygen oxidation reaction and the current density distribution by electrochemical reaction are analyzed; Then, the volume fraction of oxygen in anode and hydrogen velocity in cathode are studied to verify their influences on the current density distribution and activation overpotentials. Where oxygen gas accumulates in the porous transport layer of anode, the local current density decreases sharply; The maximum and minimum local current density are 10,263 A/m^2 and 6,921 A/m^2 at operating current density of 10,000 A/m^2, respectively. Maldistribution of the overpotentials by electrochemical reaction are also observed by oxygen gas. This study contributes to the development of numerical analysis of polymer electrolyte membrane water electrolyte.

Keywords: Polymer electrolyte membrane water electrolyte; numerical analysis; electrochemical reaction analysis; two-phase flow analysis; interner behavior analysis

1. Introduction

With the rise of interest of green energy society, the interest of hydrogen was also rising. Currently, hydrogen is produced through by product hydrogen, so the price of hydrogen is 8,000 KRW/kg in Korea; and many researchers predict that the amount of by product hydrogen will be scarce when hydrogen energy becomes popular. Therefore, many researchers have interest on new technologies to produce hydrogen continuously, which is polymer electrolyte membrane water electrolyzer (PEMWE). PEMWE can produce the hydrogen at high current density, so it can produce the large amount of hydrogen, and produced hydrogen has a high purity of 99%. Therefore PEMWE is suitable to produce hydrogen to use in green energy society. However, PEMWE has disadvantage. The oxygen generated by the oxygen oxidation reaction (OOR) at the anode can decrease performance of PEMWE. When generated oxygen gas is accumulated in porous transport layer (PTL) in anode, oxygen gas disturbs the contact between catalyst and water, so active area for reaction also decrease. This phenomenon often occurs when PEMWE is operated at high current density. Therefore, it is necessary to smoothly remove the generated oxygen when PEMWE is operated at high current density.

In this study we developed the numerical model to analyze the two-phase flow and electrochemical reaction in PEMWE. The current density distribution and activation overpotentials in anode and cathode are analyzed. This study contributes to the development of numerical analysis of PEMWE.

2. Methodology

A PEMWE comprises end plate, current density, bipolar plate, gasket, and membrane electrode assembly (MEA); and MEA comprises the membrane, catalyst, and PTL. Water decomposition reaction occurs in PEMWE and this reaction is given by Eq. (1), which the standard voltage is 1.23V

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$$H_2O \quad \rightarrow \quad H_2 \quad + \quad \frac{1}{2}O_2 \tag{1}$$

The five serpentine flow field was analyzed to confirm the internal behavior in PEMWE, which shape is in Fig. 1, and geometric parameters are listed in Table 1.

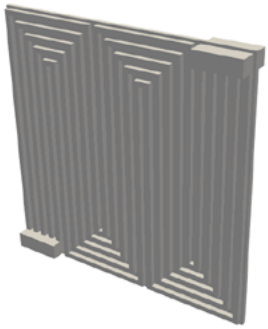


Fig. 1. Shape of the five serpentine flow field of PEMWE.

Table 1. Geometric parameters of PEMWE.

Parameter	Symbol	Value
Area of electrolyte	A_{cell}	25 cm^2
Area of inlet and outlet	$A_{in,out}$	27 mm^2
Membrane thickness	L_m	0.13 mm
PTL thickness at anode	L_A	0.36 mm
PTL thickness at cathode	L_C	0.20 mm
Chanel height	H_C	1 mm
Channel width	W_C	1 mm
Lib width	W_L	1 mm

2.1. Electrochemical model

The Nernst voltage(E^0) calculated by activities of reactant/product and the standard voltage of reaction (E_0), which can be expressed as [1]:

$$E^0 = E_0 - \frac{RT}{F} ln\left(\frac{\prod a_{product}}{\prod a_{reactant}}\right) \tag{2}$$

where F is Faraday's constant, T is temperature, and R is the gas constant. Activity of liquid is 1 and activity of gas is pressure of gas. The relation between activation overpotential (η) and current density (i) is expressed by Butler-Volmer equation, which equation is [2]:

$$i = i_0\left(e^{\frac{2\alpha F\eta}{RT}} - e^{\frac{2(1-\alpha)F\eta}{RT}}\right) \tag{3}$$

Where i_0 is the exchange current density, α is the transfer coefficients for the reaction.

2.2. Conservation equation

The mixture of liquid water and oxygen gas flow in anode, so two-phase flow model is applied in the anode. The continuity equation and momentum equation are expressed as [3,4]:

$$\begin{cases} \frac{\partial}{\partial t}\alpha_i\rho_i + \nabla\cdot(\alpha_i\rho_i U_i) = 0 \\ \nabla\cdot(\alpha_i\rho_i U_i U_i) = -\alpha_i\nabla P + \nabla\cdot\left(\alpha_i\mu_{eff}(\nabla\mu + (\nabla\mu)^T)\right) + \alpha_i\rho_i g + M_k \end{cases} \quad (4)$$

where α_i is volume fraction, ρ_i is density and U_i is velocity of species i. P is pressure of fluid, and μ_{eff} is the effective viscosity of fluid.

Only hydrogen gas is flow in cathode, so single-phase flow model is applied in the cathode. The continuity equation and momentum equation are express as [5]:

$$\begin{cases} \nabla\cdot(\rho U) = 0 \\ \nabla\cdot(\rho U U) = -\nabla P + \nabla\cdot(\mu\nabla U) \end{cases} \quad (5)$$

where ρ is density and U is velocity, and μ is viscosity of hydrogen, respectively. P is pressure of fluid.

2.3. Boundary and initial conditions

Boundary condition and initial condition is expressed as:

$$\begin{cases} U = \frac{Q}{A_{in}} \\ P_{out} = P_0 \\ T_{in} = T_0 \end{cases} \quad (6)$$

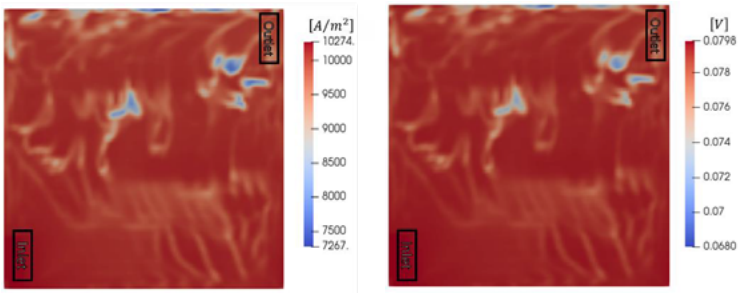
Where Q is the flow rate, P_0 is the outlet pressure, and T_0 is the inlet temperature (listed in Table 2). Simulation were conducted using OpenFOAM® (Open Field Operation and Manipulation).

Table 2. Boundary and initial condition of simulation.

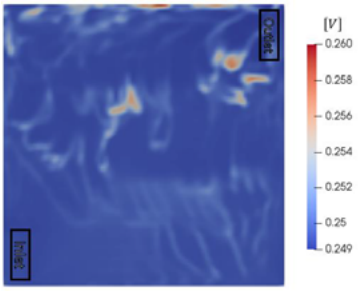
Parameter	Symbol	Value
Flow rate of water	Q	20 cm^3/min
Inlet temperature	T_0	80 ^{0}C
Outlet pressure	P_0	101,325 Pa

3. Result and discussion

Figure 2 presents the result of the electrochemical reaction in PEMWE. The current density was 10,000 A/m^2 and the flow rate was 20 cm^3/min. The maximum current density was 10,263 A/m^2 and the minimum current density was 6,921 A/m^2. The difference between maximum and minimum current density was 3,342 A/m^2. As a result, we conclude that maldistribution of current density distribution was observed. The maximum and minimum overpotential of anode reaction were 0.26 V and 0.24 V, respectively, and the maximum and minimum overpotential of cathode reaction were 0.068 V and 0.080 V, respectively. By these results we conclude that maldistribution of overpotential also occurred.



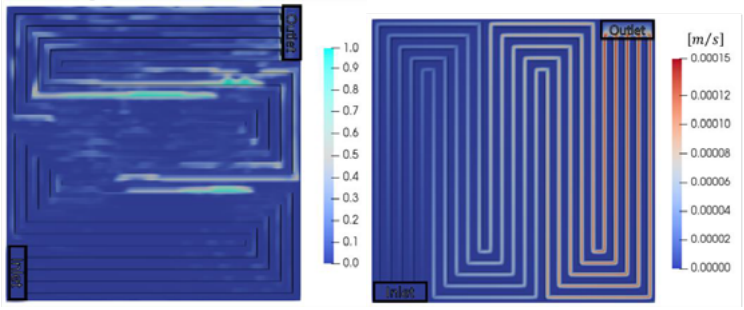
(a) (b)



(c)

Fig. 2. Electrochemical behaviors. The flow rate as 20 cm^3/min. (a) is current density distribution, (b) is overpotential of cathode reaction, and (c) is overpotential of anode reaction.

The volume fraction in anode and velocity of hydrogen are in Fig.3. The maximum volume fraction of oxygen was 0.99 in channel. When oxygen gas was accumulated in PTL, it disturbed the contact between catalyst and liquid water, so performance of PEMWE decreases. In anode, only hydrogen gas flow, so velocity of hydrogen increased continuously in channel. As a result, we conclude that oxygen gas was eliminated smoothly to increase performance of PEMWE.



(a) (b)

Fig. 3. Fluid flow distribution in PEMWE. (a) is volume fraction of oxygen in anode, and (b) is velocity of hydrogen in cathode.

4. Conclusion

In this study, we developed the numerical model for PEMWE; in this model, electrochemical reaction and fluid flows of mixture and single-phase gas in PEMWE. In cell, maldistributions of current density distribution and activation overpotential was observed; this maldistribution occurred by accumulated oxygen gas which was generated by water decomposition reaction. Therefore, to increase the performance of PEMWE, it is necessary to eliminate the oxygen gas in channel. We think that this study contributes to develop the numerical model of PEMWE.

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