

# AN IMPROVED PEMFC MODEL WITH PLUG FLOW IN CHANNELS

Valeri A. Danilov, Il Moon and Jong-Koo Lim  
Department of Chemical Engineering, Yonsei University  
Seodaemun-gu Shinchon-dong 134, Seoul 120-749, Korea

Kyoung Hwan Choi  
Materials & Devices Laboratory,  
Samsung Advanced Institute of Technology, Suwon 440-600, Korea

## Abstract

An improved PEMFC model is developed. The improvement of the model includes modification for electrochemical reaction and mass transfer limitation at cathode and anode side. Global sensitivity analysis is used for evaluating the sensitivity of the model in parameter estimation. The simulation results reveal that estimated mass transfer coefficients depend on current density. The comparison shows a good agreement between calculated and experimental polarization curves.

## Introduction

Modeling is important for optimizing and improving the design of fuel cells. The processes in a FC involve multicomponent, multiphase flow, heat and mass transfer with electrochemical reactions occurring in irregular geometries including porous media. Lots of literature contains various models for proton exchange membrane (PEM) fuel cells. However, complex interaction of chemical reaction, flow dynamics and transfer processes in fuel cells require further researches with developed models. This study presents an improved PEM fuel cell model together with a parameter estimation method. The new model is partly based on the PEMFC model by Nguyen and White (1993) which is one-dimensional, steady-state with water transport across membrane, convective heat transfer, evaporation and condensation of water in channels. The improved model includes electrochemical reactions with mass transfer limitation at anode and cathode sides. Sensitivity of the model needed for parameter estimation is studied using Sobol's sensitivity indexes.

## Model formulation

The model consists of mass balance equations for four components with plug flow condition in channels (Nguyen and White, 1993)

$$\frac{dM_{H_2}}{dx} = w N_{H_2}^A \quad (1)$$

$$\frac{dM_{H_2O,A}^L}{dx} = \frac{k_c w h}{R T} (y_{H_2O}^A P - P_{H_2O,A}^{sat}) \quad (2)$$

$$\frac{dM_{H_2O,A}^V}{dx} = -\frac{dM_{H_2O,A}^L}{dx} + w N_{H_2O}^A \quad (3)$$

$$\sum (M_i C_{p,i}) \frac{dT_A}{dx} = (H_{H_2O,A}^V - H_{H_2O,C}^L) \frac{dM_{H_2O,A}^L}{dx} + U(T_s - T_A) \quad (4)$$

$$\frac{dM_{O_2}}{dx} = w N_{O_2}^C \quad (5)$$

$$\frac{dM_{H_2O,C}^L}{dx} = \frac{k_c w h}{R T_C} (y_{H_2O}^C P - P_{H_2O,C}^{sat}) \quad (6)$$

$$\frac{dM_{H_2O,C}^V}{dx} = -\frac{dM_{H_2O,C}^L}{dx} + w N_{H_2O}^C \quad (7)$$

$$\sum (M_i C_{p,i}) \frac{dT_C}{dx} = (H_{H_2O,C}^V - H_{H_2O,C}^L) \frac{dM_{H_2O,C}^L}{dx} + U (T_s - T_C) \quad (8)$$

where  $N_{H_2}^A = -\frac{I}{2F}$ ,  $N_{H_2O}^A = -\frac{\alpha I}{F}$ ,  $N_{O_2}^C = -\frac{I}{4F}$ ,  $N_{H_2O}^C = \frac{(1+2\alpha)I}{2F}$  - molar flux for each

component. The main assumptions of the model are

1. Temperature of solid is assumed uniform.
2. Total pressure is constant.
3. Ideal gas mixture.
4. Heat- mass transfer analogy in channel.

We suggest to improve the model using equations for cathodic and anodic overpotential developed by Thampana et al. (2001)

$$\eta_k = \frac{RT}{\alpha_k F} \sinh^{-1} \left[ \frac{1}{2} \left\{ \frac{i_k / i_{k,0}}{1 - i_k / i_{k,L}} \right\} \right] \quad (9)$$

where  $i_{k,0}$  - reference exchange current density;  $i_{k,L}$  - limiting current density.

Overpotential is dependant upon exchange current density and component concentration in membrane. Exchange current density also depends on temperature. The cell potential is calculated as a function of anodic and cathodic polarizations and membrane resistance

$$V_{cell} = V_{oc} - \eta_A - \eta_C - \frac{I}{(\sigma/t_m)} \quad (10)$$

The distribution of current density is found from voltage equation with overpotential given by simplified kinetics. It should be noted that GDL and catalyst layer are porous media where saturation depends on interaction of gas and liquid flows and mass transfer. The developed model allows analyzing mass transfer in cathode and anode side which is important for water management.

### Parameter estimation

Mass transfer coefficients are found to be correlated with average current density given from experiments in parameter estimation. In this case, the number of fitting parameters can be reduced from eight to two by using additional relationship for the correlated parameters. The following set of equations is developed for the parameter estimation

$$F_{obj} = \min(I_{avg}^{exper} - I_{avg}^{calc})^2 \quad (11)$$

$$\frac{dM_{H_2}}{dx} = w N_{H_2}^A \quad (12)$$

$$\frac{dM_{H_2O,A}^L}{dx} = \frac{k_c w h}{R T} (y_{H_2O}^A P - P_{H_2O,A}^{sat}) \quad (13)$$

$$\frac{dM_{H_2O,A}^V}{dx} = -\frac{dM_{H_2O,A}^L}{dx} + w N_{H_2O}^A \quad (14)$$

$$\frac{dM_{O_2}}{dx} = w N_{O_2}^C \quad (15)$$

$$\frac{dM_{H_2O,C}^L}{dx} = \frac{k_c w h}{R T_C} (y_{H_2O}^C P - P_{H_2O,C}^{sat}) \quad (16)$$

$$\frac{dM_{H_2O,C}^V}{dx} = -\frac{dM_{H_2O,C}^L}{dx} + w N_{H_2O}^C \quad (17)$$

$$\beta_{eff}^{H_2} = \frac{N_{H_2}^{exper}}{\Delta \bar{C}_{H_2}^G}, \quad \Delta \bar{C}_{H_2}^G = \frac{1}{L} \int_0^L (C_{H_2}^G - C_{H_2,s}^G) dx \quad (18)$$

$$\beta_{eff}^{O_2} = \frac{N_{O_2}^{exper}}{\Delta \bar{C}_{O_2}^G}, \quad \Delta \bar{C}_{O_2}^G = \frac{1}{L} \int_0^L (C_{O_2}^G - C_{O_2,s}^G) dx \quad (19)$$

$$\eta_A = \frac{RT}{\alpha_A F} \sinh^{-1} \left[ \frac{1}{2} \left\{ \frac{I/i_{A,0}}{1 - I/i_{A,L}} \right\} \right], \quad \eta_C = \frac{RT}{\alpha_C F} \sinh^{-1} \left[ \frac{1}{2} \left\{ \frac{I/i_{C,0}}{1 - I/i_{C,L}} \right\} \right] \quad (20)$$

$$i_{C,L} = \left( \frac{v_{C,e^{-1}}}{-v_{C,O_2}} \right) F H_{O_2} \beta_{eff}^{O_2} C_{O_2,s}^G, \quad i_{A,L} = \left( \frac{v_{A,e^{-1}}}{-v_{A,H_2}} \right) F H_{H_2} \beta_{eff}^{H_2} C_{H_2,s}^G \quad (21)$$

$$V_{cell} = V_{oc} - \eta_A - \eta_C - \frac{I}{(\sigma/t_m)}, \quad I_{avg}^{calc} = \frac{1}{L} \int_0^L I dx \quad (22)$$

$$i_{C,0,min} < i_{C,0} < i_{C,0,max}, \quad i_{A,0,min} < i_{A,0} < i_{A,0,max} \quad (23)$$

where  $N_{H_2}^{exper} = \frac{I_{avg}^{exper}}{2F}$ ,  $N_{O_2}^{exper} = \frac{I_{avg}^{exper}}{4F}$  - experimental average molar fluxes. The objective function (11) with equality constrains (12) – (22) and inequality constrains (23) has only two parameters to be estimated (reference exchange current density  $i_{k,0}$ ). The problem (11) – (23) requires global iterations of mass transfer coefficients in gas phase  $\beta_{eff}$ . At each iteration mass transfer coefficient in gas phase is improved from (18), (19) with the mass transfer driving force. The iterations are repeated until concentration profiles convergence is achieved.

### Sensitivity analysis

Global sensitivity analysis allows us to identify the parameters having larger influence on output function defined by equation (11). We used Sobol's sensitivity indexes for global Monte Carlo (MC) based sensitivity analysis (Sobol, 2001). The total sensitivity index (TSI) is defined as sum of all indices involving the factor. TSI estimates the total contribution to the variance of outlet function that is due to a certain input variable. By definition, TSI is

$$TSI_i = 1 - \frac{D_{\sim i}}{D} \quad (24)$$

where  $D$  - the total variance of the output;  $D_{\sim i}$  - the total variance complement to factor  $i$ .

Sensitivity testing involves studying the model response for the selected model parameter combinations. Input data randomly changed in simulations were flow rates, cell voltage and reference current densities (Table 1). Sensitivity analysis shows that the improved model is sensitive to the estimated parameters (reference exchange current density of cathode and anode). The objective function is also sensitive to error in measurement of flow rate and cell voltage. The solution of the problem and confidence ranges for estimated parameters are found using Monte Carlo simulation. The estimated parameters (reference current density of cathode and anode) agree well with the data reported in literature. It should be noted that reference exchange current density indirectly includes information on the rate of electrochemical reaction and some properties of catalyst layer (catalyst loading, porosity, interfacial area).

Table 1

Ranges of parameters and total sensitivity indices

N	Parameter	Min	Max	TSI
1	$M_{H_2,0}$ , mole/s	$7.8633 \times 10^{-6}$	$7.8712 \times 10^{-6}$	4.49 %
2	$M_{O_2,0}$ , mole/s	$4.21249 \times 10^{-6}$	$4.21671 \times 10^{-6}$	3.9 %
3	$V_{cell}$ , V	$7.0 \times 10^{-1}$	$7.007 \times 10^{-1}$	22.3 %
4	$i_{C,0}$ , A/m <sup>2</sup>	1.0	210	44.9 %
5	$i_{A,0}$ , A/m <sup>2</sup>	50000	100000	24.4 %
	$F_{obj}$	$0.9 \times 10^{-3}$	$1.2 \times 10^{-1}$	100%

## Results and discussion

Because of highly reactive environment of a FC it is not possible to perform detailed measurements during operation. Modeling and simulation is valuable to improve understanding of heat and mass transfer processes and shorten the design. The improved model includes 8 parameters (mass and heat transfer coefficients, reference exchange current density) which are estimated from fitting to experimental data. Soares and Hoo, (2000) showed that parameter estimation problem can be solved for the PEMFC model for either two or four parameters. There is a way of increasing sensitivity of the model by matching the correlated parameters (Beck and Woodbury, 1998). The main finding of the present study is that mass transfer coefficients are correlated with experimental average current density in parameter estimation. Using additional relationships for the correlated parameters allows us to reduce the number of fitting parameters from eight parameters to two parameters. Sensitivity analysis revealed that the unit model with the defined outlet function is sensitive to the estimated parameters. Output data resulting from solving for the parameter estimation problem are heat and mass transfer coefficients together with the reference exchange current density. The solution of the problem and confidence ranges for estimated parameters are found using Monte Carlo simulation. Numerical simulation was carried out to predict the flow, temperature, and current distributions along channel of fuel cell with the estimated parameters. Comparison of experimental and calculated polarization curves is given in Figure 1. We used experimental data reported by Um et al. (2000). Operating condition were as follows

Channel cross section	0.762×0.762 mm
Channel length	71 mm
Air inlet temperature	80 C
Air pressure	5 atm

O<sub>2</sub> stoichiometric ratio            3.0  
H<sub>2</sub> stoichiometric ratio            2.8  
Relative humidity of inlet air/fuel 0% / 100%

Good agreement confirms applicability of the model with the developed parameter estimation method for PEMFC. The outlet of the parameter estimation includes mass transfer coefficients which contain valuable information about backing layer with porous media. As can be seen from Table 2, mass transfer coefficients decreased with current density. It should be noted that mass transfer coefficients in 1D model is a ratio of volumetric mass transfer coefficient to the electrode surface area. Volumetric mass transfer coefficient in turn is the product of local mass transfer coefficient and interfacial area.

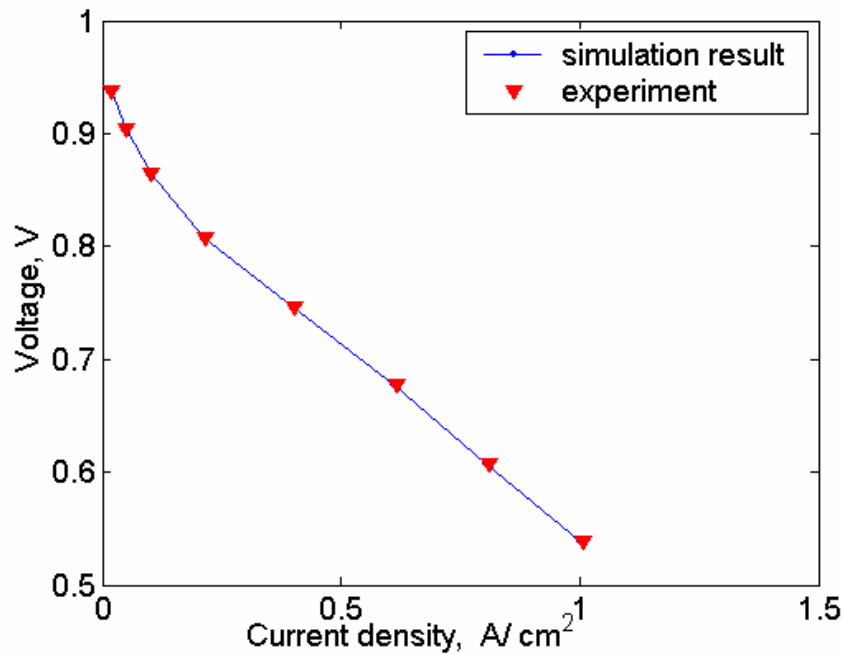


Figure 1. Comparison of predicted and experimental cell polarization. Experimental data by Um et al. (2000).

Table 2

Mass transfer coefficients estimated from cell polarization curve

Current density, A/m <sup>2</sup>	1007	2134	4004.9	6115	8034	10000
Anode mass transfer coefficient $\beta_{\text{eff}}^{\text{H}_2}$ , m/s	$4.1 \times 10^{-2}$	$9.2 \times 10^{-3}$	$7.0 \times 10^{-3}$	$8.8 \times 10^{-5}$	$5.2 \times 10^{-5}$	$5.0 \times 10^{-5}$
Cathode mass transfer coefficient $\beta_{\text{eff}}^{\text{O}_2}$ , m/s	$8.5 \times 10^{-2}$	$3.1 \times 10^{-2}$	$2.3 \times 10^{-2}$	$2.1 \times 10^{-2}$	$2.0 \times 10^{-2}$	$5.0 \times 10^{-3}$

According to simulation results reported by Wang et al. (2001), saturation of porous media is changed with current density and there is a flooding in backing layer at high current density. They used a two dimensional CFD model with detailed kinetics in channel, gas-diffusion backing layer and catalyst layer. Flooding is characterized by decrease in interfacial area in porous layer. The improved model with estimated effective mass transfer coefficients leads to the same conclusions about the effect of current density on volumetric mass transfer coefficients.

Typical current density and membrane conductivity profiles in channels are given in Figure 2. A local current density is calculated as a function of cell temperature, humidity, and partial pressure as well as cell voltage using an empirical electro-chemical equation. The predictions indicate that distributions of flow and current density are affected significantly by each other. A high current density occurs near the flow channel inlet.

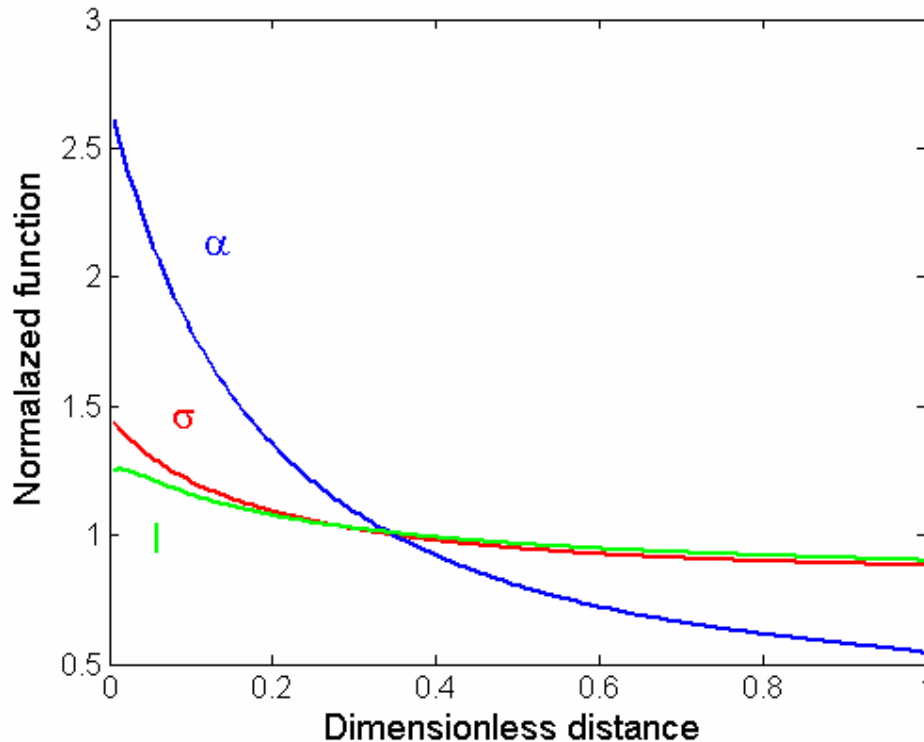


Figure 2. Current density, membrane conductivity and  $\alpha$  distribution along the flow direction.  $V_{\text{cell}}=0.8077$  V;  $I_{\text{avg}} = 2134$  A/m<sup>2</sup>.

## Conclusions

One dimensional PEMFC model presented is shown to be valuable in simulation and parameter estimation for experimental data processing. Improvement of the model includes modification for electrochemical reaction and mass transfer limitation at anode and cathode sides. Global sensitivity analysis indicates that the developed parameter estimation method is sensitive to estimated parameters. In accordance with simulation results, the coefficients of mass transfer depend on current density. Polarization curve calculated by the model with estimated parameters agree with experimental data from literature. This approach can be used to understand and investigate the effects of various parameters and operating conditions on the PEMFC performance for optimal design.

## Acknowledgements

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## Symbols used

$C$	molar concentration, heat capacity,
$F$	Faraday constant
$h$	channel height
$H$	enthalpy
$H_{H_2}$	Henry's constant for hydrogen
$H_{O_2}$	Henry's constant for oxygen
$I$	local current density
$I_{avg}$	cell average current density
$k_c$	evaporation and condensation constant
$L$	channel length
$M_i$	molar flow rate of species $i$
$M_{w,k}^L$	molar flow rate of liquid water in channel $k$
$M_{w,k}^V$	molar flow rate of vapor water in channel $k$
$P$	cell total pressure
$P_{w,k}^{sat}$	vapor pressure in channel $k$
$R$	gas constant
$t_m$	membrane thickness
$T$	temperature
$U$	heat transfer coefficient
$V_{oc}$	cell open-circuit voltage
$V_{cell}$	cell voltage
$x$	direction along the channel length
$y$	mole fraction
$w$	channel width

## Greek

$\alpha$	net water flux per proton flux
$\alpha_k$	transfer coefficient
$\beta_{\text{eff}}$	effective mass transfer coefficient
$\eta$	overpotential
$\sigma$	membrane conductivity
$\nu$	stoichiometric coefficient
$\rho_m$	molar density

## Subscripts and superscripts

A	anode
C	cathode
calc	calculation
exper	experiment
H <sub>2</sub>	hydrogen
O <sub>2</sub>	oxygen
H <sub>2</sub> O	water
N <sub>2</sub>	nitrogen
k	anode or cathode
m	membrane
s	interface, solid
V	vapor
L	liquid
sat	saturated
0	initial condition

## References

- Beck J. V., Woodbury K. A., Meas. Sci. Technol. **1998**, 9, 839.  
Nguyen T.V., R.E. White, J. Electrochem. Soc., **1993**, 140, 2178-2186.  
Sobol' I.M. Mathematica and Computers in Simulation, **2001**, 55, 271-280  
Suarez G. E., Hoo K. A. Chem. Eng. Sci., **2000**, 55, 2237-2247  
Thampana T., Malhotra S., Zhang J., Datta R., Catalysis Today, **2001**, 67, 15–32  
Um S., Wang C.-Y., Chen K. S. J. Electrochem. Soc., **2000**, 147, 4485-4493.  
Wang Z.H., Wang C.Y., Chen K.S. Journal of Power Sources, **2001**, 94, 40-50