AN ANALYSIS OF OPERATING CONDITIONS OF PEMFC TO MINIMIZE EXTERNAL HUMIDIFICATION OF GASES

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ABSTRACT

An analysis of the water management in the fuel cell is conducted to search the effective method of humidifying the gases. Four cases are considered on the basis of the ways of the humidification. Without any humidifier, the fuel cell can be operated for very low pressure ratios. The gas humidified at the cathode inlet is more effective than that at the anode inlet for the broad range of pressure ratios. Gas humidification at both inlets may cause flooding of the membrane electrode assemble for low pressure ratios but is useful for high pressure ratios. For the Case 2 and 3, the optimum relationships between the pressure ratio and the stoichiometry are suggested to insure the saturation of the air at the cathode outlet.

INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) is one of the most suitable power generation devices for future automobile applications. As well known, PEMFC has high energy efficiency, low level of noise, and almost no pollution. For decades so, lots of research efforts have been given to fuel cell itself, control systems and hydrogen reform systems. However for automobile applications, fuel cell systems still have many weak points to overcome such as high cost, heavy weight of systems, rapid dynamic responses over driving conditions, and harsh operating environment conditions.

The stable and reliable power generation of PEMFC is also essential part of basic requirements for automobile applications. The current density is strongly depended on the condition of the membrane electrode assembly (MEA). The proton conductivity of the membrane is also governed by the hydration condition so that the water management in the membrane is one of the important operating conditions. The water is produced as result of electrochemical reaction of the reactant gases. The product water is used to humidify reactant gases at the anode and cathode. Therefore, the relative humidity of the reactant gases at the anode and cathode inlets plays important role in determining the state of hydration of the membrane. To keep the proper amount of water in the membrane, external humidifiers have been used but these external systems also have consumed power generated and added more weight on the system. Also the anode and
cathode can be flooded by using external humidifiers. Several studies have been conducted to minimize using external humidifiers. The counter flow of reactant gases is introduced.\textsuperscript{1-4}

In this work a simple analytical study is conducted to investigate the operation conditions in terms of pressure ratio and stoichiometries of gases. Temperature is implicitly included into the pressure ratio which is the ratio of the partial water vapor pressure to the total pressure. A mathematical model is developed for the water transport in the MEA. Four different cases are considered based on the condition of the relative humidity of incoming gases. The relative humidity of the gas in the cathode channel is calculated to judge the operation conditions.

**ANALYSIS OF WATER MANAGEMENT**

A PEM fuel cell is modeled as in Fig. 1. It is assumed in a steady state and a uniform temperature. Also the temperatures of the incoming gases are the same as that of the PEM fuel cell. The gas at the anode outlet is assumed to be saturated. Hydrogen and air are used as reactant gases for the analysis. All the product water is assumed to be evaporated. If calculated relative humidity is greater than 100\%, water vapor is condensed and water droplet is carried away by air.

**Water balance in the MEA:**

\[
m_{an}^{i} + m_{ca}^{i} = m_{an}^{o} + m_{ca}^{o} + m_{p}
\]

Water production:

\[
m_{p} = \frac{I}{2F}
\]

where \( m \) is the mass of water, \( m_{p} \) is the product water, \( I \) is the current density, and \( F \) is the Faraday constant. The subscript \( an \) and \( ca \) indicate the anode and the cathode, respectively. The superscripts \( i \) and \( o \) are the cell inlet and the outlet, respectively.
Water at the anode inlet:
\[ m_{an}^i = m_{H_{an},an} \times \omega_{an} \]
\[ m_{an} = \frac{1}{2F} \lambda_{H} \left( \frac{X_w}{1 - X_w} \right)_{an} \]  

Water at the anode outlet:
\[ m_{an}^e = m_{H_{an},an} \times \omega_{an} = (m_{H_{an},an} - m_{H_{an}}) \times \omega_{an} \]
\[ m_{an}^e = \frac{1}{2F} (\lambda_{H} - 1) \left( \frac{X_w}{1 - X_w} \right)_{an} \]  

Water at the cathode inlet:
\[ m_{ca}^i = m_{x_{ca},ca} \times \omega_{ca} \]
\[ m_{ca} = \frac{1}{4F} \left( \frac{\lambda_{O}}{N_{O}} \right) \left( \frac{X_w}{1 - X_w} \right)_{ca} \]  

Water at the cathode outlet:
\[ m_{ca}^e = m_{x_{ca},ca} \times \omega_{ca} = (m_{x_{ca},ca} - m_{x_{ca}}) \times \omega_{ca} \]
\[ m_{ca}^e = \frac{1}{4F} \left( \frac{\lambda_{O}}{N_{O}} - 1 \right) \left( \frac{X_w}{1 - X_w} \right)_{ca} \]  

where \( m_{\text{air}} \) is the mass of air, \( m_{\text{H}_2} \) is the mass of hydrogen, \( N_0 \) is the oxygen mole fraction in air, \( \lambda_{\text{H}} \) is the stoichiometry of air, \( \lambda_{\text{H}_2} \) is the stoichiometry of hydrogen, and \( \omega \) is the humidity ratio. \( X_w = P_{H_2O}/P_t \), \( P_{H_2O} \) is the partial pressure of the water vapor in the cell, and \( P_t \) is the total pressure of gases. The partial pressure of the water vapor would be saturation pressure, \( P_{H_2O} \) when the relative humidity of gas is 100%. The subscript \( u \) indicates the mass used for electrochemical reaction.

After substitution of Eqs 2, 4, 6, 8 and 10 into Eq 1 and elimination of common terms, water balance in the MEA becomes
\[ (\lambda_{H} - 1) \left( \frac{X_w}{1 - X_w} \right)_{an} + \frac{1}{2} \lambda_{O} \left( \frac{X_w}{1 - X_w} \right)_{ca} = \lambda_{H} \left( \frac{X_w}{1 - X_w} \right)_{an} + \frac{1}{2} \lambda_{O} \left( \frac{X_w}{1 - X_w} \right)_{ca} + 1 \]  

Fraction of product water removed
Without external humidifiers, the product water is only a source and the part of the water could be used to humidify the gases in the anode and cathode. When the dry gases are coming at the inlets, the maximum water could be consumed. The expressions of the fraction of product water used are derived as follows. The fraction of product water removed at the anode is given.
\[ \frac{m^e_{an} - m^i_{an}}{m_p} = (\lambda_{H} - 1) \left( \frac{X_w}{1 - X_w} \right)_{an} - \lambda_{H} \left( \frac{X_w}{1 - X_w} \right)_{an} \]  

For dry gas entering at the anode inlet, Eq 12 becomes
\[ \frac{m^e_{an} - m^i_{an}}{m_p} = (\lambda_{H} - 1) \left( \frac{X_w}{1 - X_w} \right)_{an} \]  

The fraction of product water removed at the cathode is given
\[ \frac{m^e_{ca} - m^i_{ca}}{m_p} = \frac{1}{2} \left( \frac{\lambda_{O}}{N_{O}} - 1 \right) \left( \frac{X_w}{1 - X_w} \right)_{ca} + \frac{1}{2} \lambda_{O} \left( \frac{X_w}{1 - X_w} \right)_{ca} \]
For dry gas at the cathode inlet, Eq 14 becomes
\[
\frac{m_{a_0} - m_{a_1}}{m_p} = \frac{1}{2} \left( \frac{\lambda_a}{N_0} - 1 \right) \left( \frac{X_w}{1 - X_w} \right)_{a_0}
\]  

[15]

Relative humidity of gas at the cathode outlet

Four different cases as shown in Table 1 are considered based on the relative humidity of incoming gases. The relative humidity of the gas in the cathode channel is calculated to judge the operation conditions. When this relative humidity is much less than the saturation, the product water may be used to humidify the incoming gases and the membrane may be dehydrated.

Table 1. Summary of Conditions of Reactant Gases

| Location | Anode Inlet | Cathode Inlet | Anode Outlet |
|----------|-------------|---------------|--------------|
| Case 1   | Dry gas     | Dry gas       | Saturated gas|
| Case 2   | Saturated gas| Dry gas       | Saturated gas|
| Case 3   | Dry gas     | Saturated gas | Saturated gas|
| Case 4   | Saturated gas| Saturated gas | Saturated gas|

With dry gases at the anode and cathode inlets and saturated gas at the anode outlet such as the Case 1, Eq 11 becomes as follow
\[
(\lambda_w - 1) \left( \frac{X_w}{1 - X_w} \right)_{a_0} + \frac{1}{2} \left( \frac{\lambda_a}{N_0} - 1 \right) \left( \frac{X_w}{1 - X_w} \right)_{a_0} = 1
\]

[16]

Substituting the expression, \( \Phi = \frac{P_2}{P_1} \), of the relative humidity and \( X_w = P_x / P_1 \) into Eq 16, the relative humidity of gas at the cathode outlet is

\[
\Phi_{a_0} = \left[ 1 - (\lambda_w - 1) \left( \frac{P_x}{P_1} \right) \right] \left( \frac{1}{\lambda_a + \left( \lambda_w - 1 \right) \left( \frac{P_x}{P_1} \right)} \right)
\]

[17]

For \( \Phi_{a_0} = 100\% \), Eq 17 is simplified further as follow
\[
\left( \lambda_w + \frac{\lambda_a}{2N_0} - \frac{1}{2} \right) = \frac{1}{P_1}
\]

[18]

This equation expresses the optimum relationship of the pressure ratio and the stoichiometries of gases to obtain the saturation state at the cathode outlet. The same procedure can be applied to three other cases and the results are summarized in Table 2.

RESULTS AND DISCUSSION

Without external humidifier, the product water is only a source to humidify the gases in the anode and cathode to prevent dehydration of the membrane. The amount of water for humidification depends on the partial pressure of the water vapor and the

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stoichiometries of gases. When the partial pressure is lower than the saturation pressure of the vapor, the gases entering the anode and cathode would absorb the product water. So, higher pressure ratio leads to consume more water. Also, the gas with higher stoichiometry needs more water. For $\lambda_a = 2.0$ and $\lambda_H = 2.0$ of dry gases, the maximum fractions of water consumed at the anode or cathode are estimated by using Eqs 13 and 15 for various pressure ratios as shown in Fig. 2. More water is used at the cathode than at the anode because it is assumed that pure hydrogen is used at the anode and air is supplied at the cathode. Also, it shows that all of the product water could be removed by hydrogen and air at the pressure ratio of about 0.15. The dry air alone flowing into the cathode could consume entire product water at the pressure ratio of about 0.17.

For the hydrogen stoichiometry of 3, the relative humidity of air at the cathode outlet is calculated to examine the operating condition without external humidifiers corresponding to the Case 1. The results in Fig. 3 show that for only very low pressure ratios, $Pr$, the relative humidity of air in the cathode becomes the saturation condition. For most of pressure ratios, the relative humidity is not only low but also decreases sharply as the air stoichiometry is increased. Therefore the operation of the PEM fuel cell without external humidifiers is limited in the range of very low pressure ratios.

Table 2. Summary of relative humidity, and optimum relationships of pressure ratio and stoichiometry

| Case   | Relative Humidity ($\Phi^o_{ca}$)                                                                 | Optimum Relationship for $\Phi^o_{ca} = 100\%$ |
|--------|---------------------------------------------------------------------------------------------|-----------------------------------------------|
| Case 1 | $\Phi^o_{ca} = \frac{1 - (\lambda_H - 1) \left( \frac{P_i}{P_t} \right)}{\frac{\lambda_a}{2N_o} + \frac{1}{2} (\lambda_H - 1) \left( \frac{P_i}{P_t} \right)} \left( \frac{P_t}{P_t} \right)$ | $\left( \lambda_H + \frac{\lambda_a}{2N_o} \right) = \frac{P_i}{P_t} + \frac{1}{2}$ |
| Case 2 | $\Phi^o_{ca} = \frac{1 + \left( \frac{P_i}{P_t} \right)}{\frac{\lambda_a}{2N_o} + \frac{1}{2} \left( \frac{P_i}{P_t} \right)} \left( \frac{P_t}{P_t} \right)$ | $\lambda_a = 2N_o \left( \frac{P_i}{P_t} + \frac{1}{2} \right)$ |
| Case 3 | $\Phi^o_{ca} = \frac{1 + \left( \frac{\lambda_a - \lambda_H + 1}{2N_o} \left( \frac{P_i}{P_t} \right) \right) \left( \frac{P_t}{P_t} \right)}{\frac{\lambda_a}{2N_o} + \frac{1}{2} \left( \frac{\lambda_a - \lambda_H + 1}{2N_o} \left( \frac{P_i}{P_t} \right) \right) \left( \frac{P_t}{P_t} \right)}$ | $\lambda_H = \frac{P_i}{P_t} + \frac{1}{2}$ |
| Case 4 | $\Phi^o_{ca} = \frac{1 + \left( \frac{\lambda_H - 1}{2N_o} \left( \frac{P_i}{P_t} \right) \right) \left( P_t \right)}{\frac{\lambda_a}{2N_o} + \frac{1}{2} \left( \frac{\lambda_H - 1}{2N_o} \left( \frac{P_i}{P_t} \right) \right) \left( P_t \right)}$ | None |
When hydrogen is humidified at the anode inlet such as the Case 2, the product water can be solely used to humidify the air at the cathode so that the air is saturated until up to the pressure ratio of 0.5 for the low stoichiometry of air as shown in Fig. 4. However, the reasonable value of the air stoichiometry such as 2, applicable pressure ratio is very low. Also the relative humidity decreases as the air stoichiometry and the

![Fig. 2. The maximum fraction of product water to be consumed at the anode or cathode.](image)

![Fig. 3. The relative humidity vs. air stoichiometry for the air at the cathode outlet with the hydrogen stoichiometry of 3 for the Case 1.](image)

![Fig. 4. The relative humidity vs. air stoichiometry for the air at the cathode outlet for the Case 2.](image)
pressure ratios increase. So, with the limited product water, the air in the cathode could remove water from the membrane assembly as the pressure ratio and air stoichiometry are raised. Even though the relative humidity is higher than 100% for the low air stoichiometry in Fig. 4, the relative humidity greater than 100% is theoretically impossible. It implies that condensed water droplets may be carried by the air.

In the Case 3, a humidifier is used at the cathode inlet for entering air while dry hydrogen enters at the anode inlet. Fig. 5 shows the variations of the relative humidity of the exit air for the air stoichiometry of 3. For the hydrogen stoichiometries between 1 and 3, near the saturation condition is well established for high pressure ratios and water vapor may be condensed at low pressure ratio. When the stoichiometry of hydrogen is increased, the relative humidity of air decreases because more water is consumed at the anode.

![Fig. 5](image)

Fig. 5. The relative humidity vs. hydrogen stoichiometry for the air at the outlet of the cathode for $\lambda_A = 3$ of the Case 3.

Fig. 6 shows the results for the hydrogen stoichiometry of 3. When the air stoichiometry is one, the relative humidity is very high for the low pressure ratios and decreases below 100% as the pressure ratio increases. This indicates that all the product water is used to humidify hydrogen and extra water vapor in the air is transported from the cathode to meet the saturation condition constrained at the anode outlet. However, air is near saturation state for most of the air stoichiometries and the high pressure ratios. Thus, the Case 3 is the most promising one among the cases for the broad ranges of pressure ratios and air stoichiometries.

![Fig. 6](image)

Fig. 6. The relative humidity vs. air stoichiometry for the air at the cathode outlet with the hydrogen stoichiometry of 3 for the Case 3.
For the Case 4, humidifiers are used at both inlets so that the incoming gases are saturated. The relative humidity of air is always greater than 100% because the product water is added to the saturated air. The MEA is always hydrated and may be flooded when the excess water is not carried out by gas in the cathode. The results obtained by using Eq 23 show that for the high pressure ratios, the relative humidity is close to 100% in the broad ranges of the air stoichiometries. For the low pressure ratios, much more water than necessity is provided so that the proper control of humidifiers is required.

The proper operation of fuel cells requires that the relative humidity of the exit air is about 100% to avoid dehydration of the membrane. This is obtained by setting the proper stoichiometries of gases for each operating pressure ratio. The optimum relationships, Eqs 20 and 22, for the Case 2 and Case 3 are used to calculate the results. Fig. 7 shows the variations of the optimum stoichiometries to keep the cathode outlet air in the saturation condition. Both stoichiometries decrease with increasing the pressure ratio. For the Case 2, it is meaningful to only low pressure ratios otherwise the hydrogen stoichiometry is less than 2. For the Case 3, the optimum air stoichiometry is applicable to the broad range of the pressure ratio.

![Fig. 7. The optimum stoichiometry vs. pressure ratio for the Case 2 and 3.](image)

**CONCLUSIONS**

The analytical results show that without external humidifier the hydration condition of MEA can be obtained at very low pressure ratios. The gas humidified at the cathode inlet is more effective than that at the anode inlet for the broad range of pressure ratios. Humidifying gases at both inlets may cause flooding of MEA due to the excess amount of water at low pressure ratios but is useful for high pressure ratios. For the Case 2 and 3, the optimum relationships between the pressure ratio and the stoichiometry are given to obtain the saturation condition of the air at the cathode outlet.

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