

Effect of inlet Stoichiometry in to Anode and Cathode Channels on Performance of Polymer Electrolyte Membrane Fuel Cell by using Three-Dimensional Mathematical Modeling

Mona. Roshdi benam, Ahmad. Jamekhorshid , Mahyar.Saleh, Mohamad. Samipourgiry, and Amir Sahand. Gooyavar, *Member, IACSIT*

Abstract—One of the most important performance in polymer electrolyte membrane fuel cell, is the problem in the water balance.

At the same time being so that wet membrane for proton transfer, it can prevent from the cathode flooding and anode drying. Inlet stoichiometry to anode and cathode channels is one of the most important parameters in maintaining this balance. In this study, the effect of inlet stoichiometry on distribution of local current density, oxygen concentration and activation overpotential investigated by three-dimensional mathematical modeling which is according to conservation law, electrochemical reactions, ohmic losses and mass diffusion with assuming the spiral arrangement of the flow channel, ideal gas mixture and being fully hydrated membrane. Modeling results, shows that increasing the inlet stoichiometry to cathode channel due to more air entering channel, resulting in more water leaving channel and lead to reduce water flooding and thus increase in electrochemical reaction and result to increase current density, activation overpotential and decrease Oxygen concentration.

Increasing stoichiometry of anode also has a similar effect with the cathode stoichiometry. Because of this increase resulting to increased the hydrogen concentration along the anode channel, and thus, the electrochemical reaction speed up and therefor results to current density and activation overpotential increment

Index Terms—Polymer electrolyte membrane fuel cell, current density distribution, stoichiometry, three-dimensional modeling

I. INTRODUCTION

Hydrogen as the most abundant element in Earth's surface, provides energy as one of the best options for playing the role of energy in new systems. Hydrogen energy system due to the independence of the primary sources of energy is a system of permanent, indestructible, inclusive and non-renewable. It is predicted that in the not too distant future as an energy producing and consuming it spreading

Manuscript received March 11, 2012; revised May 5, 2012.

M. benam, A. Jamekhorshid. M. Saleh, and M. Samipourgiry are with the Department of Chemical Engineering, North Branch, Islamic Azad University, and Tehran, Iran. (Corresponding author :phone +(98 21 88787204); fax: +(98 21 88787204), e-mail: mona.roshdibenam@yahoo.com Jamekhorshid@Gmail.com, mahyar_saleh@yahoo.com)

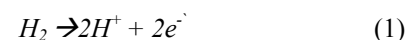
A. Gooyavar is with Metallurgy and Material science Engineering Department, Faculty of Engineering, University of Tehran, Tehran, Iran. e-mail: Sub_zeron2@yahoo.com)

throughout the global economy , it is established the hydrogen economy. Conversion of the chemical energy of hydrogen into electrical energy is done by fuel cell [1] That one of its variants is a polymer electrolyte membrane fuel cell (PEMFC). Due to the low sensitivity and low setup ratio to postural mobile devices usually are used. In the recent years many studies for increasing of polymer electrolyte membrane fuel cell performance were carried out. In this studies, current density is derived according to the parameters used in modeling. And finally, is investigated the effect of operating parameters such as humidity, temperature, stoichiometry, cell voltage and pressure on PEM fuel cell performance.

Yoon et al [2] divided a fuel cell into 81 parts and obtained each part of current density .and finally, they were investigated Stoichiometry changes in the inlet gas on the fuel cell performance . Ahmad and Song [3] calculated the current density distribution in a direct channel of the fuel cell by non-isothermal cell and a three-dimensional models and investigated the effect of cathode Stoichiometry on PEM fuel cell performance. In this paper a three-dimensional model is used to investigate the effect of inlet Stoichiometry to anode and cathode channels on current density distribution, oxygen concentration and activation overpotential. For this purpose, first, is derived current density, oxygen concentration and activation overpotential in the Stoichiometry = 1.5 and = 1.6 and so is investigated the effect of increasing anode and cathode Stoichiometry on current density, oxygen concentration and activation overpotential .

II. MATHEMATICAL MODELLING

Fig. 1 show the performance of a PEM fuel cell , Hydrogen enters at the anode side and diffuses through the porous electrode until it reaches the anode catalyst layer. At this layer the hydrogen broken into proton and electron during the electrochemical reaction in the reaction below[4]



Proton ion transfer through the membrane and electron leave by an external circuit towards the cathode and reacts in the cathode catalyst layer with oxygen and will produce water and electricity (current density). The overall electrochemical reaction occurring at the reaction site represented by the reaction

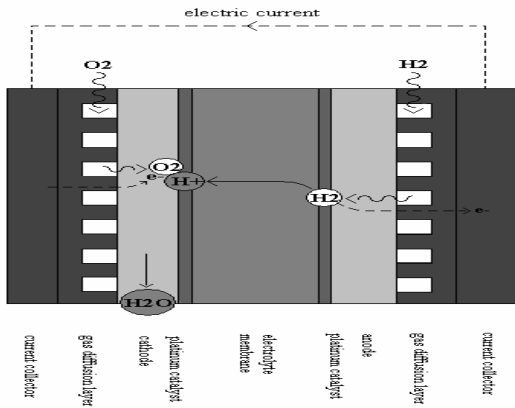
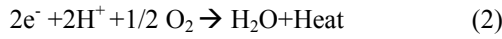


Fig. 1. Schematic of a PEM fuel cell.

Ideal gas mixture, steady state condition and completely hydrated of membrane is the assumption in this study[5]. Using the following formula, Oxygen concentration changes depending on the depth of the cathode catalyst layer is provided by conservation equation and Fick's law in the equation below[5]

$$\frac{dC}{dz} = \frac{I - I_\delta}{4FD_{O_2}^{\text{eff}}} \quad (3)$$

where $D_{O_2}^{\text{eff}}$ is the effective diffusion coefficient of oxygen in the catalyst layer and is obtained by Bruggeman relation. [6]

$$D^{\text{eff}} = D(\phi)^{3/2} \quad (4)$$

I_δ is the current density along the length of catalyst layer and starting in the reaction zone (interface between membrane and catalyst layer) and calculated from cell voltage using the following formula,

$$E_{\text{cell}} = E_r - \eta_{\text{act,c}} - \eta_{\text{ohm,m}} \quad (5)$$

where [7]-[8]

$$\eta_{\text{act,c}} = \frac{RT}{0.5F} \ln \left(\frac{I(\delta)}{I_0 P_{O_2}^{\text{cat}}} \right) \quad (6)$$

I_0 is the Exchange current density at the reference pressure. $P_{O_2}^{\text{cat}}$ is calculated assuming the ideal gas mixture from the following equation:

$$P_{O_2}^{\text{cat}} = c_{O_2}^{\text{cat}} RT \quad (7)$$

$c_{O_2}^{\text{cat}}$ is the oxygen concentration at interface of the catalyst layer and membrane.

The ohmic overpotential associated with the membrane and the reversible voltage is calculated from [7]-[8]

$$\eta_{\text{ohm,m}} = 0.01I(\delta) \frac{t_m}{\sigma_m} \quad (8)$$

$$E_r = 1.229 - 0.85 \times 10^{-3} (T - 298.15) +$$

$$4.31 \times 10^{-5} T \left[\ln P_{H_2} + \frac{1}{2} \ln P_{O_2} \right] \quad (9)$$

where t_m is the membrane thickness and σ_m is the Membrane conductivity, is a function of the membrane water content at the anode interface: [8]

$$\sigma_m = \left(0.00514 \frac{M_{\text{m,dry}}}{\rho_{\text{m,dry}}} c_{w,a} - 0.00326 \right) \times \exp \left(1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right) \quad (10)$$

The change of current density at the depth of catalyst layer assuming constant proton concentration is provided by the Butler-Volmer equation, as follows[5]

$$\frac{dI}{dz} = A_v I_0 \left(\frac{C}{C_{\text{ref}}} \right)^\gamma \left\{ \frac{\exp \left(\frac{\alpha_c F \eta_{\text{act}}}{RT} \right) - \exp \left(-\frac{\alpha_a F \eta_{\text{act}}}{RT} \right)}{\right\} \quad (11)$$

where the cathodic and anodic transfer coefficients are denoted by α_c and α_a . C_{ref} and I_0 are the reference Oxygen concentration and the reference current density. The reaction order is denoted by γ and can be found analytically from the procedure in Newman [9]

A_v is the specific reaction surface and calculated from the following equation:

$$A_v = \frac{m_{pt} A_s}{t_c} \quad (12)$$

where m_{pt} is the catalyst mass loading per unit area of cathode and A_s is the catalyst surface area per unit mass of the catalyst and is the function of the amount of platinum catalyst on its carbon support (f_{pt}) that here is one. also t_c is the thickness of the catalyst layer [5]

The changes of activation overpotential at the depth of catalyst layer is derived by Ohm's law, as follows: [5]

$$\frac{d\eta_{\text{act}}}{dz} = \left(\frac{1}{K_m^{\text{eff}}} + \frac{1}{K_s^{\text{eff}}} \right) I - \frac{I_\delta}{K_s^{\text{eff}}} \quad (13)$$

where K_m^{eff} and K_s^{eff} are the effective conductivities of the membrane and the catalysed solid and obtained from the following relations :

$$K_m^{eff} = (l_m \phi_c)^{3/2} K_m \quad (14)$$

$$K_s^{eff} = (1 - \phi_c)^{3/2} K_s$$

where K_m and K_s are the buk conductivites of the membrane and the solid catalyst.and ϕ_c is the void fraction of the catalyst layer[5]

III. CALCULATION PROCEDURE

In this section, the model that is in the form of a differential equations system as mentioned above are solved using MATLAB software and is investigated the effect of inlet Stoichiometry changes as the fuel cell control parameters on its performance on the current density, oxygen concentration and the activation overpotential.

For this purpose we need the following three boundary conditions:[5]

$$I(z = 0) = 0$$

$$I(z = \delta) = I_\delta \quad (15)$$

$$C(z = 0) = C_{cat}$$

C_{cat} is the Oxygen concentration in the interface between catalyst layer and gas diffusion layer and calculated from the following relations :[5]

$$C_{O_2}(z = 0) = \frac{P_{O_2}(z = 0)}{H_{O_2}}$$

where, H_{O_2} is the Henry's constant and obtained from the following relations [10]:

$$H_{O_2} = 0.1033 \exp\left(14.1 - \frac{666}{T}\right)$$

Thus, $I(x, z)$, $C_{O_2}(x, z)$, $\eta_{act}(x, z)$ are obtained at the catalyst layer.

IV. RESULTS

In this section, we'll examine the results of equations that is shown in Table I

Fig. 2-4 show the results of modeling for the current density, oxygen concentration and the activation overpotential in different conditions of S_c , S_a .

As is shown in Fig.2-4 increasing inlet Stoichiometry to cathode channel leads to more air entering the channel, therefore the amount of water that comes out of channel is more and result to reduce or eliminate component flooding in the catalyst layer and gas diffusion layer. Thus, Increases the current density and activation overpotential due to increased the rate of electrochemical reaction and oxygen concentration due to more consumption in the reaction is reduced the greater amount.

TABLE I: PARAMETERS USED IN MODELING

Parameteres	value
E_{cell}	0.5(V)
T_{cell}	80 (c°)
P_{cell}	1.1 (atm)
RH_c^{in}	40%
RH_a^{in}	70%
S_c	1.5-2.5
S_a	1.6-3.5
I_0	100 (A/m ²)
C_0	1.2 mol/m ³
α	0.5
γ	0.5
t_{GDL}	250 μm
t_c	18 μm
t_m	220 μm
K_m	0.17S/cm
K_s	727 S/cm
A_s	28 m ² /g
m_{pt}	0.003kg/m ²
Φ_c	48%
Φ_{GDL}	60%

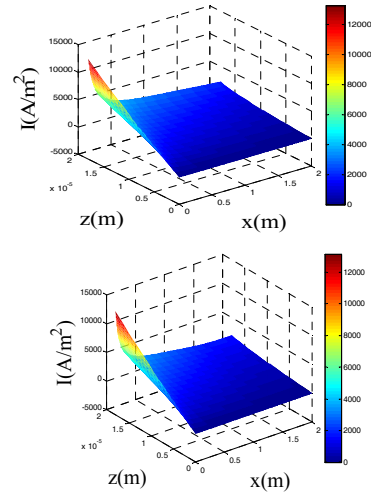


Fig. 2. Current density distribution in the cathode catalyst layer for two cathode stoichiometry : 1.5(top) and 2.5 (bottom)

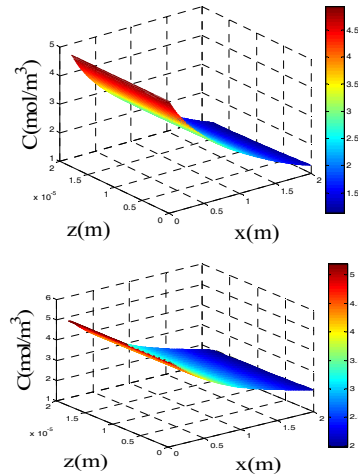


Fig. 3. Oxygen concentration distribution in the cathode catalyst layer for two cathode stoichiometry : 1.5(top) and 2.5 (bottom)

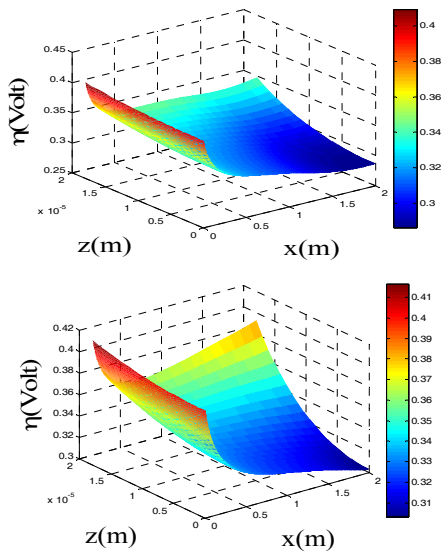


Fig. 4. Activation overpotential distribution in the cathode catalyst layer for two cathode stoichiometry : 1.5(top) and 2.5 (bottom)

The effect of inlet gas Stoichiometry to anodic channels on the current density, oxygen concentration and the activation overpotential is shown In Fig. 5-7.

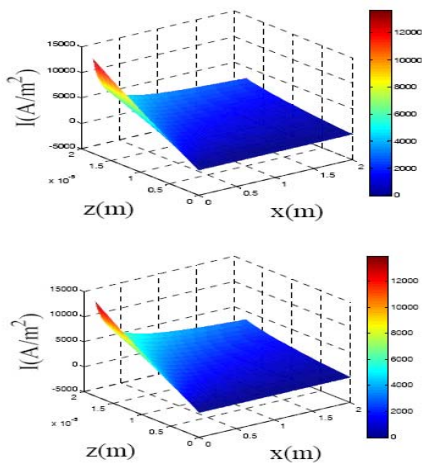


Fig. 5. Current density distribution in the cathode catalyst layer for two anode stoichiometry : 1.6 (top) and 3.5 (bottom)

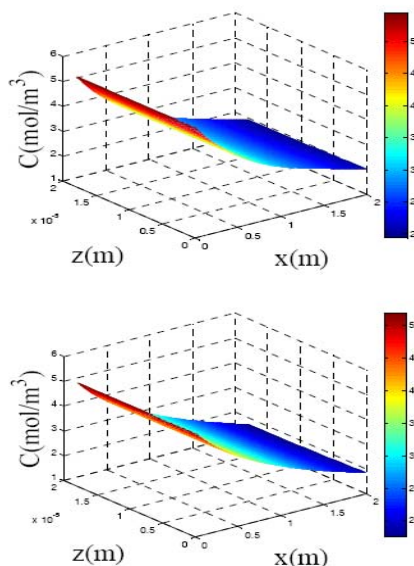


Fig. 6. Oxygen concentration distribution in the cathode catalyst layer for two anode stoichiometry : 1.6 (top) and 3.5 (bottom)

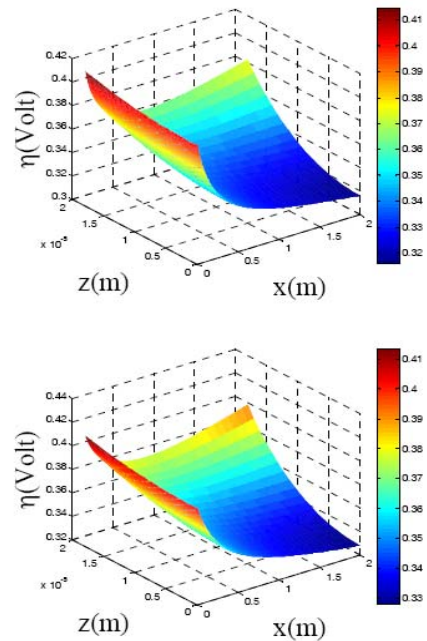


Fig. 7. Activation overpotential distribution in the cathode catalyst layer for two anode stoichiometry : 1.6 (top) and 3.5 (bottom)

Due to increased the hydrogen concentration(available) along the anode channel with increase in anode Stoichiometry lead to higher Electrochemical reaction rate and therefore the current density and the activation overpotential and the oxygen concentration due to consumed in the reaction are faced with greater reduction.

V. CONCLUSIONS

Many studies in recent years, pay the effects of various parameters such as Stoichiometry, temperature, pressure, etc Up to obtain the effect of these parameters on the cell performance . In this study, mathematical modeling based on conservation laws, mass transfer, Ohm's law and electrochemical reactions investigated to understand the performance of fuel cells under the influence of different stoichiometry. The obtained model can give consideration behavior of current density, Oxygen concentration and activation overpotential in effect of increase in the stoichiometry.

Effect of stoichiometry as one of the control parameters on the fuel cell performance, shows increasing Stoichiometry of inlet cathode due to air entering the channel and leaving more water from the channel and reduce the component of flooding in the cathode side and therefore Increases the current density and activation overpotential and Oxygen concentration decreases. Increased in inlet Stoichiometry to the anode side channel has the similar effect by increased inlet Stoichiometry to the cathode side channel. Because of this increase will lead to increased concentrations of Hydrogen and finally the electrochemical reaction rate is increased.

REFERENCES

- [1] X. Li, "Principles of fuel cells. New York: Taylor & Francis Group," 2006.

- [2] Y. G. Yoon, W.Y. Lee, T. H. Yang, G. G. Park and C.S. Kim. "Current distribution in a single cell of PEMFC," *Journal of Power Sources*, Vol. 118, pp. 193-199, 2003.
- [3] D.H. Ahmed, H.J. Sung. "Local current density and water management in PEMFCs." *International Journal of Heat and Mass Transfer*, vol. 50, pp. 3376-3389, 2007.
- [4] J. J. Baschuk and X. Li, "Modelling of polymer electrolyte membrane fuelcellswithvariable degrees of water flooding," *Journal of Power Sources*, vol. 86, pp. 181-196, 2000.
- [5] C. L. Mar and X. Li. "Composition and Performance modeling of catalyst layer in a proton exchange membrane fuel cell," *Journal of Power Sources*, vol. 77, pp. 17-27, 1992.
- [6] T. E Springer, T. A Zawodzinski, and S. Gottesfeld, "Polymer Electrolyte Fuel Cell Model," *Journal of the Electrochemical Society*, vol. 138, no. 8, pp. 2334-1342,1991.
- [7] T.V Nguyen and R.E White, "A Water and Heat Management Model for Proton-Exchange-Membrane Fuel Cells" *Journal of the Electrochemical Society*, vol. 140, no. 8, pp. 2178-2186.
- [8] J. S. Newman. *Electrochemical systems*, 2th edition. Prentice-Hall, 1991.
- [9] D. M. Bernardi, M. W. Verbrugge, "A Mathematical Model of the Solid-Polymer-Electrolyte Fuel Cell," *Journal of the Electrochemical Society*, vol. 139, no. 9, pp. 2477-2491,1992.

Mona.roshdi benam she was born in Tehran, Iran, on 2 October 1985, she received M.S degree chemical engineering at the azad university of Tehran north branch, Iran. In 2011. Her current research interest includes PEM FUEL CELL/modeling/reactor design/renewable energy.



Ahmad. Jamekhorshid he was born in Dashtestan, Iran, on 6 august 1984, he is studding P.H.D chemical engineering at the university of Terabit modares, Iran. . His current research interest includes energy/ phase change materials/ PEM FUEL CELLS/ simulation.



Mahyar. Saleh He was born in Tehran,Iran,on 10 august 1982, he received ms degree the azad university of Tehran north branch,Iran. in 2011. He worked in Iranian Offshore Oil Company, his current research interest include applied energy/integration/rheology/ FUEL CELLS /polymer technology/ modeling /reactor design/ simulation.



Mahamad. Samipourgiry He was born in Iran,on 23 August 1974 , he received PhD degree the university of Tehran, Tehran, Iran. In 2003.



AmirSahand. Gooyavar He was born in Tehran, Iran on 23 march 1991. He is studying Metallurgy and material science at the University of Tehran, Tehran,Iran. His current research interest include modeling/ Nano material/ Physical metallurgy/ Thermodynamic/ FUEL CELLS.