

직접메탄올 연료전지내 전달현상에 대한 전산 모사

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Simulation for transport phenomena of DMFC (Direct Methanol Fuel Cell)

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Abstract : The results of simulation of direct methanol fuel cell fed with liquid-state methanol feed are shown. This numerical process is based on mass and current conservation equations. The results showed that over low current density($<200\text{mA}/\text{cm}^2$) IV polarization curve was well-presented compared to experimental result. Methanol fed from anodic side moved into cathodic side through electrolyte membrane and the pressure near cathode electrode increased according to amount of methanol crossover and production of water. Besides change of overpotential on each electrode were checked by x-axis.

1. Introduction

The direct methanol fuel cell is attractive power source for portable electronic devices such as battery for laptop computer, cellular phone and etc. Because methanol has advantages of a much higher energy density and easier storage and transport. Unfortunately, compared to hydrogen fuel cell direct methanol fuel cell has a lot of difficulty during investigation in that methanol and water have similar chemical properties. In addition, not methanol, however, reacts at the anode side. Unreacted methanol moves into cathode side, occurring another oxidation reaction of methanol at the cathodic electrode. As the result, it makes performance of fuel cell lower than the ideal case. it is called by methanol crossover. Lots of investigation has been so far excuted so as to overcome the problem and try to find the mechanism of transport behaviors on operating of direct methanol fuel cell. The representative group is A.A. KULIKOVSKY¹⁾⁻³⁾ who has studied a model of a DMFC with liquid methanol feed, elucidate the mechanism of transport of liquid methanol and finding methods of decreasing methanol crossover. In this work, based on the theory above our experimental preliminary-data is fitted onto voltage-current curve. In addition to IV-polarization curve, transport behavior of methanol is shown.

2. The model

Generally this model is based on mass and current conervation equations. There are the following assumptions:

System of single cell unit is isothermal and keeps steady-state condition. flows of gas and liquid mixture are laminar in the channel as well.

Anode side - methanol is mixed with water sufficiently. It allows using the liquid density instead of one of mixture. No effect hydrophobicity of carbon electrode.

Anode catalyst layer - an electrochemical reaction takes place on the surface of catalyst. Not

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methanol reacts with water, the rest of methanol transports into the cathode side through a membrane, reacting with oxygen.

Electrolyte membrane - membrane is fully humidified one, remaining constant proton conductivity. No diffusion of oxygen and carbon dioxide in the cathode electrode into the membrane. during operation it is dominantly electroneutral inside the membrane.

Cathode catalyst layer - all of the rest of methanol reacts in this part, the concentration should be zero.

Cathode electrode - oxygen is fed in excess and compressible ideal gases. On flowing to the cathode it is fully saturated with water vapor and there is no diffusive terms for the liquid water flux. In addition no interactions between the gases and the liquid water in the pores of diffusion layer. There is no condensation of water through reaction on the cathode catalyst as well.

2.1 Electrochemical reaction rates

There is two kinds of electrochemical reaction; one is methanol oxidation at the anode and the other is oxygen reduction at the cathode. Both are originated from Butler-Volmer theory.

$$\frac{\partial^2 \eta_a}{\partial x^2} = \frac{R_a}{\sigma_n} = \frac{A_1}{\sigma_n} \exp(A_2(\eta)) = A_{1,2} \exp(A_2(\eta))$$

$$\eta_a = \varphi_a - \varphi_m$$

$$\frac{\partial^2 \eta_c}{\partial x^2} = \frac{-R_c}{\sigma_n} = \frac{-B_1}{\sigma_n} \exp(B_2(-\eta)) = -B_{1,2} \exp(B_2(-\eta))$$

$$-\eta_c = \varphi_m - \varphi_c$$

2.2 Pressure

The liquid is mixture with methanol and water. Pressure depends on two forces on the fluid: drawing effect under the electro-osmotic force and the water production at the cathode.

$$\frac{\partial^2 P}{\partial x^2} = -C_1 \left(\frac{\partial^2 \eta}{\partial x^2} \right) - C_2$$

2.3 Methanol transport

Methanol flux is formed from the concentration gradient(Fick's law) and the flux created by the flow of mixture. As you see, the flow of mixture is proportional to the electro-osmotic flux and water production at the cathode side. The continuity equation depends on the condition of each position. the methanol concentration at intersection of cathode electrode and cathode catalyst layer should be 'zero'.

$$\begin{aligned} \frac{\partial^2 C_m}{\partial x^2} + [D_1 \frac{\partial \eta}{\partial x} + D_2 \frac{\partial p}{\partial x}] \frac{\partial C_m}{\partial x} + [D_1 \frac{\partial^2 \eta}{\partial x^2} + D_2 \frac{\partial^2 p}{\partial x^2}] C_m \\ = D_1 A \exp(A_2(\eta)) = D_1 A \exp(B_2(-\eta)) \end{aligned}$$

2.4 Gas transport in the cathode

Oxygen is consumed in reduction reaction and extra-methanol oxidation reaction at the cathode side.

$$\frac{\partial^2 \xi_{O_2}}{\partial x^2} = E_1 [B_1 \exp B_2(-\eta) + A_1 \exp A_2(\eta)]$$

3. Result and Discussion

Fig. 1 displays the voltage-current curves of experimental result and evaluated one. Over the whole range, evaluated value was close to real operation data. However, above 200 mA the deviation took place up to 50% of experimental data. The reason is that rate of methanol consumption according to current density was not considered in the governing equations.

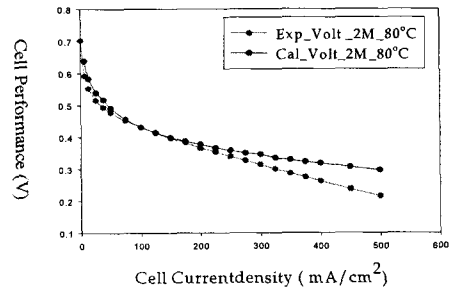


Fig. 1 Cell Voltages at 2M methanol, 80°C

Fig. 2 shows the change of methanol concentration by x-axis between each electrode and membrane. Inside reaction site methanol was consumed rapidly. At the result, unreacted methanol got to move into membrane and transported one still reacted with water produced at the cathode reaction. And then at the surface of cathode electrode methanol completely exhausted.

Moreover, the efficiency of methanol consumption at the anodic electrode was under 50%.

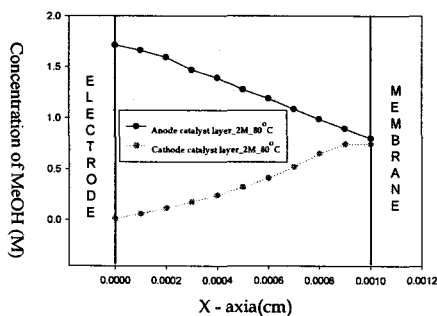


Fig. 2 Concentration of Methanol at 20mA/cm² 80°C

4. Conclusions

From these results, the comparison between preliminary experiment data and calculated values by fitting model, given assumptions were quite proper on our real single cell unit system at the low current density (under 200 mA/cm²). But at high current density more correlated formular between current density and methanol concentration is needed in order to explain the behavior of overpotential.

Besides from concentration profile of methanol inside single cell we could guess the efficiency of fuel at each current density as well. In this work it was absolutely true that our system has not optimized so far. And this fitting model made it possible to estimate the qualitative performance of electrolyte membrane and the amount of methanol-crossover.

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Nomenclature

- σ : conductivity, S/cm
- i_{ref}^o : exchange current density on each electrode at reference composition, A/cm³
- p_{ref} : pressure of methanol at the reference, atm
- $p_{mehtnaol}$: pressure of mehtnaol, atm
- α : transfer coefficient
- c_{O_2} : concentration of oxygen at the reference state, mol/cm³
- c_{H^+} : concentration of proton in the membrane phase, mol/cm³
- R_{H_2O} : rate of water production on the cathodic reaction
- μ : hydrdraulic permeability, cm/s
- μ_{el} : elektrokinetic permeability, cm/s
- D_{MeOH} : diffusion coefficient of Methanol in the mixutre
- D_{H^+} : proton diffusion coefficient, cm²/s
- D_{O_2} : knudsen diffusion coefficient of Oxygen
- ν : stoichiometric coefficient
- F : faraday constant, 96500C/s
- R : gas constant
- T : cell Temperature (K)
- n : number of electro related to the electrochemical reaction
- η : fluid viscosity, kg/m s
- ρ : liquid density, mol/cm³
- λ : a volume fraction of membrane in the catalyst layer
- r_p : mean pore radius
- γ : correction factor
- ϵ : porosity
- ϕ_m : potential of membrane phase, volt
- ϕ_a : potential of anode electrode, volt
- ϕ_c : Potential of cathode electrode, volt
- c_{MeOH} : concentration of methanol, mol/cm³
- c_{O_2} : relative oxygen concentration
- p : pressure in the cell, atm
- R_a : rate of charged particle production
- R_c : rate of charged particle loss
- R_{c*} : rate of charged particle loss with methaol crossover