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


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 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. MATEMATICAL 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]

$$H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

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
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 ficks law in the equation below[5]

$$\frac{dC}{dz} = \frac{I - I_s}{4FD_{eff}}$$  \hspace{1cm} (3)$$

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

$$D_{eff} = D(\phi)^{3/2}$$  \hspace{1cm} (4)$$

$I_s$ 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,

$$E_{act} = E_f - \eta_{act} - \eta_{mem}$$  \hspace{1cm} (5)$$

where [7]-[8]

$$\eta_{act} = \frac{RT}{0.5F} \ln \left( \frac{I(\delta)}{I_{act}} \right)$$  \hspace{1cm} (6)$$

$I_s$ is the Exchange current density at the reference pressure. $P_{act}^o$ is calculated assuming the ideal gas mixture from the following equation:

$$P_{act}^o = c_{act}^oRT$$  \hspace{1cm} (7)$$

c_{act}^o 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]

$$\eta_{mem} = 0.01(\frac{t_m}{\sigma_m})$$  \hspace{1cm} (8)$$

$$E_f = 1.229 - 0.85 \times 10^{-3}(T - 298.15) + 4.31 \times 10^{-3}T[ln P_{act} + \frac{1}{2} ln P_{o}]$$  \hspace{1cm} (9)$$

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

$$\sigma_m = \left( 0.00514 \frac{M_{m,0}}{P_{o}} c_{act} - 0.00326 \right) \times \exp \left( 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right)$$  \hspace{1cm} (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]

$$\frac{dI}{dz} = A_i \exp \left( \frac{\alpha F \eta_{act}}{RT} \right) - \exp \left( \frac{-\alpha F \eta_{act}}{RT} \right)$$  \hspace{1cm} (11)$$

where the cathodic and anodic transfer coefficients are denoted by $\alpha_c$ and $\alpha_a$. $C_{act}$ and $I_0$ are the reference Oxygen concentration and the reference current density. The reaction order is denoted by $\gamma$ and can be found analytically from the procedure in Newman [9]

$A_i$ is the specific reaction surface and calculated from the following equation:

$$A_i = \frac{m_p A}{t_c}$$  \hspace{1cm} (12)$$

where $m_p$ is the catalyst mass loading per unit area of cathode and $A_i$ 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 ($f_w$) 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]

$$\frac{dn_{act}}{dz} = \left( \frac{1}{K_{m}} + \frac{1}{K_{s}} \right) \left( 1 - \frac{I_s}{K_{s}} \right)$$  \hspace{1cm} (13)$$

where $K_{m}$ and $K_{s}$ are the effective conductivities of the membrane and the catalysed solid and obtained from the following relations :
\[ K_m = \left( I_0 \phi \right)^{1/2} K_m \]
\[ K_s = \left( 1 - \phi \right)^{1/2} K_s \]  

(14)

where \( K_m \) and \( K_s \) are the bulk conductivities of the membrane and the solid catalyst, and \( \phi \) 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]

\[ I(z = 0) = 0 \]
\[ I(z = \delta) = I_i \]
\[ C(z = 0) = C_{oa} \]  

(15)

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

\[ C_{oa} (z = 0) = \frac{P_o (z = 0)}{H_o} \]

where, \( H_o \) is the Henry’s constant and obtained from the following relations [10]:

\[ H_o = 0.1033 \exp \left( 14.1 - \frac{666}{T} \right) \]

Thus, \( I(x, z) \), \( C_o (x, z) \), \( \eta_{act}(x, z) \) 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>
<thead>
<tr>
<th>TABLE I: PARAMETERS USED IN MODELING</th>
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<td>Parameteres</td>
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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)
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.

Due to increased inlet stoichiometry, 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

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